Sediment Budgets 1 (Proceedings of symposium S1 held during the Seventh IAHS Scientific Assembly at Foz do Iguaçu, Brazil, April 2005). IAHS Publ. 291, 2005.

Contributions of authigenic iron compounds to fluvial suspended sediment concentrations and fluxes in the Nete sub-basin, Belgium

ELIN VANLIERDE[1], JAN DE SCHUTTER[2], JORIS F. A. MEYS[3], FRANK MOSTAERT[2] & PATRIC JACOBS[1]

1 *Department of Geology and Soil Science, Research unit for Sedimentology and Engineering Geology, University of Ghent, Krijgslaan 281 S8, B-9000 Ghent, Belgium*
elin.vanlierde@ugent.be

2 *Flanders Hydraulics Research, Ministry of the Flemish Community, Berchemlei 115, B-2140 Borgerhout (Antwerp), Belgium*

3 *Laboratory for Ecophysiology, Biochemistry and Toxicology, University of Antwerp – UA, Groenenborgerlaam 171, B2020 Antwerp, Belgium*

Abstract In the Nete Basin (Flanders, Belgium), there are indications that the chemical precipitates derived from groundwater-associated Fe(II) seeping into the overlying surface water significantly contribute to the composition, concentration, and fluxes of suspended sediment. For purposes of evaluation, model-derived concentrations were compared with those determined from actual samples. Missing suspended sediment concentrations were estimated from a site-specific rating curve (a stepwise linear regression model) generated from log-transformed data for suspended sediment concentration, gauge height, baseflow, and interflow). Based on various estimates of the concentration of Fe(II) in groundwater, as well as several other factors, authigenic iron compounds may constitute from 36 to 97% of the sediment load in the basin. However, the best current estimate, based on a rating curve model relating groundwater flow to authigenic mineral formation is 70%.

Key words authigenic iron compounds; Belgium; suspended sediment concentration; suspended sediment flux

INTRODUCTION

Flanders Hydraulics Research (FHR) has installed and maintains a sediment-monitoring network on seven tributaries of the River Scheldt in Belgium, to address issues such as dredging, flood control, erosion and water quality. The monitoring stations are located in different sub-basins of the river. Suspended sediment in the basin is derived from detrital, anthropogenic and authigenic sources (Vervaet, 2002).

The Nete sub-basin, situated in northern Flanders, contains the Kleine Nete and the Grote Nete and their tributaries, and drains about 1670 km^2 (Fig. 1). About 590 km^2 lie upstream of the Grobbendonk suspended sediment concentration (SSC) monitoring station located on the Kleine Nete (Fig. 1). The landscape in the region is mostly flat, thus minimizing erosion potential (VMM, 2003; Vervaet, 2002). Additionally, ditches and trenches adjacent to the fields further limit the dispersion of eroded material.

The Nete sub-basin is characterized by thick Tertiary deposits overlain by a thin layer of Quaternary sediment (Fig. 2). Because of its very low permeability, the clayey Boom Formation serves as an aquitard that divides the Nete groundwater system into two separate hydrogeological units (AMINAL, 1995; Envico, 2001). Therefore all groundwater seepage into the surface water system is contributed by the upper

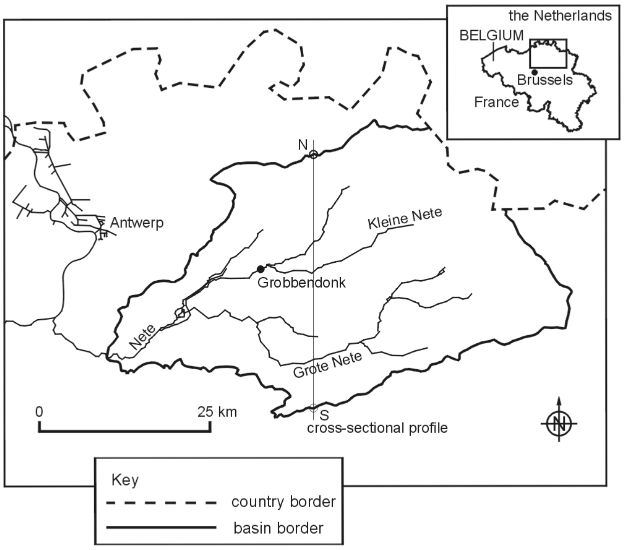

Fig. 1 Map of the Nete sub-basin and its river system.

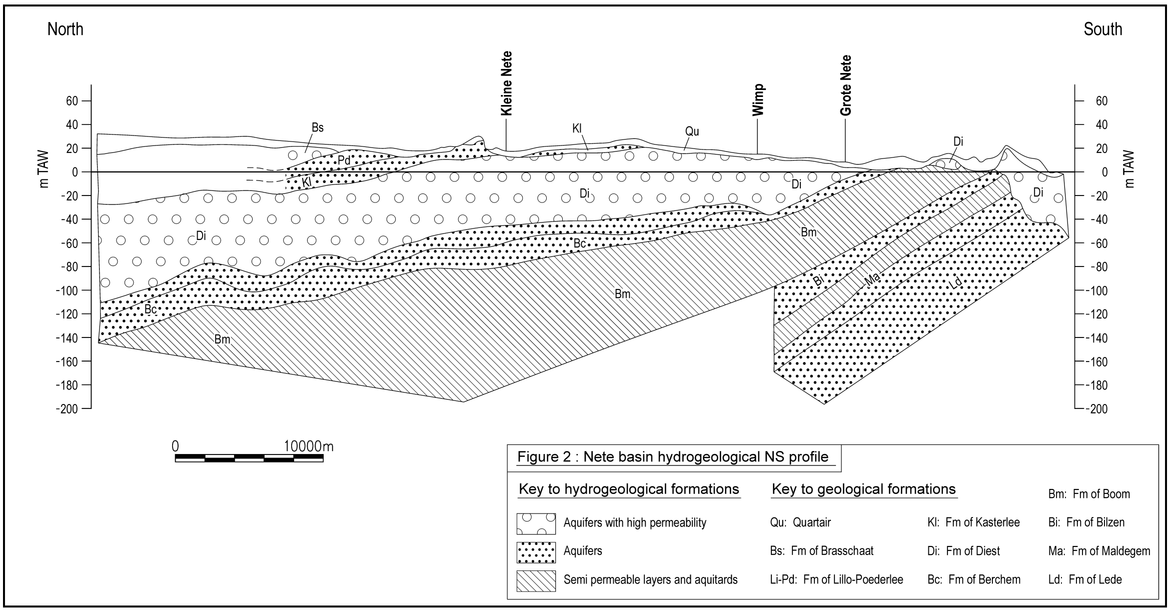

Fig. 2 North–south cross-sectional hydrogeological profile through the Nete sub-basin (modified from Envico, 2001).

hydrogeological unit consisting of three Neogenic sand aquifers: (1) the Merksplas, Brasschaat, and Mol Formations; (2) the Lillo, Poederlee, and Kasterlee Formations; and (3) the Berchem and Diest Formations (AMINAL, 1995; Envico, 2001). The latter appears to be the most important of the three. Additional groundwater contributions are derived from the Campine Plateau that lies east of the Nete sub-basin. Most of the geological formations throughout the region contain iron minerals (e.g. glauconite, iron sulphides) and because the groundwater is both acidic and reducing, it contains substantial concentrations of Fe(II) (Blommaert *et al.*, 1988; AMINAL, 1995; VLM, 1997).

When the acidic, reducing, Fe(II)-rich groundwater seeps into the oxidized surface water system, various Fe compounds (e.g. iron oxyhydroxides and phosphates) begin to precipitate/flocculate (Stumm & Morgan, 1970). Observations (e.g. iron stains along the river bank) and SSC samples collected at Grobbendonk indicate that these authigenic iron compounds could constitute a significant proportion of the SSC, and hence the suspended sediment fluxes derived from the Nete sub-basin. An attempt to estimate that authigenic contribution for the period 1 February 1999 to 31 January 2000 is described here.

METHODS, RESULTS AND DISCUSSION

Actual suspended sediment fluxes at Grobbendonk

Between 1 February 1999 and 31 January 2000 the Grobbendonk site was instrumented with an automatic sampler that was programmed to collect material every seven hours. Upon retrieval, the samples were analysed gravimetrically for SSC, after filtration through a 0.45-µm membrane filter and air drying. Mean daily SSC values were generated from these data. The site also was instrumented with a stage recorder; discharge was estimated based on a site-specific stage/discharge relation. The combination of mean daily SSC and mean daily discharge was used to calculate the total suspended sediment flux for the site for the period of record.

Data on mean daily discharge were available for the entire period of record; however, mean daily SSC only was available for 336 days of the 365-day period. To determine the total load for the period more accurately, missing mean daily SSC concentrations were estimated using a pair of site-specific sediment rating curves. The rating curves were developed based on a conceptual model that required consideration of both surface water flow (to account for detrital material) and groundwater flow (to account for authigenic material), both derived from NAM (rainfall–runoff model) (Nielsen & Hansen, 1973). Two different approaches were compared, a single rating curve, and a combination of two rating curves. In the latter approach, a discharge breakpoint was estimated together with the other parameters. An initial analysis indicated that inserting a breakpoint in the model significantly improved its predictive power. Multiple rating curves for the same site have been used before to deal with such issues as seasonality and/or for different parts of a storm hydrograph (e.g. Walling & Webb, 1988). The rating curves took the form:

$$C = a_1 + a_2(Q) + a_3(Q_p) + a_4(F) \qquad \text{for } Q < BR \quad (\text{in m}^3\ \text{s}^{-1})$$

$$C = b_1 + b_2(Q) + b_3(Q_p) + b_4(F) \qquad \text{for } Q > BR \quad (\text{in m}^3\ \text{s}^{-1})$$

where C = SSC in mg l^{-1}; Q is surface water discharge in m^3 sec^{-1}; F is groundwater baseflow in m^3 sec^{-1}; Q_p is surface water discharge for the previous day in m^3 sec^{-1}; and BR is the breakpoint.

Although groundwater flow is composed of both baseflow and interflow, both terms could not be used in the regressions due to issues of co-linearity. The Q_p term was added because SSC levels tend to decline when elevated surface water discharges extend over periods longer than 24 hours. The a_1–a_4 and b_1–b_4 coefficients were estimated together with the breakpoint using the Hooke-Jeeves pattern search algorithm. Asymptotic standard deviations were calculated, and the results evaluated with a Student's *T* test. Non-significant parameters were discarded, and the procedure was repeated until the final forms of the rating curves were developed. The final rating curves took the form:

$C = 6.32(Q) - 2.28(F)$ for $Q < 18.8$ m^3 sec^{-1}

$C = 216 + 10.3(Q) - 2.31(Q_p) - 26.7(F)$ for $Q > 18.8$ m^3 sec^{-1}

The difference between the measured and the model-derived suspended sediment flux for Grobbendonk for the 336-day period where actual data were collected was <<1%, and amounted to 12 400 tonnes. Based on actual measurements, plus model-derived SSCs for the missing 29 days, the suspended sediment flux at Grobbendonk, for the period from 1 February 1999 to 31 January 2000, was 13 400 t.

Groundwater-derived authigenic contributions to SSC and suspended sediment fluxes at Grobbendonk

The determination of groundwater-derived authigenic contributions to the suspended sediment fluxes at Grobbendonk requires a variety of hydrological, mineralogical, and chemical data (shown schematically in Fig. 3). These include estimates/measurements of: (1) groundwater discharge; (2) groundwater Fe(II) concentrations; (3) the mineralogical composition of the authigenic precipitates (a stoichiometric factor), and (4) the mass of sorbed chemical constituents to the authigenic precipitates (a sorption factor). The need for the first two types of data are self-evident; however the latter two are not. Mineralogical composition is important because it has a direct bearing on the mass of authigenic contributions. This accrues because the same amount of Fe(II) can generate different masses of authigenic material, depending on the final mineralogical composition. The sorption factor is an issue because authigenic Fe-oxides have extremely high surface areas capable of concentrating a number of different trace elements (e.g. Cu, Zn, Cd, Pb, Ni) that could increase the mass of the authigenic contribution (Stumm & Morgan, 1970; Horowitz; 1991; Tessier, 1992).

As noted previously, the Nete sub-basin displays flat topography and is overlain with high permeability soils (VMM, 2003; Vervaet, 2002). Further, the nearby Campine Plateau also is highly permeable as it consists of coarse sand overlying gravels (Wouters & Vandenberghe, 1994). It has been estimated, based on a water balance model, that between 1901 and 1986 the groundwater contribution to surface-water discharge in the sub-basin averaged 62% (Van Der Beken & Huybrechts, 1990). Further, based on NAM (rainfall–runoff model) (Nielsen & Hansen, 1973), groundwater contributions to surface water discharge, during the 1 February 1999–31 January 2000 period of record, accounted for about 88% of the flow (Swings *et al*., 2003). Hence, groundwater discharge for the period averaged some 185 500 000 m^3 year^{-1}.

Examination of a number of databases containing information on Fe(II) in groundwater in the Nete sub-basin indicate that concentrations throughout the region vary over a wide range, and even vary quite locally [PIDPA (public water supply) (personal communication), AMINAL (Division Water) (personal communication), the Belgian

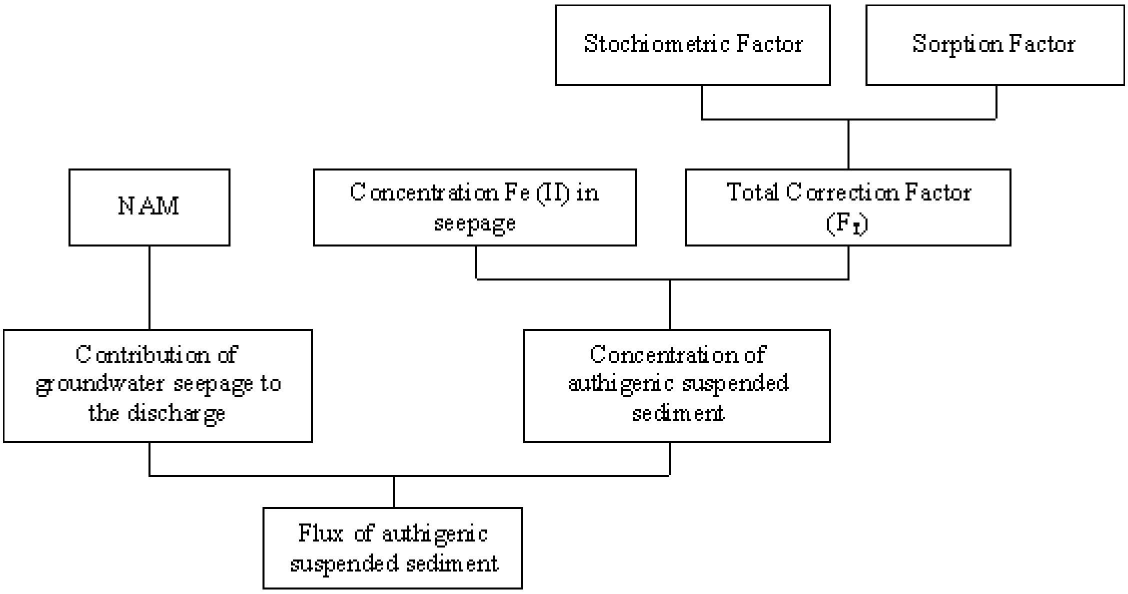

Fig. 3 Schematic overview of the methodology and correction factors used to calculate the theoretical contribution of authigenic material to the suspended sediment load at Grobbendonk.

Nuclear Research Centre (Blommaert *et al.*, 1988), Institute of Nature Conservation (personal communication)]. However, the Kleine Nete and the Grobbendonk monitoring site, directly overlie the highly permeable Diest Formation. In fact, the river actually incises it; as such, it is plausible that groundwater from this formation largely outweighs contributions from other aquifers. As the Fe(II) concentration data from the formation are highly skewed (Table 1), the median concentration of the AMINAL dataset of 15.7 mg l^{-1} was used for groundwater baseflow contributions. Values for Fe(II) concentrations in the interflow should be higher than those in the baseflow due to rainwater infiltration into the phreatic layer. As the overlying soil has little buffering capacity, pHs as low as 4 have been observed; median Fe(II) concentrations ranging from 15 to 25 mg l^{-1} have been estimated (VLM, 1997).

As noted above, the mass of authigenic iron compounds generated by the same amount of dissolved Fe(II) can vary significantly, depending on the wide variety of mineralogical forms that can occur in freshwater (Stumm & Morgan, 1970). For example, stoichiometrically, 1 g of Fe(II) can form 1.51 g of ferrihydrite, 1.59 g of lepidocrocite, 3.35 g of strengite, or 3.79 g of mitridatite. Hence, theoretically, the stoichiometric factor could range from 1.5 to 3.8. The high capacity of iron oxides to sorb cations also is likely to add to the mass of the authigenic precipitates; however, this is likely to be substantially smaller than the stoichiometric factor. In practice it is difficult to determine the amount of mass added by sorption; however, for the purposes of this exercise, a mass of 0.2 g per g of Fe(II) was assumed. This means that the theoretical range for the combined stoichiometric and sorption factors (F_T) is 1.7 to 4.0.

Examination of actual suspended sediment from the Grobbendonk site, using Mössbauer spectroscopy, provides some insight into the possible mineralogical forms that the authigenic iron precipitates might take. Possible candidates include iron hydroxides, ferrihydrite, or lepidocrocite. On the other hand, the same analyses indicate a

Table 1 Statistical overview for groundwater-associated iron concentration in the Nete sub-basin.

Source	Inst. Nature Conservation	PIDPA median values	AMINAL			Belgian Nuclear Research Centre
	Depth <10 m	Fm Diest	Fm Lillo	Fm Diest	Fm Berchem	Fm Diest
No. values	41	44	16	28	27	18
Average	22.69	23.43	5.97	29.98	6.75	7.70
Mean	11.5	22.83	2.36	15.68	1.56	2.88
Min.	0.25	2.11	0.03	0.05	0.07	0.01
Max.	117	46.57	26.04	148.01	42.80	78

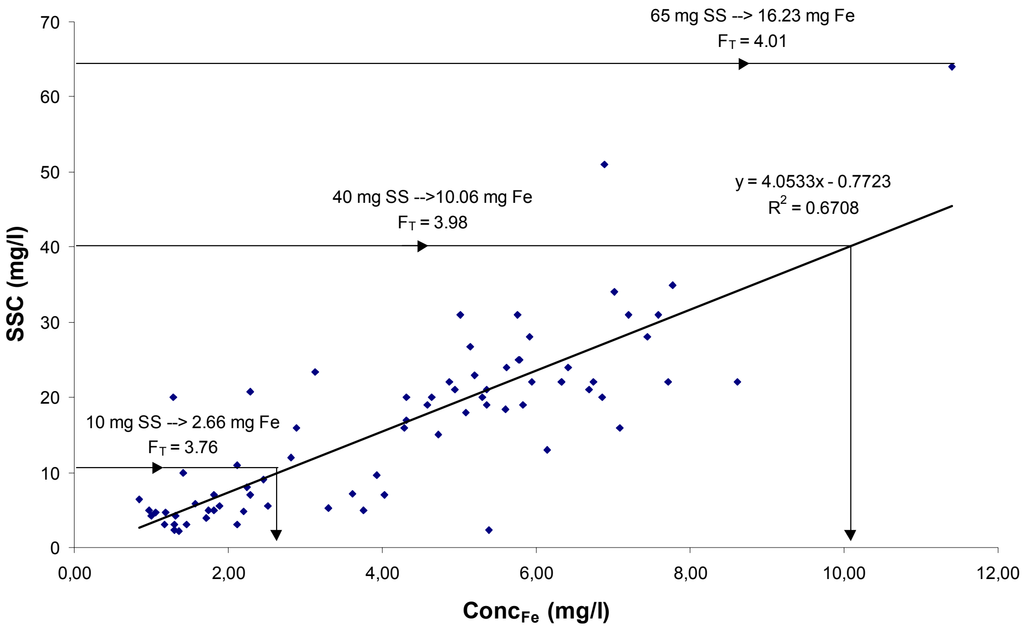

Fig. 4 The relation between total iron concentrations and SSCs for the Grobbendonk monitoring site (data from VMM, 2004).

lack of goethite or hematite. An alternative approach to estimating F_T entails examining how the concentration of iron varies with increasing SSC. Calculated data from the Flemish Environment Agency indicate that 10, 40 and 65 mg l^{-1} concentrations of SSC contain, respectively, about 2.6, 10.1, and 16.2 mg of Fe (VMM, 2004, Fig. 4). A maximum value for F_T can be determined assuming that all the suspended sediment-associated Fe is authigenic. If no detrital Fe is present, F_T can range from 3.8 to 4.0. These values do fall within the upper limits of the theoretical range.

Based on the various ranges for the requisite factors (groundwater discharge, concentration of Fe(II), and the combined stoichiometric/sorption factor (F_T)) it is possible to calculate a range for the flux of authigenically derived suspended sediment for the period of record (Table 2). That range is between 4900 and 13 000 t year^{-1}. As the estimated suspended sediment flux for that same period is 13 400 t year^{-1}, the range of authigenic contributions lies between 36 and 97%.

A more refined estimate of the total authigenic contributions to the suspended sediment flux for the period of record can be obtained by using a mathematical model (rating curve). This model predicts daily authigenic SSCs and subsequent calculations

Table 2 Ranges for iron concentrations, the total correction factor, and predicted SSCs and fluxes for the Grobbendonk site.

	Fe (mg l^{-1})		F_T		Authigenic SSC (mg l^{-1})		Q (m^3 $year^{-1}$)	Flux (t $year^{-1}$)	
	Min	Max	Min	Max	Min	Max		Min	Max
Baseflow	15.68		1.7	4	26.66	62.72	144 774 213	3859	9080
Interflow	15	25	1.7	4	25.5	100	40 581 228	1035	4058
Total seepage							185 355 441	4894	13138

Table 3 Summary of the different parameters used as input for the groundwater/authigenic suspended sediment rating curve model.

Source	Specification	Unit	Variability
NAM	Total discharge	m^3 s^{-1}	Time variable
	Interflow	m^3 s^{-1}	Time variable
	Baseflow	m^3 s^{-1}	Time variable
IN PIDPA	Conc'n Fe(II) baseflow	mg l^{-1}	Median form of Diest = 15.68
AMINAL BNRC	Conc'n Fe(II) interflow	mg l^{-1}	15 < range < 20
Model parameters	F_T		1.70 < range < 4.00
	F_{acc}		Accumulation is variable in two discharge classes. 1. Q < 10.6 m^3 s^{-1} > accumulation 2. Q > 10.6 m^3 s^{-1} > erosion

of daily suspended sediment fluxes. The input values (Table 3) consist of (1) daily groundwater discharges derived from NAM (Swings *et al.*, 2003), (2) the various predetermined factors (e.g. Fe(II) concentration, F_T) which can vary within the assumed ranges, and (3) an accumulation factor. The latter was used to further refine the mathematical model, relative to the theoretical model. The SSC at any given moment can be defined as the amount of supplied authigenic sediment multiplied with the accumulation factor. This factor moderates the SSCs depending on the surface-water discharge conditions. During low flow conditions a fraction of the generated authigenic suspended sediment will accumulate on the bottom, lowering the instantaneous transported SSC, while during higher flow conditions, a fraction of the previous accumulated authigenic suspended sediment will be remobilized, increasing the suspended sediment concentration. The break point for physical remobilization appears to occur at 10.6 m^3 sec^{-1}, and was determined by examining the SSC as a function of the frictional velocity (Fig. 5), and the corresponding discharge, at the Grobbendonk site. The model was further refined by comparing the predicted daily authigenic SSCs and fluxes with the measured total SSCs and fluxes (Fig. 6).

After fine-tuning, the model generated the best fit when using 3.6 for the total correction factor (F_T), and 15.7 mg l^{-1} and 25 mg l^{-1} for the Fe(II) concentrations in the base- and interflow, respectively. Note that as is typical for rating curves, the model tended to overpredict the low SSCs and underpredict the high SSCs (e.g. Horowitz, 2003). However high flow conditions generate higher contributions of detrital suspended sediment and will erode more of the riverbed than only the accumulated authigenic sediments taken into account by the mathematical model. Therefore the amount of sediment underpredicted during high flow conditions is most likely of non-authigenic origin.

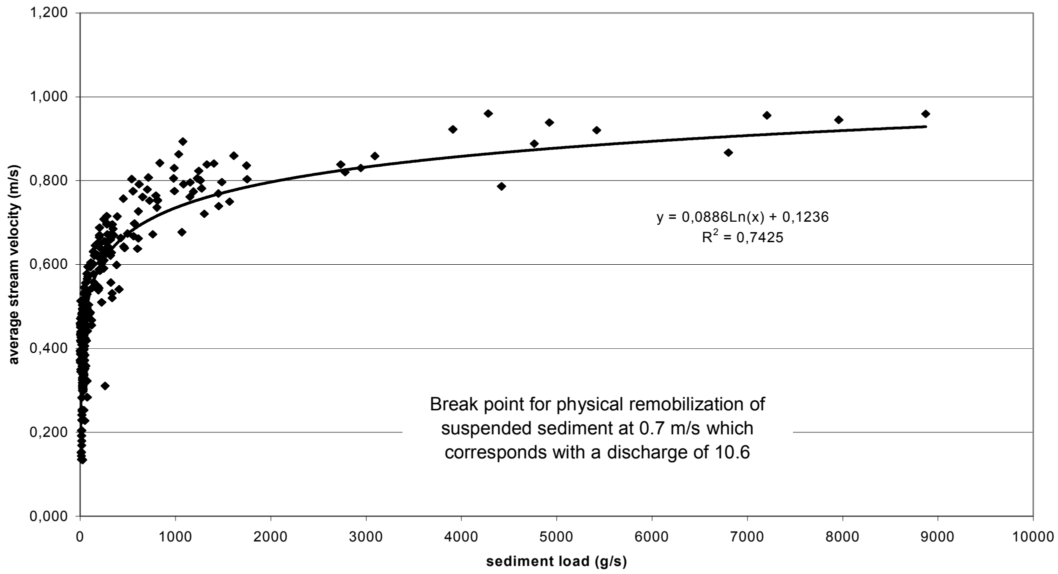

Fig. 5 The break point for physical remobilization of suspended sediment determined by examining the SSC as a function of the frictional velocity.

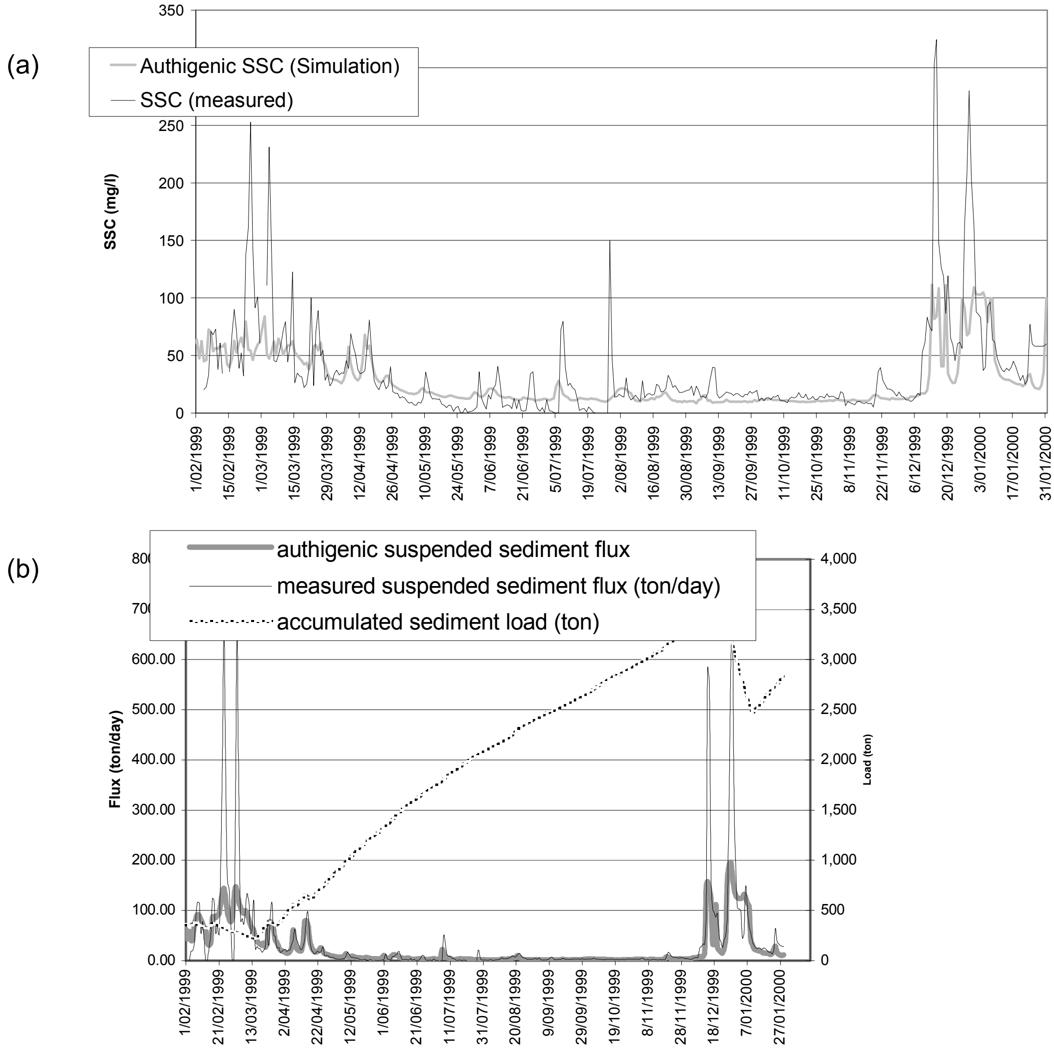

Fig. 6 Simulation of authigenic suspended sediment concentrations (a), and fluxes (b) against measured values for the 1 February 1999 to 31 January 2000 period.

The model-derived authigenic suspended sediment flux at the Grobbendonk site for the 1 February 1999– 31 January 2000 period of record was 9400 t year^{-1}. Based on a total suspended sediment flux of 13 400 t year^{-1} for the site, the mathematical model estimates the account of authigenic contributions at around 70% of the load.

CONCLUSIONS

1. In the Kleine Nete sub-basin of the Scheldt River, the suspended sediment flux at the Grobbendonk suspended sediment monitoring site for the period 1 February 1999–31 January 2000, based on actual measurements and a pair of site-specific rating curves was estimated at some 13 400 t year^{-1}.
2. Groundwater inflow at Grobbendonk makes a substantial contribution to the surface water discharge; based on the NAM rainfall–runoff model, groundwater may account for as much as 88% of the surface water flow for the period of record.
3. The groundwater discharge at Grobbendonk is rich in Fe(II) as a result of lowered pHs, and reducing conditions within the aquifer; when the reduced groundwater enters the surface water system, substantial quantities of authigenic iron minerals precipitate/flocculate.
4. Theoretical calculations indicate that the authigenic precipitates could account for 36–97% of the suspended sediment fluxes, for the period of record at the site.
5. However, the best current estimate for authigenic mineral contributions to the suspended sediment flux at the site for the period of record, is based on a rating curve relating groundwater flow to authigenic mineral formation, and amounts to about 70%.

Acknowledgements The authors would like to thank A. J. Horowitz for his continuous support, critical remarks and expert insight combined with a wonderful sense of humour. We couldn't have done this without you. Further more we would like to thank Prof. E. De Grave for his technical support and J. Ronsijn and P. Peeters for their hydrological calculations. Finally we would like to thank the field personnel of FHR for their continuous effort in collecting data.

REFERENCES

AMINAL – Division Water (1995) *Grondwaterkwaliteit in de provincie Antwerpen.* Ministry of the Flemish Community, Belgium

Blommaert, W., de Marmol, P. & Patyn, J. (1988) Hydrochemical Research within the Hades Project (Disposal of high radioactive waste into the Boom clay). Internal report, Ministry of the Flemish Community, Belgium.

Envico (2001) Uitwerking van thema's ter invulling van de omgevingsanalyse in het kader van de opmaak van waterhuishoudingsplannen en bekkenbeheerplannen voor een aantal pilootprojecten - Bekken van de Nete. Report ed. by W. Mennen. AMINAL - Division Water, Ministry of the Flemish Community, Belgium.

Horowitz, A. J. (1991) *A Primer on Sediment Trace Element Chemistry* (second edn). Lewis Publishers Inc., Chelsea, Michigan, USA.

Horowitz, A. J. (2003) An evaluation of sediment rating curves for estimating suspended sediment concentrations for subsequent flux calculations. *Hydrol. Processes* **17**, 3387–3409.

Nielsen, S. A. & Hansen, E. (1973) Numerical simulation of the rainfall–runoff process on a daily basis. *Nordic Hydrol.* **4**, 171–190.

Stumm, W. & Morgan, J. J. (1970) *Aquatic Chemistry, An Introduction Emphasizing Chemical Equilibria in Natural Waters*. Wiley-Interscience, New York, USA.

Swings, J., Vanderkimpen, P., Smets, S. & Blankaert, J. (2003) *Actualisatie Sigmaplan*, Deelopdracht 3: Hydrologische en hydraulische modellen, vol. 1b: Statistiek/Hydrologie Rupelbekken. AWZ—Sea Scheldt Division, Ministry of the Flemish Community, Belgium

Tessier, A. (1992) Sorption of trace elements on natural particles in oxic environments. In: *Environmental Particles* vol. 1 (ed. by J. Buffle & H. P. van Leeuwen). Lewis Publishers Inc., Chelsea, Michigan, USA.

Van Der Beken, A. & Huybrechts, W. (1990) De Waterbalans van het Vlaams Gewest, Een rationeel Waterbeheer via kennis van de Waterbalans. *Water* **50**, 88–92.

Vervaet, C. (2002) Uitwerking van het onderwerp sedimenttransport in het kader van de Omgevingsanalyse van het Bekkenbeheerplan van de Nete. Studie uitgevoerd door Soresma in opdracht van het Ministerie van de Vlaamse Gemeenschap. AMINAL—Water Department. Ministry of the Flemish Community, Belgium.

VLM (Flemish Land Agency) (1997) Fosfaatverzadiging van zandige bodems in Vlaanderen. Flemish Land Agency Report. Ministry of the Flemish Community, Belgium.

VMM (Flemish Environment Agency) (2003) *Mira-T 2003, Milieu- en natuurrapport Vlaanderen: thema's* (ed. by Marleen van Steertegem). LannooCampus, Leuven, Belgium.

VMM (Flemish Environment Agency) (2004) Meetdatabank Vlaamse Milieumaatschappij. http://www.vmm.be

Walling, D. E. & Webb, B. W. (1988) The reliability of rating curve estimates of suspended sediment yield: some further comments. In: *Sediment Budgets* (ed. by M. P. Bordas & D. E. Walling), 337–350. IAHS Publ. 174. IAHS Press, Wallingford, UK.

Wouters, L. & Vandenberghe N. (1994) *Geologie van de Kempen—Een synthese.* NIRAS, Belgium.