A mass-balance approach to estimate in-stream processes in a large river

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Abstract:

A mass-balance approach was used to estimate in-stream processes related to inorganic nitrogen species ($NH_4{}^+$, $NO_2{}^-$ and $NO_3{}^-$) in a large river characterized by highly variable hydrological conditions, the Garonne River (south-west France). Studies were conducted in two consecutive reaches of 30 km located downstream of the Toulouse agglomeration (population 760 000, seventh order), impacted by modification of discharge regime and high nitrogen concentrations. The mass-balance was calculated by two methods: the first is based on a variable residence time (VRT) simulated by a one-dimensional (1-D) hydraulic model; the second is a based on a calculation using constant residence time (CRT) evaluated according to hydrographic peaks. In the context of the study, removal of dissolved inorganic nitrogen (DIN) for a reach of 30 km is underestimated by 11% with the CRT method. In sub-reaches, the discrepancy between the two methods led to a 50% overestimation of DIN removal in the upper reach (13 km) and a 43% underestimation in the lower reach (17 km) using the CRT method. The study highlights the importance of residence time determination when using modelling approaches in the assessment of whole stream processes in short-duration mass-balance for a large river under variable hydrological conditions.

KEY WORDS mass balance; in-stream processes; inorganic nitrogen; hydraulic perturbations; large river

INTRODUCTION

Studying the concentration variations in flowing water is the easiest way to study how a river functions. However, knowledge of flux variations is necessary to quantify in-stream processes. Most of the time, processes are studied under controlled conditions (laboratory, flume, artificial river); but real *in situ* studies are necessary to overcome scale difficulties when laboratory processes are generalized to the *in situ* scale (Stream Solute Workshop, 1990).

An *in situ* function can be studied by concentration measurements along a river at different points at a given date in order to have an idea of variations in space and time. If hydrological data can be obtained on the same scale of space and time, then mass balance can be calculated via fluxes. The methodology chosen depends on space and time variations. For example, in order to have an idea of space and time variations between seasons in a river reach, one sampling in different points of the reach at a given date (one or more sampling dates for each season) can be sufficient. In this first method, data give information about seasonal mean function of the river (Améziane *et al*., 2003). Another method consists in measuring continuous concentration variations over time at several sites. Here, the data obtained provide information on the how the river functions between sites, the accuracy depending on sampling frequency (Brunet and Astin, 1996; Garnier *et al*., 1999; House *et al*., 2001). These last two methods are complementary and allow mass balance to be calculated over large reaches (>100 km) (Sjodin *et al*., 1997).

The best way to estimate the activity of a reach of stream is to follow the water body by Lagrange sampling and compare the same circulating water by calculating mass balance. With this method, the mass balance is known more precisely and reveals the constituent dynamics. In this case, the contributions in streams are integrated (tributaries, outputs, exchanges with underground). This approach allows a real estimation of the intensity of the processes taking place in the river (retention and/or production).

For mass-balance studies, when the sampling duration is greater than the transient time, knowledge of transit time is not necessary (House and Warwick, 1998). However, knowing the transit time does allow the correspondence between discharge and concentrations to be known for large variations of discharge and/or concentrations during the sampling period.

In this paper, it is proposed that two methods be compared to estimate in-stream processes by a mass-balance approach. The study reach on the Garonne River

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(largest in south-west France) was 30 km long at the seventh order. It is influenced by the Toulouse conurbation (760 000 inhabitants), and the study was performed during a low water period with daily hydrological perturbations. To show the importance of residence times for determining in-stream processes by mass balance, the same mass balance was calculated by two different methods:

(i) the first is the variable residence time (VRT) method which is calculated by a hydraulic model based on one-dimensional (1-D) Saint Venant equations.
(ii) the second is a convenient method using a constant residence time (CRT) mass balance calculated from peaks in the hydrograph from the data for the sampling period as used by House and Warwick (1998).

MATERIAL AND METHOD

Studied site

The Garonne River is the largest river of the south-west France (eighth Strahler order at its mouth), with a watershed area of 60 000 km^2 and a length of 600 km. The region has a general temperate oceanic climate. Annual rainfall averages 900 mm and can reach 2000 mm in the upper part of the basin. The reach of stream under study is located in the seventh order part of the river directly downstream of Toulouse, an conurbation with a population of 760 000 inhabitants (Figure 1). In the study reach, the width of the river was 130 m, the mean depth 1·25 m during low water discharge (around 50 m^3 s^{-1}) and the overall slope 0·85‰. At the nearest gauging station [Verdun sur Garonne site downstream (DS)], located at the downstream end of the section studied, the mean annual discharge is 200 m^3 s^{-1} and ranges between 17 to 8000 m^3 s^{-1} Garonne river discharge for the year of the study is given (Figure 2). In this part of the Garonne River, the flow regime is characterized by two hydrological maxima, one in February and one in May, and a low-flow period from August to September (Tables I and II).

Along the section studied, hydrology is perturbed daily by releases from dams situated further upstream, flow fluctuations reaching 50% of the discharge during low-water periods (Figure 3). The river is also under the influence of Toulouse wastewater treatment plant and for some parameters notably for the inorganic nitrogen species,

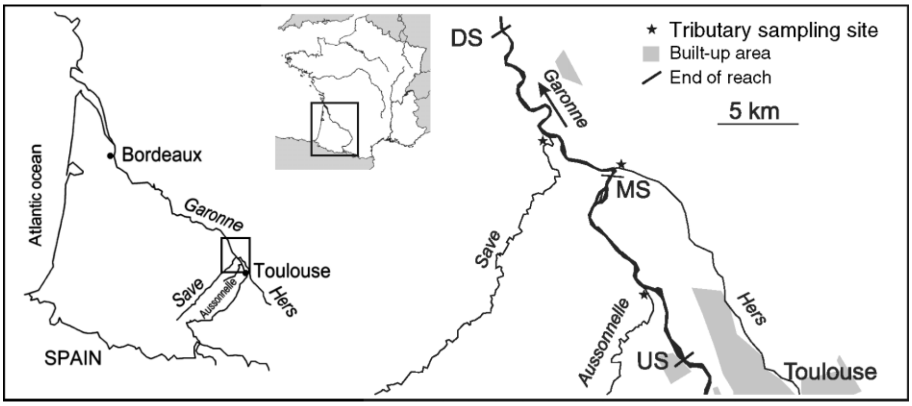

Figure 1. Regional and local maps showing reaches and tributaries studied

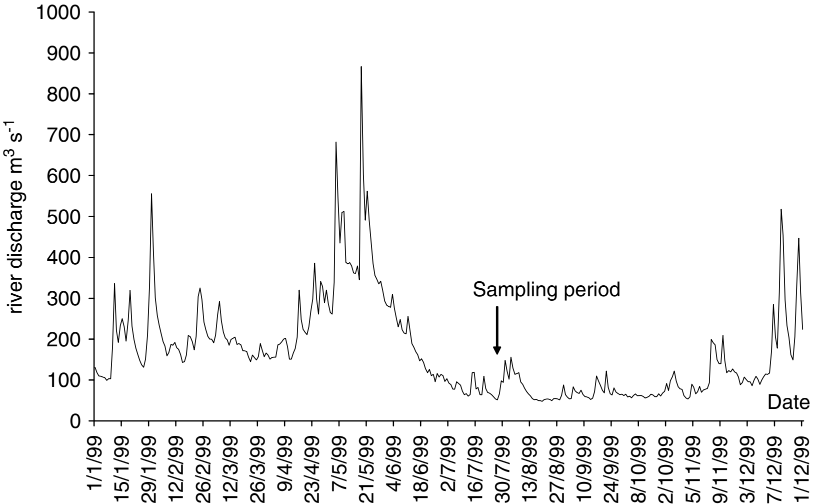

Figure 2. Garonne River discharge at Verdun sur Garonne (seventh order) for the year 1999. The arrow symbolizes the sampling period

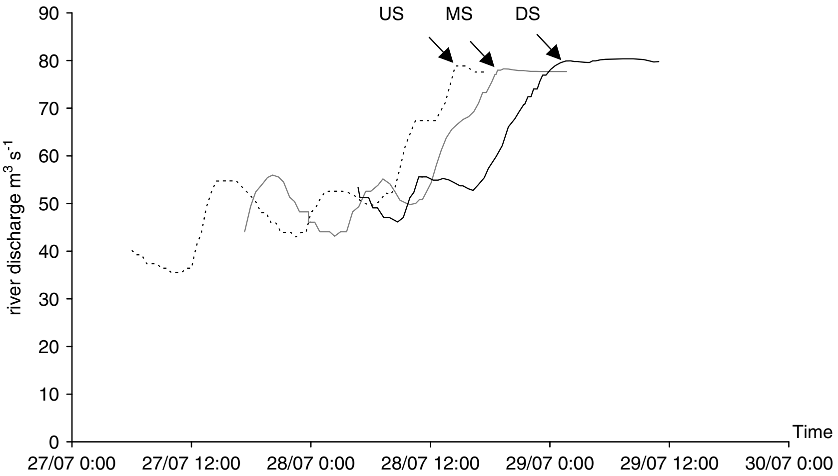

Figure 3. River discharge simulated in US (upstream), MS (midstream) and DS (downstream) sampling points (sites are represented by a dashed line, grey line and black line, respectively) during the study period. The arrows symbolize the high discharge peaks chosen for CRT calculations of the mass balance

Table I. Monthly mean discharge

Month	Discharge (m^3 s^{-1})	Month	Discharge (m^3 s^{-1})
January	209	July	130
February	251	August	82
March	242	September	86
April	302	October	126
May	351	November	157
June	266	December	200

Table II. Hydrological characteristics (in m^3 s^{-1}) for 30 years (1972–2001) at Verdun sur Garonne [mean ± standard deviation (SD)], located 30 km downstream of Toulouse

Annual mean discharge	Mean low water discharge	Flood return period (2 years)	Flood return period (5 years)
200 ± 22	60 ± 20	1500 ± 200	2100 ± 300

which undergo large hourly fluctuations (Figure 4 at the upstream sampling point).

Data collection

The study was carried out from 27 July to 29 July 1999 in three sampling sites named upstream site (US), middle site (MS) and downstream site (DS), delimiting two consecutive reaches of 13 and 17 km, extending from Fenouillet (US site) to Verdun sur Garonne (DS site). The US site is located at the mixing point where the river receives the outlet from the wastewater treatment plant of Toulouse city (serving about 550 000 people). Three little tributaries were also sampled: one in the upper river reach (the Aussonnelle) and two in the lower river reach (the Hers-Mort and the Save). The samples from the tributaries were taken just upstream of their confluence with the Garonne. In the Garonne, each sampling site was located sufficiently far downstream of any tributary source or other point source that the water column was fully mixed.

During the *in situ* experimentation, the beginning of the sampling period was synchronized for each sampling sites with the upstream site in order to have the same water body sampled at all sites. For tributaries sampling sites, the sampling period begins when the water body arrived at the confluent with the river. This first calculation of the water body residence time was performed with a 1-D hydraulic model which used Saint Venant equations (Sauvage *et al.*, 2003).

At all sampling sites in the river and tributaries, water was collected by automated samplers for 48 h except for the US site which was sampled for 35 h. For the three river sites (US, MS, DS), the 1 l samples were 2-h means: each sample being a mixture of 10 subsamples (one taken every 12 min) of 100 ml of water. For the three tributaries, 4-h mean samples of 1 l (250 ml subsamples were taken hourly) were collected over the 48-h period. After field collection, all the water samples were stored at 4 °C until laboratory analysis performed within 48 h. Raw discharge data were obtained from hourly monitoring of Direction Régionale de l'Environnement (water authorities) at the DS site gauging station on the Garonne and on tributaries. For the tributaries, a daily mean discharge was used for calculations, as the hourly variations were low. During sampling (3 days), daily mean discharges recorded at the DS were 52, 67 and 98 m^3 s^{-1} respectively. This progressive increase is due to the beginning of a small flood coming from upstream which peaked on 31 July 1999 at 148 m^3 s^{-1} (Figure 2). During sampling (3 days), the mean discharge for the Aussonnelle, the Hers-Mort and the Save tributaries recorded at the gauging stations was 0·16, 1·2 and 1·7 m^3 s^{-1} respectively. At each Garonne site, discharge evolution was simulated by the 1-D hydraulic model based on Saint Venant equations (see paragraph on calculating mass-balance VRT method).

Data analysis

Measurement of inorganic nitrogen species was carried out on samples filtered through Whatman GF/F filters

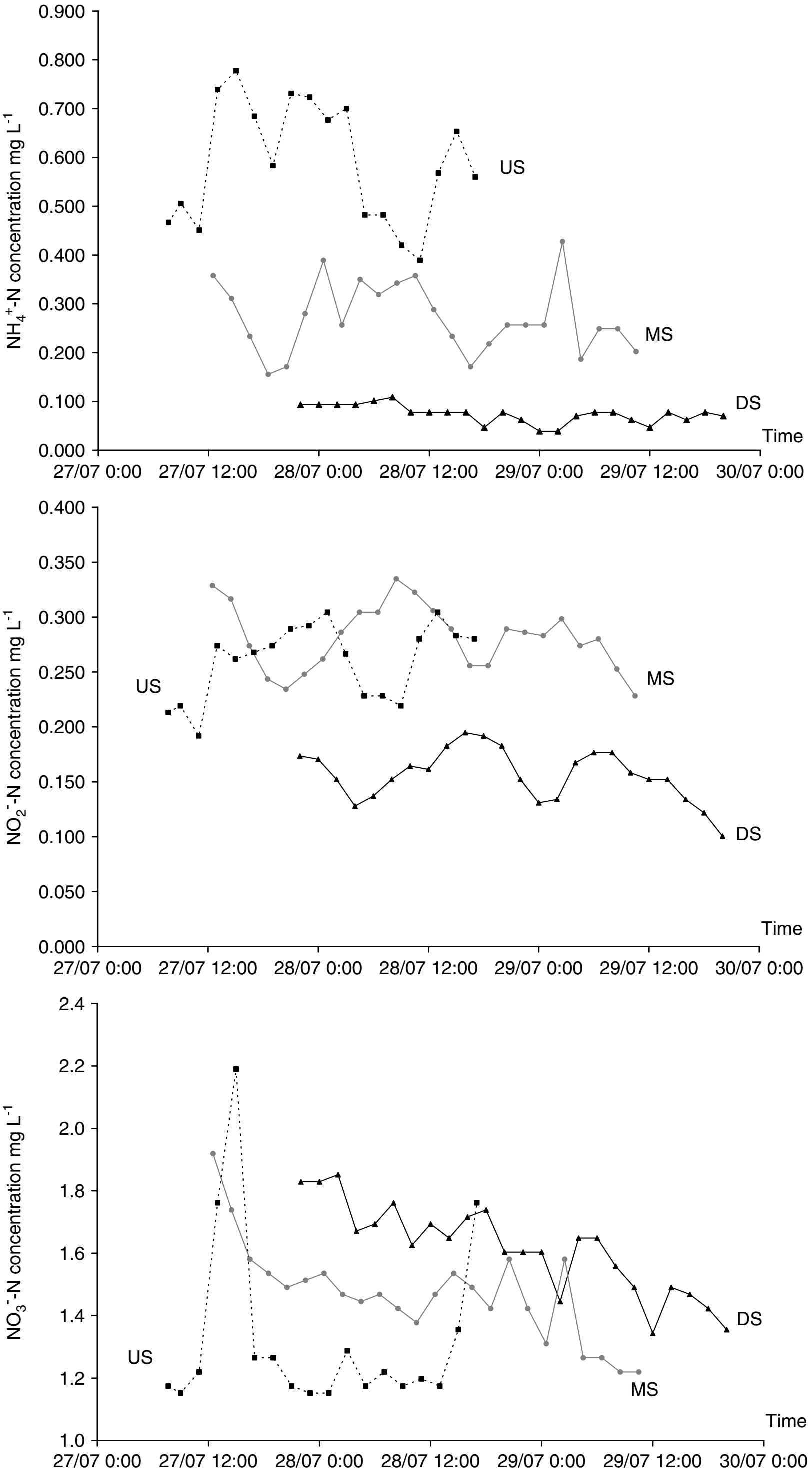

Figure 4. NH_4^+-N, NO_2^--N and NO_3^--N river concentrations for the upstream (US), midstream (MS) and downstream (DS) sampling points (sites are represented by a dashed line, grey line and black line, respectively)

(0·7 μm). NH_4^+, NO_2^- and NO_3^- concentrations were determined using standard methods with an autoanalyser: the indophenol blue method, the diazotation method and diazotation after cadmium reduction, respectively (APHA, 1985).

Calculating the mass balance

In order to estimate the intensity of in-stream processes in the studied reach of river, mass balance on inorganic nitrogen species was calculated according to the standard expression (see Burns, 1998; House and Warwick, 1998):

$$M_{\mathrm{dn}}(\alpha) = M_{\mathrm{up}}(\alpha) + M_{\mathrm{t}}(\alpha) + \Delta m(\alpha)$$

where M_{dn} (α) is the mass of constituent α at the downstream (dn) end of the reach in M T^{-1}, M_{up} (α) is the mass of constituent α at the upstream (up) end of the reach in M T^{-1} and M_{t} (α) is the mass of constituent

α from tributaries (t) in M T^{-1}. The value Δm is the mass variation in M T^{-1} for constituent α due to in-stream processes: gain or loss of mass along the reach (including dispersion, transient storage, ground water and hyporheic zone exchange, biotic and abiotic in-stream transformations, etc.), reflect the net activity of the reach for in-stream processes.

Each term M_γ ($\gamma =$ dn, up, t) in this equation corresponds to the total mass of dissolved element in individual water body crossing a site during the sampling period. Each M_γ is characterized by the concentration (c_i) and water discharge (q_i):

$$M_{(i)} = (c_i q_i + c_{i+1} q_{i+1})/2 \times \Delta t \text{ with}$$

$$M_\gamma = \sum M_{(i)} \text{ for } i = 1, n$$

with n is the number of water bodies that cross all the sites, $\Delta t = (t_{i+1} - t_i)$ is the time between two successive water bodies characterized by $M_{(i)}$. In fact, Δt corresponds to the frequency of calculation for each sampling site.

For CRT, Δt was constant and the residence time was estimated from peaks in the hydrograph for the sampling period as in House and Warwick (1998) (Figure 3).

For VRT, Δt was chosen constant for the US site (discharge and concentrations were calculated every 30 min), and Δt (or the frequency of calculation) for the other sites is variable depending of the residence time of the water between sampling sites. The residence time was variable accordingly to the results given by the hydraulic 1-D model.

In order to compare mass-balance results, Δm was integrated during the whole monitoring period and in-streams processes were expressed per area of river bottom (in mg N m^{-2} h^{-1}) as follows: Δm/mean monitoring time/river bottom area in the studied segment. The river bottom area (in m^2) was calculated by multiplying the mean wetted perimeter (in m) (simulated by the hydraulic model in space and time) by the distance (in m) between the two sampling sites concerned. Δm describes in fact "in-stream processes".

Discharge

For CRT methodology, residence times correspond to the time spent by the maximum discharge of the flood between each site. In fact, to estimate instantaneous discharge q_i with the CRT method, the constant residence time between the sites means the discharge curve at the two upstream sites can be predicted by translating the discharge curve obtained from one upstream site to downstream.

To estimate instantaneous discharge q_i with the VRT method at the three sampling sites and residence time between sites the outputs of the 1-D hydraulic model developed on the Garonne River detailed elsewhere (Sauvage *et al.* 2003) was used. The physical part of this model is composed of a 1-D unsteady hydrodynamic model, allowing the resolution of the complete Saint-Venant equations. The entry data are discharges entering the river (at the entry of the reach and lateral inflows) and morphology of the river (77 transects along the 30 km of the river). In each transect, the model can simulate temporal evolution for each time step of the Froude number (adim), width of the river (in m), cross-sectional area (in m^2), wetted perimeter (in m), mean water depth (in m), mean current velocity (in m s^{-1}), and residence time (in s) between two transects. This hydraulic model has been validated for discharges between 50 and 120 m^3 s^{-1} in the sector under study. Relative errors in the discharge estimation (from 5 to 15% according to the discharge) are greatest for low discharge because of the difficulty in obtaining precise quantitative data. This error is the same for the two methods (CRT and VRT). Instantaneous discharges are shown in Figure 3.

Concentrations

To calculate c_i for each water sample at the corresponding sampling site, simulated residence times between each site were used to calculate, by linear interpolation, the chemical data (versus time) for the river and the tributaries from measured concentrations.

Residence times between sampling points for tributaries and the confluent with the river were assumed to be negligible because the distances between the tributary sampling sites and the confluence were less than 1 km.

RESULTS

Inorganic nitrogen concentrations

At the US site, concentrations of NH_4^+ were high and varied strongly with time ranging from 0·389 to 0·778 mg N-NH_4^+ l^{-1}. At the MS site NH_4^+ decreased and after 30 km, the DS site was submitted to a relatively low level of NH_4^+ (0·074 mg l^{-1}) Table III.

NO_2^- concentrations are also variable but did not follow the trend of NH_4^+ concentrations and the highest values were monitored at the MS site. Between MS and DS sites, the NO_2^- concentrations were roughly halved (Table III). NO_3^- concentrations presented daily peaks and increased from upstream to downstream. For sites MS and DS the NO_3^- concentrations decreased with time, which may be explained by dilution from increasing discharge (Figure 4).

Residence time calculated by the two methods

The residence times for CRT (estimated from the peaks in the hydrograph of the data for the sampling period) were fixed at 4·5 h for the upstream reach and 6 h for the downstream one.

The average residence times for VRT (calculated from the discharge for each 30 min interval) were around 10 h for both the upstream and downstream reaches (Tables IV and V). As a result, the calculated mean current velocity for the mass balance duration was double for CRT (Table V).

Table III. Mean concentration (mean ± SD) during the whole sampling period for each site: US (upstream site), MS (middle site), DS (downstream site)

	NH_4^+-N (mg l^{-1})	NO_2^--N (mg l^{-1})	NO_3^--N (mg l^{-1})
US	$0{\cdot}589 \pm 0{\cdot}124$ ($n = 18$)	$0{\cdot}260 \pm 0{\cdot}034$ ($n = 18$)	$1{\cdot}325 \pm 0{\cdot}285$ ($n = 18$)
MS	$0{\cdot}272 \pm 0{\cdot}073$ ($n = 24$)	$0{\cdot}282 \pm 0{\cdot}030$ ($n = 24$)	$1{\cdot}470 \pm 0{\cdot}159$ ($n = 24$)
DS	$0{\cdot}074 \pm 0{\cdot}019$ ($n = 24$)	$0{\cdot}156 \pm 0{\cdot}024$ ($n = 24$)	$1{\cdot}614 \pm 0{\cdot}144$ ($n = 24$)

Note: *n*, number of data points.

Table IV. Mass-balance results for the two methods

	Variable residence time (VRT)			Constant residence time (CRT)		
	US site	MS site	DS site	US site	MS site	DS site
Duration of mass-balance calculations (h)	35 : 30 : 00	32 : 20 : 00	30 : 12 : 00	29 : 30 : 00	29 : 30 : 00	29 : 30 : 00
Mean discharge (with tributaries)	52·8	59·7	65·6	56·0	56·2	59·2

Discharges

Discharges at each sampling point for each step of the mass-balance calculation are shown in Figure 5, for the two methods. For the CRT method, the variation of discharge for the same step in each sampling station was low. For the VRT method, the temporal variation of discharge for the same step in each sampling station was very high. Mean discharges of tributaries (Aussonnelle, Hers, Save) correspond to respectively 0·3, 2·0, 2·7% of the Garonne discharge (with a minimum/maximum respectively of 87/214, 1080/1280, 1000/2480 l s^{-1}).

The volume of water transferred at each site during the mass-balance calculation was considered as constant as the between-site discrepancy for the two methods was less than 1%. However, the discrepancy between the two methods was around 10%: for the US site it was for the VRT method $6{\cdot}75 \times 10^6$ and $5{\cdot}95 \times 10^6$ m^3 for CRT (Table V).

Mass balance

In-stream load (Δm, in mg N m^{-2} h^{-1}) are presented in Figure 6 for NH_4^+-N and NO_3^--N for the two sub-reaches. The two methods give the same trend for NH_4^+-N: the results show a negative Δm during the whole study period but the values are quite different. For NO_3^--N the trend and the values of Δm are quite different.

The dynamics of inorganic nitrogen species were highly variable in time. NO_3^- was mainly gained but can be lost along the two reaches and NH_4^+ was always removed from the water column. Overall DIN was removed from the water column as the lost of NH_4^+ (and NO_2^- in lower river reach) is higher than gain of NO_3^- (and NO_2^- in the upper river reach) irrespective of the mass-balance method used (Figure 7). For the entire reach, removal of DIN was underestimated by 11% with the CRT method compared to the VRT method: at the scale of each reach, CRT method led to an overestimation of DIN removal of 50% in the upper reach and an underestimation of 43% in the lower river reach.

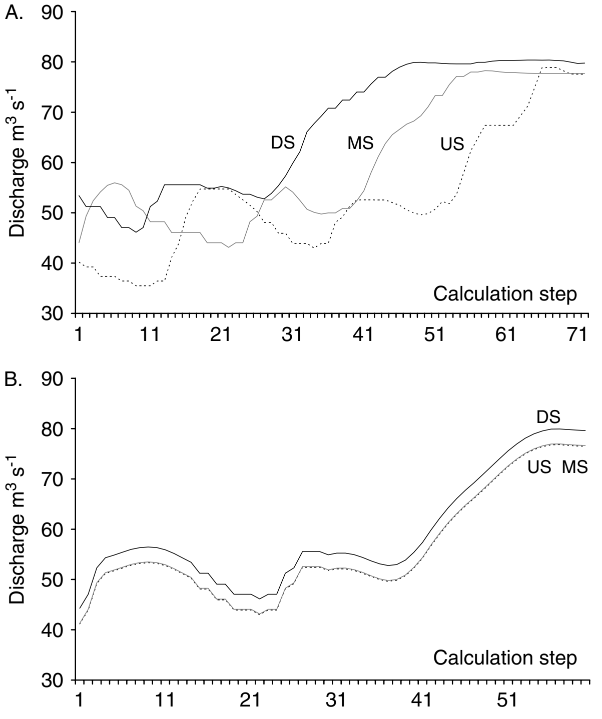

Figure 5. Discharge at each sampling point for each step of the calculation of the mass balance. US, MS and DS sampling points are represented by a dashed line, grey line and black line, respectively. (A) VRT method: one step represented half an hour only for the US site. (B) CRT method: one step represented half an hour at each site. US and MS curves are almost the same because of the low discharge variation between the sampling points

Mass-balance results for the inorganic and other features of the calculation are summarized in Tables IV and V.

DISCUSSION

Discharge and water mass balance

In mass-balance studies, obtaining a good water balance is critical because all input and withdrawal of

Table V. Mass-balance results for the two methods

	Variable residence time (VRT)			Constant residence time (CRT)		
	US to MS	MS to DS	US to DS	US to MS	MS to DS	US to DS
Distance from sampling sites (km)	13·3	16·9	30·2	13·3	16·9	30·2
Bottom area (m^2)	$1·76 \times 10^6$	$2·14 \times 10^6$	$3·90 \times 10^6$	$1·76 \times 10^6$	$2·14 \times 10^6$	$3·90 \times 10^6$
Mean residence time (h)	10:09	10:19	20:28	04:30	06:00	10:30
Mean current velocity ($m\ s^{-1}$)	0·36	0·45	0·41	0·82	0·78	0·80
Water mass balance (m^3)[a]	$6·75 \times 10^6$	$6·93 \times 10^6$	$6·77 \times 10^6$	$5·95 \times 10^6$	$5·95 \times 10^6$	$5·98 \times 10^6$
Δm NH_4^+ ($mg\ N\ m^{-2}\ h^{-1}$)	−35·6	−20·8	−27·4	−38·8	−18·1	−27·4
Δm NO_2^- ($mg\ N\ m^{-2}\ h^{-1}$)	2·8	−12·2	−5·0	1·2	−10·9	−5·5
Δm NO_3^- ($mg\ N\ m^{-2}\ h^{-1}$)	18·4	7·7	12·6	16·1	14·6	15·3
Δm DIN ($mg\ N\ m^{-2}\ h^{-1}$)	−14·3	−25·2	−19·8	−21·5	−14·4	−17·6

[a] Volume of water transferred at one site during the whole duration of the mass-balance calculation (tributaries are not taken into account).

water should be taken into account. However, in this study discharges were obtained from the downstream site gauging station and simulated by a hydraulic model where only tributaries are taken into account and water exchanges with ground water are assumed to be negligible with respect to the river discharge.

As CRTs are fixed for high flow periods, current velocities are high and residence times are low compared to field conditions during the sampling period. These discrepancies are a source of error during the mass-balance calculation.

In the CRT method, the shapes of the discharges curves are the same at all sampling points and are exclusively modified by discharges coming from the tributaries. In this case the water mass balance is obviously correct because discharges at the upstream points are extrapolated from the DS site records by subtracting the tributaries' contribution. However, with this method, a satisfactory water mass balance is easy to obtain because the same discharge record is transferred (in time) at each sampling site. With CRT, residence time is calculated from peaks in the hydrograph, the duration of the mass balance is therefore constant at each site and there is an obvious discrepancy in hydraulic parameters (discharge, mean residence time, mean current velocity) between this method and the values described by VRT methods.

CRT mean residence time is twice the one of VRT because the peak stream flows used, i.e. 80 $m^3\ s^{-1}$, are

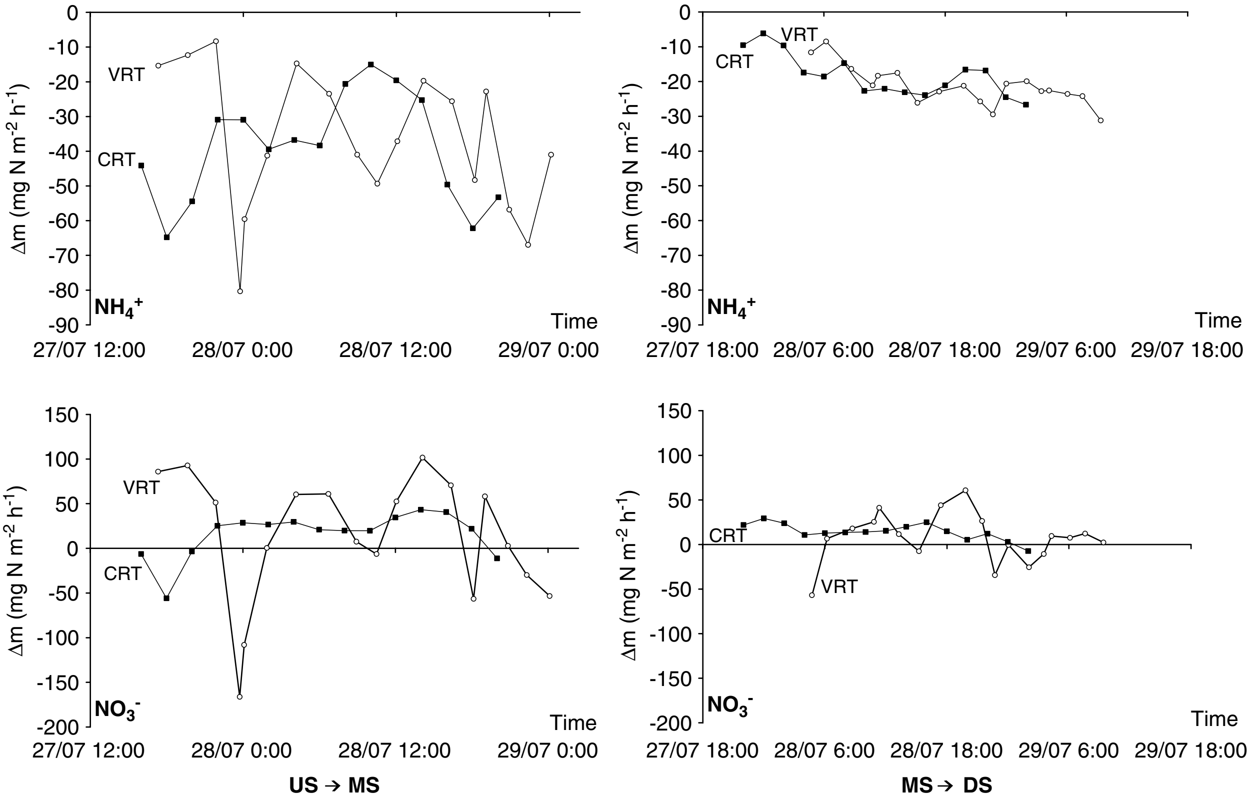

Figure 6. The values of Δm for NH_4^+ and NO_3^- for the two sections calculated for variable (open circles) and constant (dark squares) residence times. Values are integrated by 2-h periods

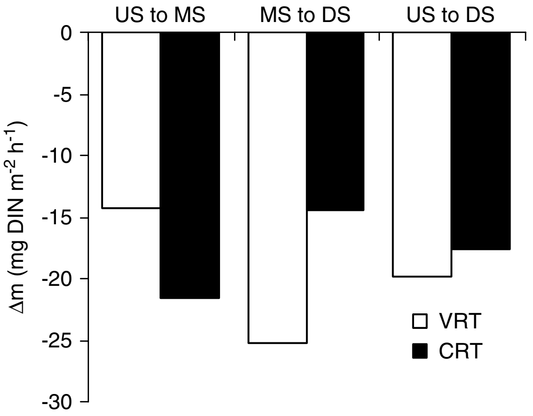

Figure 7. The values of Δm expressed per unit of bottom area for dissolved inorganic nitrogen for the two sub-reaches and the whole reach. Calculations with the two methods: white bars symbolize a VRT mass balance; black bars symbolize a CRT mass balance

faster than the actual downstream transfer of the water body taken into account in the VRT method (Tables IV and V).

In VRT, mean discharges increased along the river with the flood transfer. With higher discharge, the residence time decrease and the duration of the mass balance decrease: 35 h 30 for US site to 30 h 12 for DS site in order to integrate the same water volume at each site (without the tributaries' contribution).

Nitrogen dynamics

The dynamics of in-stream load integrated in 2 h steps show a distinct pattern between the two methods and Δm can be highly variable (flux of NO_3^- ranging from -166 to 93 mg N m^{-2} h^{-1} in a 6-h period, Figure 6). In the VRT method this high variability is mainly due to changes in discharge during the downstream transfer of a water body (discharge can be lower at the downstream site than at the upstream site for some intervals of time, Figure 5) and as a result the shape of the Δm dynamics is similar for each compound. This is particularly clear for NH_4^+ and NO_3^- in the upper reach (US to MS, Figure 6). In contrast, CRT mass balance is mainly driven by the variation of concentrations because the discharges are conserved between sampling sites and are only changed by tributaries.

Because the nitrogen dynamics calculated in this study is driven by variable discharge rather than by other biotic or abiotic processes, the whole duration of the monitoring period needs to be integrated to better assess the nitrogen dynamics of the whole reach. Therefore, nitrogen dynamics related to the circadian cycle can not be studied within these reaches with hourly disturbances of the discharge. More generally, to study the circadian cycle, the limits of the reach should be chosen such that the residence time in the studied stretch of river is short enough (<6 h in summer) for the body of water to be transferred exclusively in the dark.

Most mass-balance measurements are carried out in rivers without knowing the residence time. They often concern a great length of stream or last for a whole annual time scale, as for example in the studies of Brunet and Astin (1996), House and Warwick (1998), Garnier *et al.* (1999). More precise assessment of the mass balance during a limited time and spatial scale does not necessarily require the residence time water body in the studied section to be known; for example, when the period of time between samplings at two stations is greater than the water residence time. In that case concentration evolutions obtained for the upper reach can be compared with those obtained for the lower reach (Burns, 1998).

Moreover, when discharges are constant over the study period, it is not necessary to evaluate residence time for each water body.

However, when discharge is highly variable in a large river, the most effective method is to know the residence time for the various rates of discharge. This implies using a hydraulic model integrating the river morphology. For small rivers (less than the third order), it is possible to use conservative tracers to determine an average residence time (Stream Solute Workshop, 1990).

Another method for all streams is to have, close to each site, a gauging station in order to measure on each sampling site at the same time step the water level and the corresponding discharge variation in time.

Whatever the method, the mass balance will be determined more precisely if discharge is constant over the period studied.

SUMMARY AND CONCLUSIONS

The study of flux variations is necessary to quantify in-stream processes. If hydrological data can be obtained with the same space and time scale at each sampling point, mass balance can be calculated via fluxes. it must also be calculated for the same volume of water so the residence time between sampling sites has to be known.

It is not necessary to know time variation of residence time when discharge is constant over the study period. Moreover, for small rivers (less than the third order) without any discharge variation, it is possible to use a conservative tracer to determine an average residence time (Stream Solute Workshop, 1990).

So, the principal difficulty is to study in-stream processes in a large river under variable discharge. By comparing two methods in this study, it is shown that the use of a hydraulic model allows variable discharges to be taken into account on any reach length of a large river with any sampling time step. It also allows variation of time residence to be known depending on discharge variation which is indispensable to obtain a precise calculation of the mass balance to evaluate in-stream processes. The residence time is thus a determining factor that is often underestimated in the case of large rivers with highly variable discharges.

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