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Uncertainty of solute flux estimation in ungauged small streams: potential implications for input-output nutrient mass balances at stream reach scale

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Abstract

Input-output mass balances within stream reaches provide *in situ* estimates of stream nutrient retention/release under a wide spectrum of hydrological conditions. Providing good estimates of the mass balances for nutrients depends on precise hydrological monitoring and good chemical characterisation of stream water at the input and output ends of the stream reach. There is a need to optimise the hydrological monitoring and the frequencies of water sampling to yield precise annual mass balances, so as to avoid undue cost – high resolution monitoring and subsequent chemical analysis can be labour intensive and costly. In this paper, simulation exercises were performed using a data set created to represent the instantaneous discharge and solute dynamics at the input and output ends of a model stream reach during a one year period. At the output end, stream discharge and water chemistry were monitored continuously, while the input end was assumed to be ungauged; water sampling frequency was changed arbitrarily. Instantaneous discharge at the ungauged sampling point was estimated with an empirical power model linking the discharge to the catchment area (Hooper, 1986). The model thus substitutes for the additional gauge station. Simulations showed that 10 days was the longest chemical sampling interval which could provide reach annual mass balances of acceptable precision. Presently, the relationship between discharge and catchment area is usually assumed to be linear but simulations indicate that small departures from the linearity of this relationship could cause dramatic changes in the mass balance estimations.

Keywords: nutrients, fluxes, stream reach mass balance, rivers, ungauged stream, monitoring

Introduction

Nutrient retention and/or release in small streams have received increasing attention over the last decade. The assessment of in-stream biogeochemical processes is considered crucial to preserve the quality of continental waters across the entire stream network, from small headwaters to large rivers (Lowe and Likens, 2005). The enhancement and diffusion of these studies is supported by a solid theoretical background based on the nutrient spiralling concept (Newbold *et al.*, 1981) and a well established experimental methodological approach (Stream Solute Workshop, 1990). Studies in this field provide the basis of knowledge of stream biogeochemistry and interactions between solutes and biota. However, these results are obtained typically under base-flow conditions. From a hydrological perspective, however, biogeochemical studies conducted largely for baseflow are restricted to a small window of the entire spectrum of hydrological conditions of the stream and therefore cannot describe completely the biogeochemical functioning of its ecosystem. To overcome this restriction, alternative approaches are needed to provide a more inclusive estimation of in-stream biogeochemical processes across the wide range of flows occurring during any given year and this requires intensive monitoring programmes, both hydrological and chemical, at long and short term time scales.

An important method for exploring solute retention/release is an input-output mass balance approach in large stream reaches. This approach has already been used successfully to estimate *in situ,* under natural conditions and without manipulation of the system, the nitrate retention at the daily time scale (Burns, 1998) and at the annual time scale (Bernhardt *et al*., 2003, 2004; Houlton *et al.*, 2003). The power of this approach depends on the frequency and strategy of the sampling programme and on the accurate estimation of the hydrological parameters; the hydrological monitoring and chemical sampling have to be carried out at two sites, i.e. the two ends of the stream reach. Therefore, when precise mass balance estimates are needed at the daily scale (i.e. day–night changes, or changes during storm events) or at a seasonal or annual scale, the hydrological monitoring and chemical sampling effort must be doubled and two fully equipped hydrological and water sampling stations are necessary. As field automatic samplers have become relatively affordable, detailed long-term monitoring studies have multiplied. However, water samples for nutrient analyses collected with these automatic samplers cannot be stored in the field for long periods. This demands continuous field work, constant maintenance of field equipment and rapid response chemical analysis and raises two important issues:

- To what extent is the estimated mass balance sensitive to relatively small changes in the hydrological and chemical parameters used for the mass balance estimation?
- How can the sampling effort be reduced by varying at one end of the stream reach, the frequency of water sampling, without an undue increase of the uncertainty associated with the estimation of the annual solute fluxes and, thus, of mass balances?

Here, these questions are explored by performing a series of simulations based on a data set obtained for a hypothetical catchment in an arbitrary drainage area.

Methods

Two sampling points were selected in this hypothetical stream to consider the input and output ends of the experimental stream reach. The output end drained the entire catchment while the input end drained only a portion of it. For this study, it is assumed that, at the output end, both the stream discharge and the water chemistry were monitored continuously to obtain high-resolution data about discharge and solutes. From these data, reference solute flux estimates considered ‘exact’ were obtained. At the input end, the instantaneous discharge was estimated with a log-log empirical model relating discharge to the catchment area. The frequency of water sampling was changed arbitrarily. This empirical model was used to estimate water fluxes at different points of a stream by using only one gauging station, thereby optimising the equipment setting and economic resources (a situation which is common within field studies — only one gauging site within a given river). This model was proposed by Hooper *et al*. (1986) for a small catchment in humid regions and then used by Lawrence and Driscoll (1990) in other similar catchments.

The stream discharge and solute dynamics

The annual discharge regime in the experimental catchment was generated for the output end of the study reach using the INCA model (Whitehead *et al*., 1998). Daily data were obtained and the discharge regime ranged between 0.1 and 200 l s^{-1}. Several storm events of different magnitude were distributed within the sampling period to generate two high base-flow periods separated by a drier period with low discharge in the middle of the series (Fig. 1a).

Similarly, the solute daily series was generated assuming a positive log-log relationship between solute concentration and discharge (Moosmann *et al*., 2005) (Fig. 1b). This has been widely observed for nitrate, dissolved organic carbon (DOC) and phosphate (Butturini *et al*., 2005; Moosmann *et al*., 2005). This relationship is caused by the mobilisation during rains of reactive solutes stored in forest and riparian top soils (Sickman *et al*., 2003; McGlynn and McDonnell, 2003). To avoid creating a perfect, unrealistic log-log relationship, a random noise (ψ) parameter was introduced in the formula (Fig. 1c):

$$C_{O(t)} = \phi Q_{O(t)}^{\varepsilon} \pm \psi(Q_{O(t)}) \qquad (1)$$

where $C_{O(t)}$ and $Q_{O(t)}$ are the instantaneous solute concentration and the discharge at the output end of the stream reach, and coefficients ϕ and ε are empirical parameters. The subscript t denotes that C_O and Q_O are functions of time. In this study, $\phi = 1$ and $\varepsilon = 0.3$ and the magnitude of the random noise parameter ψ is directly proportional to discharge. Concentration values were standardised to values between 0 and 100.

In this study, it is assumed that the input end of the study reach drained 40% of the total catchment area. According to Lawrence and Driscoll, 1990, in small catchments, the instantaneous discharge at the upstream sampling point can be approximated by an empirical relationship proposed by Hooper (1986):

$$Q_{I(t)} = \alpha Q_{O(t)}^{\gamma} \qquad (2)$$

For this equation, α is the proportion of the catchment drained through the input end of the stream reach ($\alpha = 0.4$ in this case) and γ is an exponential fitting parameter.

For the situation where the temporal dynamics of solute concentrations at the input end of the stream reach ($C_{I(t)}$)

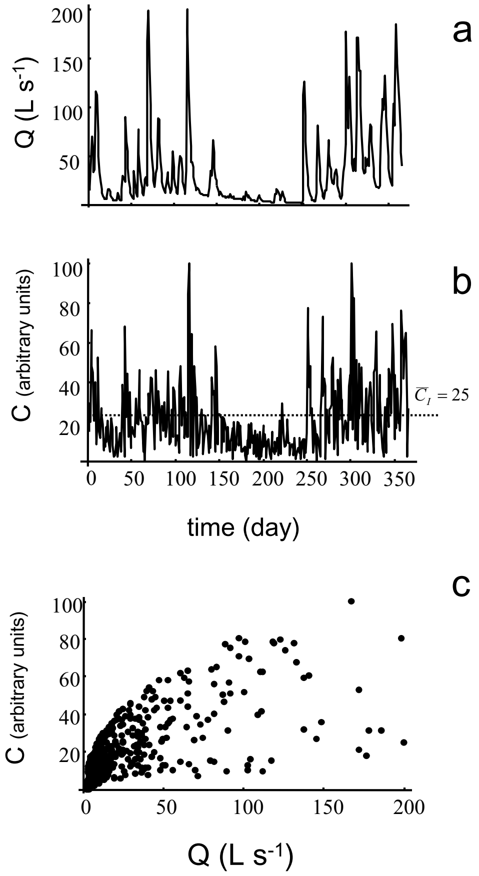

Fig. 1. *Example data set used in the analyses. Panel* a *shows the temporal dynamics of discharge. Panel* b *shows those of solute concentration (estimated from Eqn. 1) at the output end of the stream reach. Panel* c *is a scatter plot of discharge* vs. *concentration.*

were identical with those observed at the output end and the absolute concentration values at the output end were increased by a factor of β, then

$$C_{I(t)} = \beta C_{O(t)} \tag{3}$$

For this situation, β is higher than $1/\alpha$.

Stream reach mass balance model

In this study, the mass (M) of a solute is estimated over an annual time interval by the equation:

$$M_P = \sum_{t=1}^{365}(Q_{P(t)}C_{P(t)}) \tag{4}$$

For this equation, $Q_{P(t)}$ and $C_{P(t)}$ are the instantaneous (daily) discharges and concentrations at the input (I) and output (O) sampling points and groundwater (G). The annual solute mass balance in the experimental stream reach was estimated according to the equation:

$$M_O = M_I + M_G + \delta \tag{5}$$

Here, δ is the annual absolute mass balance in the stream reach and, the relative annual mass balance (η) is:

$$\eta = \frac{Input}{Output} = \frac{M_I + M_G}{M_O} \tag{6}$$

From Eqn. 6, the relative retention/release of solutes in the stream reach is:

$$\ln(\eta) = \begin{Bmatrix} \text{solute retention} & if & > 0 \\ \text{nil retention} & if & = 0 \\ \text{solute release} & if & < 0 \end{Bmatrix} \tag{7}$$

Incorporating Eqns. 2 and 3 into Eqns. 4 and 5 and assuming that the differences in stream water flow between the input and output sites of the experimental stream reach were due exclusively to groundwater discharge (i.e. $Q_{G(t)} = Q_{O(t)} - Q_{I(t)}$), then,

$$M_I = \alpha\beta\sum_{t=1}^{365}(Q^{\gamma}_{O(t)}C_{O(t)}) \tag{8}$$

$$M_G = \sum_{t=1}^{365}(Q_{O(t)} - \alpha Q^{\gamma}_{O(t)}C)_{G(t)} \tag{9}$$

The relative solute balance η depends on the value of the exponent γ, the ratios β and $C_{G(t)}$.

Simulation exercises

Simulation exercises were organised into two subsets. The first subset explores the sensitivity of the annual mass balance η to changes of the hydrological (γ) and chemical (β, $C_{G(t)}$, $C_{O(t)}$) parameters. The second subset is focused on the monitoring effort, and explores the impact of sampling frequency at the two ends of the stream reach on the annual mass balance.

At the stream reach ends, discharge and solute concentration were assumed to be measured continuously (daily) ($1/f$=1 *d*) and the estimated annual solute mass represents the 'exact' solute mass. At the input end, the discharge was estimated by using Eqn. 2. According to Lawrence and Driscoll (1990), the values of γ in small humid catchments are close to 1 but never exactly 1. These authors report that the approach to unity of γ depends on the area drained, ranging between 0.8 and 0.99 at sites draining 5.6% to 63.2% of a small catchment. To evaluate the sensitivity of the mass balance to small departures from 1 of the γ parameter, simulations were performed varying the value of γ from 0.9 to 1 while increasing the ratio β from 2.5 to 7. This ratio describes the difference between input and output ends of solute concentrations (Eqn. 3). In this exercise, the contribution of groundwater to the solute flux is assumed negligible, therefore $C_{G(t)} = 0$ and, from Eqn. 6,

$$\eta = \frac{Input}{Output} = \frac{M_I}{M_O} \tag{10}$$

Thus, the solute balance depends uniquely on the values of γ and β. Decreasing the exponent γ led to an increase in the contribution of the groundwater flux to the total water flux (Eqn. 9). Therefore, if the assumption that $C_{G(t)} = 0$ is violated, the entire solute mass balance changes. To assess the relevance of solute concentration in groundwater ($C_{G(t)}$) and of the exponent γ on the relative mass balance η, simulations were performed varying γ from 0.9 to 1 and increasing the concentration $C_{G(t)}$ from 0 to 4 times the average solute concentration at the output reach end ($\overline{C}_{O(t)} = 25$ arbitrary units).

The impact of sampling effort on the accuracy of mass balance estimation at the reach scale was evaluated by varying the frequency (f) of measurements of solute concentration at the input (f_I) and output (f_O) ends of the reach. The optimal combination was assessed between the requirement to obtain a reasonably precise relative (η) or absolute (δ) mass balance and that of reducing the sampling effort. Four hypothetical scenarios were considered on the basis of changes in sampling frequency at the two ends of the reach and their effects on mass balance estimation. The first three scenarios explored how the relative mass balance (η) was altered when the sampling frequency at the input end was lower than at the ouput end (i.e. $f_O > f_I$). The sampling frequency at the input end varied within a restricted range, while frequency at the output end was fixed. In the first scenario, water samples at the output end were collected at daily intervals, while at the input end the sampling frequency decreased from daily to monthly (Fig. 2). In the second scenario, the sampling frequency at the output end was weekly, while at the input end it gradually decreased from weekly to monthly. In the third scenario, the sampling frequency at the output end was bi-weekly, while at the input end it decreased from bi-weekly to monthly.

The fourth scenario explored how decreasing the sampling frequency affected the estimation of the absolute solute mass balance in the stream reach (δ). In this scenario, both the input and output ends were sampled with the same frequency, decreasing from daily to monthly. The absolute solute mass balance estimated with the data collected at sampling frequencies lower than daily (i.e. $2<1/f<30$ days) was then standardised with respect to the δ estimated using daily data ($\delta_{(1)}$).

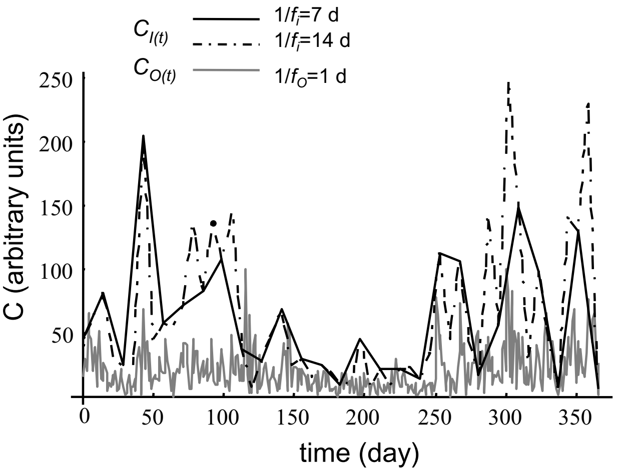

Fig. 2. *Temporal dynamics of solute concentration at the output end* ($C_{O(t)}$) *of the stream reach measured at daily intervals (gray solid line) and at the input end* ($C_{I(t)}$) *measured at weekly (solid black line) and bi-weekly (dotted line) intervals. In this example,* $C_{I(t)}=3\ C_{O(t)}$.

In each scenario, the mass balance equation (Eqn. 10) was run simultaneously 1000 times. In each run, γ ranged randomly between 0.95 and 1, while β ranged randomly between 2.5 and 5. Thus, the probability of obtaining a reasonably precise relative (or absolute) mass balance was estimated: i.e. differing by less than 20% ($P_{20\%}$) compared to the 'exact' balance. In scenarios 1 to 3, the 'exact' relative balance ($\eta_{(exact)}$) was that obtained when the sampling frequency was the same at the output and input ends (f_O=f_I). In scenario 4, the exact absolute mass balance is that estimated with daily data $\delta_{(1)}$.

When the sampling frequency was lower than daily, solute data at daily frequency were estimated using the weighted interpolation method (Alewell *et al*., 2004).

Results

THE RELEVANCE OF THE HYDROLOGY AND OF THE CHEMICAL PARAMETERS

According to Eqns. 8 and 10, when $\beta=1/\alpha$ and $\gamma=1$, the retention is nil (i.e. $\ln(\eta)=0$) and the solute behaves as a conservative tracer. Figure 3 provides evidence that small variations of γ determine dramatic changes in the relative mass balance (i.e. in $\ln(\eta)$). For instance, assuming $\beta=5$ (i.e. that the concentration at the input end is five times higher than at the output end), solute retention occurs when $\gamma >$ 0.952. Thus, when, for instance, $\gamma=0.97$, the stream reach retains 25% of the solute flux at the output end. However, a reduction of only 3% in γ gives rise to a negative mass balance, with weak solute release (21%). Although this example is an unusual case, it shows that, if the solute flux from groundwater is nil, only values of the exponent γ close to unity will lead to robust, unambiguous solute retention

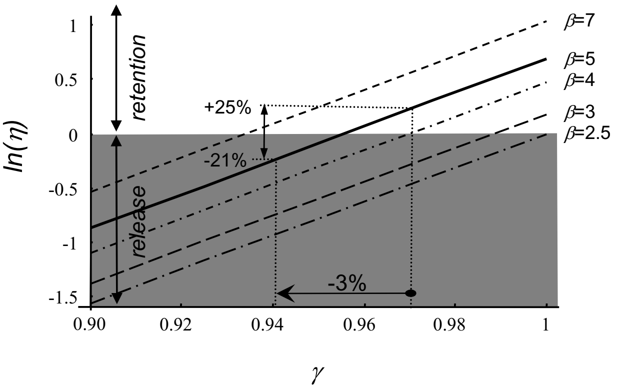

Fig. 3. *Relationship between stream reach relative mass balance (η) and the hydrological parameter γ (Eqn. 2) for varyious values of* β. *The shaded area indicates negative balances (i.e. solute release predominates over retention, Eqn. 7).*

in the stream reach. This condition becomes more restricted at lower values of β (Fig. 3). For instance, if β=3, solute retention occurs only when $\gamma > 0.989$.

Under more realistic conditions, the groundwater solute flux cannot be ignored. In this same example, when β=3, it is patent that when the groundwater solute concentration ($C_{G(t)}$>0) increases, the relevance of the exponent γ in the solute mass balance gradually decreases: when $C_{G(t)} \geq 2\overline{C}_{O(t)}$, solute retention was clearly predominant, even at relatively low β values (Fig. 3). This example illustrates the importance of accurate estimation of both $C_{G(t)}$ and γ. For instance, if β=3 and γ=0.97, the solute mass balance shifts from weak release, if $C_{G(t)} = 0.25\overline{C}_{O(t)}$, to nil when $C_{G(t)} = 0.5\overline{C}_{O(t)}$, to solute retention when $C_{G(t)} = 1\overline{C}_{O(t)}$. On the other hand, if γ=0.94, the mass balance can change from strong release, for instance when $C_{G(t)} = 0.25\overline{C}_{O(t)}$, to no retention when $C_{G(t)} = 1\overline{C}_{O(t)}$ (Fig. 4).

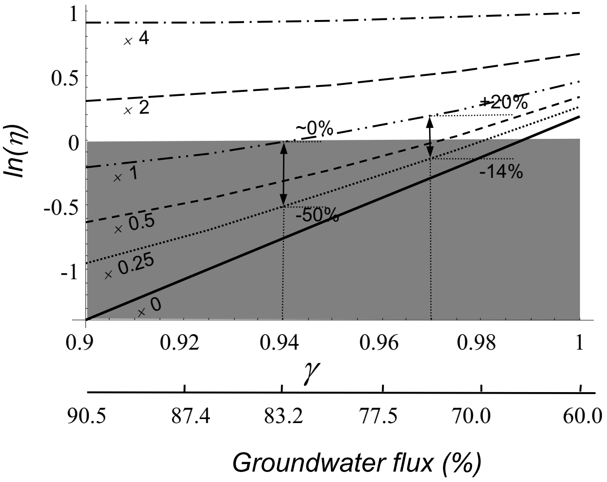

Fig. 4. *Relationship between stream reach relative mass balance (η) and the hydrological parameter γ (Eqn. 2) under different values of solute concentration in groundwater ($C_{G(t)}$, where, $0 \leq C_{G(t)} \leq 4\ \overline{C}_{O(t)}$). In these simulations,* β=*3. The shaded area indicates negative balances (i.e. solute release predominates over retention, Eqn. 7).*

THE RELEVANCE OF THE WATER MEASUREMENT STRATEGY

Figure 5 shows an example of scenario 1 and illustrates the impact on the estimates of relative solute balance (η) of an increase in water sampling interval at the input end of the stream reach. It indicates that when f_I/f_O> 10, most estimates of relative solute balance depart by more than 20% from the exact balance.

The random simulations of scenarios 1–3 indicate that estimates of the relative mass balance approached the exact balance (i.e. $0.8 \leq \eta/\eta_{(exact)} \leq 1.2$) with high probability (i.e. $P_{20\%}$ > 55%) when water samples were collected daily at the output end, while, at the input end, samples were collected at least every 10 days (Fig. 6a). At lower sampling frequencies (i.e. scenarios 2 and 3, Figs. 6b and 6c, respectively), the probability of estimating a reasonably precise mass balance is strongly decreased (in most cases it was lower than 40%). Therefore, random simulations under scenarios 1 to 3 clearly advise avoiding the estimation of η when water measurements at one reach end are collected less frequently than at the other end. This is because the approximate relative balance could under- or over-estimate the retention (or release) in the stream reach and, therefore, provide unrealistic results. The results clearly indicate the need to estimate the relative mass balance using data only from dates when both ends had been sampled (i.e. $1/f_O = 1/f_I$). This condition is described in scenario 4. Figure 7 illustrates the impact on the absolute mass balance (δ) of decreases in the sampling frequency at both reach ends. This example shows that when sampling less frequently than every 10 days, most of the estimated δ values will be at least 20% higher (or lower) than the exact δ value ($\delta_{(I)}$). The random simulations of scenario 4 show that the relative mass balance estimate (η) changes negligibly with decreases in water sampling frequency (i.e. $\eta/\eta_{(exact)}$ is always ~1). However, there is a very high probability of obtaining a good absolute mass balance ($P_{20\%}$>95%) when sampling is performed every 5 days or more frequently. This probability decreased to ~72% when water samples are collected every 5–10 days and oscillated widely between 70% and 2% with less frequent sampling (Fig. 8).

Discussion

Knighton (1998) contends that the power function is an extremely useful formulation for empirical hydrogeomorphological studies. For instance, the power function

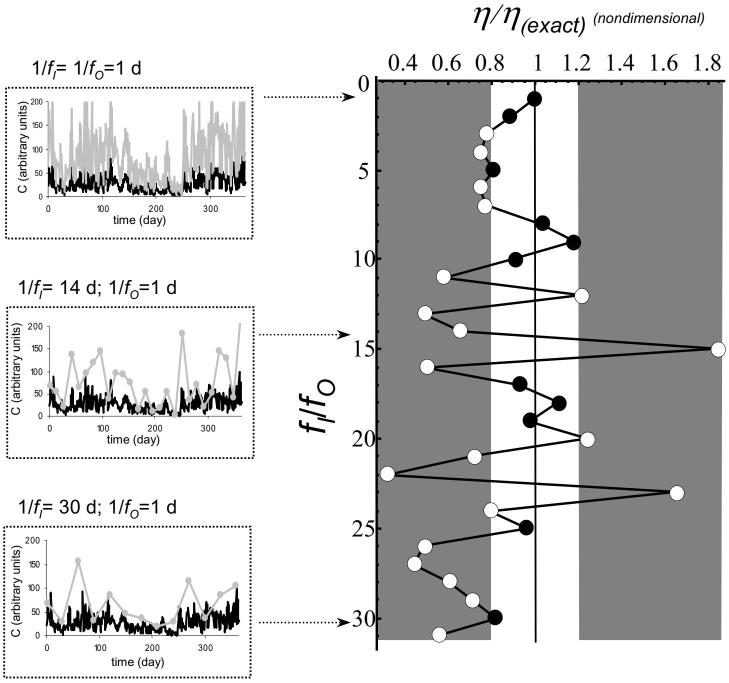

Fig. 5. *Example of the impact of changes in sampling frequency at the input end of the stream reach (left plots) on the estimation of relative solute mass balance (right large plot). In this example,* $\alpha=0.4$; $\beta=3$ *and* $\gamma=1$. *The relative solute mass balances* (η) *were standardised with respect to the exact balance* ($\eta_{(exact)}$). *Open circles represent* η *estimates which are 20% higher (or lower) than the exact balance* $\eta_{(exact)}$.

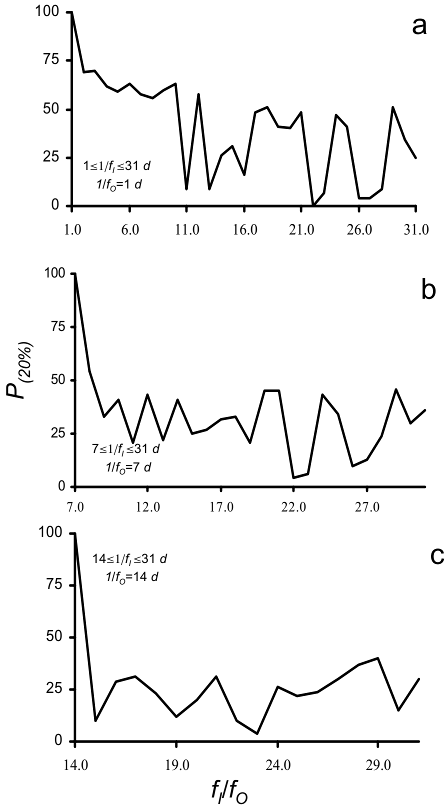

Fig. 6. *Percentage of relative mass balances* (η) *estimates which differ by less than 20% compared to the exact balance, as increasing the water sampling interval between the input and output ends. In panel* a, *the sampling frequency at the output end was set as daily* ($1/\mathrm{f}_O=1$ *day), while at the input end, the sampling frequency decreased from daily to monthly* ($1\leq1/\mathrm{f}_I\leq30$ d). *In panel* b: $1/f_O=7$ *days and* $7\leq1/\mathrm{f}_I\leq30$ *days. In panel* c: $1/\mathrm{f}_O=14$ *days and* $14\leq$£$1/\mathrm{f}_I\leq30$ *days. In these simulations, Eqn. 8 was run simultaneously 1000 times and the parameters* γ *and* β *ranged randomly between 0.95 and 1, and between 2.5 and 5, respectively.* $\mathrm{C}_G(\mathrm{t})=0$.

fits reasonably well the relationships between stream discharge and channel morphology and current velocity (Leopold *et al*., 1964) and the relationships between the area of catchment and the length of the main channel within the catchment (Maritan *et al*., 1996). Similarly, Leopold *et al.* (1964) have reported that flood discharge (Q_f) is highly related to drain area (A), following:

$$Q_f \sim A^b \tag{11}$$

where b is an empirical exponent varying between 0.65 and 0.8, which approaches to 1 at mean annual flows in humid regions. Clearly, the model proposed by Leopold and colleagues (1964) fits data from large catchments and provides rough water fluxes which are grossly inaccurate for the present purposes. On the other hand, the empirical power model proposed by Hooper (1986) is designed from and for small catchments in humid regions, but it cannot be assumed applicable in all systems. Furthermore, in this model it is highly improbable that a unique value of the exponent γ in Eqn. 2 can describe, satisfactorily, the relationship between discharge and catchment area under

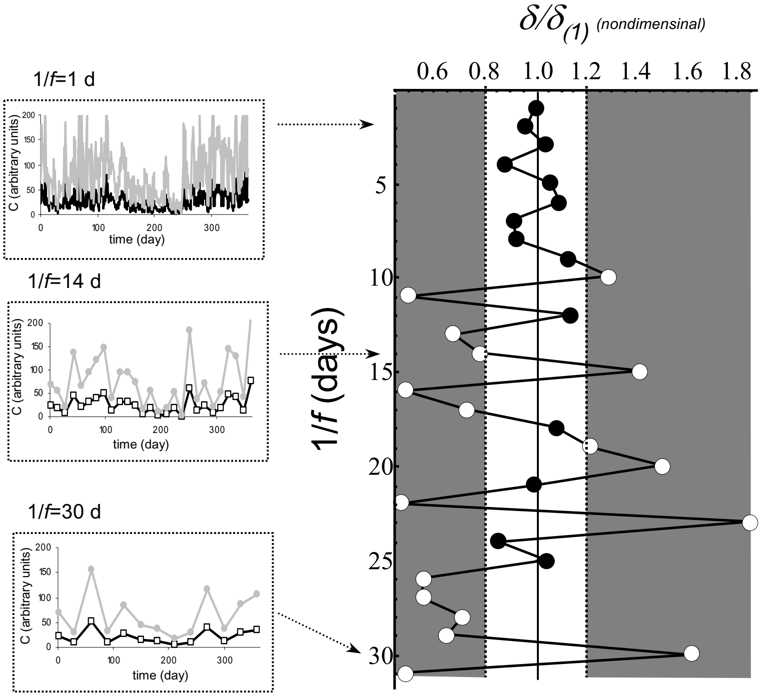

Fig. 7. *Example of the influence of the sampling frequency (see left plots) on the estimation of the absolute solute mass balance (large right plot). In this example,* $\alpha=0.4$*;* $\beta=3$ *and* $\gamma=1$*. The absolute solute mass balances (*δ*) were standardised with respect to the exact balance (*$\delta_{(1)}$*). Open circles represent estimates which are 20% higher (or lower) than the exact balance* $\delta_{(1)}$*.*

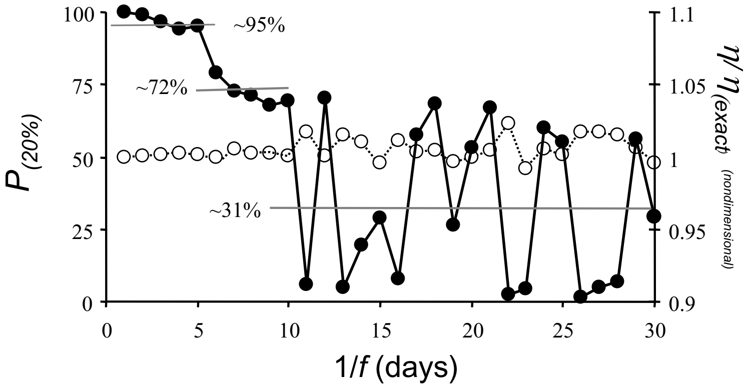

Fig. 8. *Percentage of absolute mass balances (*δ*) estimates which differ by less than 20% compared to the exact difference (*$\delta_{(1)}$*), as the water sampling frequency is decreased at both reach ends. In these simulations,* γ *and* β *ranged randomly between 0.95 and 1, and between 2.5 and 5, respectively, while* $C_{G(t)}=0$*. The right axis shows the ratio of the relative mass balance* η *over the exact mass balance (i.e. obtained with daily measurements,* η_{exp}*) (open circles).*

the entire range of hydrological conditions occurring during a given year. Nevertheless, the description contained in these power models suggests that, when necessary to estimate solute fluxes in ungauged points, it may be pertinent to verify, accurately, the correlation existing between stream flows at different sampling points and under different hydrological conditions, rather than assume *a priori* that a simple linear relationship exists between discharge and catchment area (Bernhardt *et al*., 2003; Houlton *et al*., 2003). According to Lawrence and Driscoll (1990), the linear approximation can lead to errors due to spatial heterogeneity of precipitation, local topography or soil–vegetation properties and/or perturbations. The simulations provided in the study presented here for γ close to 1 show that relatively small departures from unity can cause dramatic changes in the mass balance estimation of the stream reach. Such changes may easily lead to the formulation of divergent conclusions about the magnitude of the in-stream processes.

The groundwater flow is the main water input in small and large catchments under base flow conditions. Equation 2 provides a tool for estimating the groundwater contribution to the total stream reach discharge. Accurate estimation of solute concentrations in groundwater is essential to estimating correctly the contribution of groundwater to the mass balance of the stream reach. Correct descriptions of solute concentration in groundwater are difficult to obtain and the assumption of constant solute concentration in time and space of both groundwaters and hillslope waters is most often arbitrary. Thus, high resolution good-quality data on the chemistry of ground and hillslope waters are needed to evaluate the uncertainty of their estimations (Bishop *et al*., 2004; Joerin *et al*., 2002, Hornberger *et al*., 2001; Genereux, 1998; Bazemore, 1994; Hooper *et al*., 1990; Neal e*t al*., 1990).

Often, research programme time scales influence the degree of accuracy of description of groundwater chemistry. In short-term studies performed under base flow conditions (Burns, 1998) relatively few measurements may be adequate. However, these data will not be adequate for long-term studies, which integrate a wide spectrum of hydrological conditions (Bernhardt *et al.*, 2003).

High discharge episodes contribute a large proportion of the annual solute flows. Experimental studies have revealed that, under high discharge conditions, streams have a reduced capacity for retaining nutrients (Butturini and Sabater, 1998). Hydrological studies at the catchment scale based on the mixing model approach have demonstrated that stream storm flows may be associated with multiple inputs: rapid hillslope water (overland flow, subsurface flow through soil macropores, throughfall and direct channel interception) and slow groundwater and subsurface soil water inputs (Chanat and Hornberger, 2002). Inevitably, catchment end-member mixing models represent a simplification of the hydrological processes intervening (Kirchner *et al*. (2000). Nevertheless, this model should be considered to improve the mass balance model (Eqn. 5), especially for long-term studies that integrate a wide range of hydrological conditions. As a first step, at least one additional input component should be added, i.e.

$$M_O = M_I + M_G + M_H + d \tag{12}$$

where H refers to the hillslope water flowing through organic soil before entering the stream water. This hydrological component is considered negligible at baseflow (i.e. $Q_{H(t)}$=0). However, its relevance may increase noticeably during storms, especially for those solutes that are leached from forest and riparian soils, such as nitrate and dissolved organic carbon; these are often more concentrated in hillslope waters than in the stream water (i.e. $C_{H(t)} >> C_{I(t)}$). Unfortunately, adding a new term to the formulation implies a new source of uncertainty, due to the spatial and temporal variability of $C_{H(t)}$.

Most of the current scientific literature on catchment hydrology and biogeochemistry is based on streams draining catchments of a few hectares in humid regions. Bernhardt *et al*. (2003, 2004) give one example of the utility of the stream reach mass balance approach. Using monthly measurements, they demonstrate the ability of small streams in humid regions to damp anomalous nitrate inputs to streams from their catchments. According to Hall (2003), these results have established for the first time that in-stream processes affect catchment nitrogen exports. Findings from these studies are relevant to the whole scientific community interested in freshwater and terrestrial biochemistry (Jackson and Hedin, 2004). They could impinge substantially on researches approaching the study of the self-purifying capacity of lotic systems and the management of water quality of those streams which may be affected by long-term point-source nitrogen inputs. From a basic research perspective, the stream reach mass balance approach is of value to researchers interested in comparing nutrient retention estimates obtained under experimental conditions with those obtained without having to interfere with the natural system.

There is a large literature on the effects of data availability on the quality of solute flux estimation in large catchments (Marcé *et al*., 2004). In small catchments, Alewell *et al*. (2004) have shown that a bi-weekly sampling monitoring programme provides a reasonably accurate picture of solute variability and therefore an accurate annual mass balance estimation for time series longer than a year. Clearly, no unique monitoring programme is adequate to address all scientific questions in all systems (Alewell *et al*., 2004). Kirchner and colleagues (2004) have called for more high frequency (at daily or hourly intervals) chemical sampling monitoring programmes. They argue that, as knowledge of the hydrochemical behaviour of catchments increases with the high-frequency sampling programmes, new research lines are emerging. Simulations performed in this study suggest that research programmes interested in obtaining accurate annual estimates of relative (η) and absolute (δ) mass balances at the stream reach scale should plan to collect water samples at both sampling sites every 10 days or more frequently. This sampling strategy is more demanding and resource consuming than that suggested by Alewell *et al.* (2004). The requirement for estimating an accurate mass balance in the stream reach may well lead to minimising the errors in the mass flux estimations at the two sampling sites and, therefore, to increasing the sampling frequency compared to the bi-weekly sampling monitoring programme proposed by Alewell and colleagues (2004). Nevertheless, an acceptably accurate relative mass balance estimation can be obtained even using monthly data, as long as data are collected concurrently at both sites with equal frequency.

Conclusion

Accurate annual estimates of the stream reach mass balance can be obtained using time series of chemical data with sampling dates spaced every 10 days or less. However, when stream discharge needs to be estimated for an ungauged point, the uncertainty of the solute flux estimates and therefore of the entire mass balance needs to be reduced. Thus, it is strongly recommended to verify accurately the correlation between stream flows at different sampling points under the wider spectra of hydrological conditions: that a simple linear relationship always exists between discharge and catchment area should not be assumed. Indeed, a small departure from linearity can cause substantial changes in the mass balance estimates.

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