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Compared performances of different algorithms for estimating annual nutrient loads discharged by the eutrophic River Loire

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Abstract:

Good estimates of pollutant fluxes are required for Earth systems sciences and water quality management. The gradual accumulation of water quality data records over the past few decades has increased the value of these data for examining long-term trends. On many major rivers, however, infrequent sampling of most pollutants makes flux estimates and their analysis difficult. This paper explores the performance of different methods for estimating nutrient fluxes. The objective is to assess the accuracy (bias) and precision (dispersion) of annual nutrient fluxes based on monthly sampling, which is the frequency with which 80% of French water quality surveys have been carried out since 1971. The study is based on a data set of nutrient concentrations surveyed at high frequency during a 5 year pilot study (1981–85) at the Orléans station in the middle reaches of the River Loire, France. The mean specific fluxes were 641 (nitrate-N), 96 (total-P) and 37 kg year^{-1} km^{-2} (orthophosphate-P). For each year, the data set was then 'resampled' by randomly simulating 12 sampling dates. 100 simulated monthly samplings were generated, upon which seven estimation methods were tested. The evaluations indicate that, when concentrations of specific substances in large rivers exhibit seasonal variation, a simple method based on linear interpolation between samples taken at approximately monthly intervals is advocated. With the monthly sampling interval, the precision (confidence level of 95%) of annual nutrient fluxes obtained by the appropriate methods was 13% for nitrates, 20% for total-P, 26% for orthophosphates, and 34% for particulate-P. The frequency of water quality surveys required to obtain an annual nutrient flux with 10% precision was around 15 days for nitrate, 10 days for orthophosphate-P and total-P, and about 5 days in the case of particulate-P. Copyright © 2004 John Wiley & Sons, Ltd.

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INTRODUCTION

The demand for riverine flux estimates is growing for Earth systems sciences and water quality management in order to: (i) evaluate mechanical and chemical denudation rates; (ii) estimate output from catchment ecosystems and source apportionment between point and diffuse sources (Behrendt, 1993; Kronvang *et al*., 1996; Lidén *et al*., 1999); (iii) evaluate nutrient and pollutant losses from land to sea for international commissions (e.g. OSPARCOM: Oslo–Paris Commission; HELCOM: Helsinki Commission) (Laznik *et al*., 1999); (iv) carry out a long-term analysis of annual flux in response to changes in land use activities and atmospheric deposition (Heathwaite *et al*., 1997; Littlewood *et al*., 1998; Grimvall *et al*., 2000); (v) evaluate riverine carbon fluxes to oceans (Meybeck, 1982). This demand has directed attention to the accuracy of flux calculation techniques and to the reliability of available information (Walling, 1977a; Walling and Webb,

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1981; Stevens and Smith, 1978; Dolan *et al.*, 1981; Ferguson, 1987; Olive and Rieger, 1988; Thomas, 1988; Burn, 1990; Littlewood, 1992; Phillipps *et al.*, 1999; Horowitz, 2003).

The total load over a given period T, such as a hydrological or calendar year, is given by integration of instantaneous flux, i.e. the product of concentration C and discharge Q. In practice, continuous and exact measurement of the streamflow and concentration required to calculate mass fluxes is not possible, principally due to lack of continuous concentration records. River flow is recorded with high temporal resolution, but in some circumstances uncertainty in streamflow data can be appreciable (ISO, 1997). However, concentration data are still commonly the limiting factor on the quality of river flux estimates. Uncertainty may, therefore, come from both the measurement of the concentration and the temporal integration of instantaneous fluxes. This paper will focus on the latter issue.

A practical means of evaluating the flux integral equation over a period T is to approximate it by the sum

$$\text{Flux} = \sum_{i=1}^{T/\delta t} C_i Q_i \delta t \tag{1}$$

with a fixed sampling interval δt shorter than the minimum time over which discharge or concentration can vary significantly. This will be a matter of minutes to months depending on water quality indicators, river sources and pathways, and river size. Multiple categories of concentrations versus discharge relationships have been described, particularly for total suspended solids (TSS; Williams, 1989; Meybeck *et al.*, 1992), and for nitrogen and phosphorus (Stevens and Smith, 1978; Behrendt, 1993).

Regular water quality surveys are generally based on a fixed sampling frequency. The most common frequency is monthly; although a bimonthly strategy is increasing, it is not adapted to the specific temporal variability of each indicator, which depends on various control factors, including the basin size (Chapman, 1992; Meybeck *et al.*, 2003).

The best way of using discrete concentration data sets and continuous discharge records for flux estimation is not clear, and several methods have been proposed. The main methods have been evaluated previously by empirical studies (Walling and Webb, 1981; 1985; Littlewood, 1995), and by theoretical and statistical studies (Ferguson, 1987; Clarke, 1990). However, many of these studies focus mainly on the assessment of suspended sediment loads (Crawford, 1991; Philipps *et al.*, 1999; Horowitz, 2003).

The reliability of any estimation method is usually assessed in terms of both the accuracy (systematic error) and precision (degree of dispersion) of a particular sampling strategy. Accuracy measures the distance and direction of the estimated flux distribution centre from the reference value. Precision reflects how tightly the distribution of the estimate is clustered about its centre (Walling and Webb, 1981).

The specific variability of suspended sediment concentrations, characterized by marked and rapid fluctuations during flood events, leads in most instances to serious underestimation (bias) and lack of precision of the load in the absence of detailed records (in the case of infrequent samples) (Walling and Webb, 1985). Nutrient concentrations are very rarely surveyed at high frequency (i.e. daily); therefore, there are few published evaluations of nutrient load estimation methods. For nitrates, Littlewood (1995) investigated the performance of two mass-load algorithms and sampling frequencies based on a generated time series of synthetic concentrations for two hypothetical concentration behaviours (increase and decrease with flow).

Our study is based on a 5 year data set of near-daily concentrations (nitrate, orthophosphates, total phosphorus (total-P)) surveyed during a pilot study at the Orléans station in the highly eutrophic middle Loire, France. Based on these data, the study had the following objectives:

1. To explore the performance and provide indicative levels of accuracy and precision of different methods of annual river flux estimation for these nutrients.
2. To assess the degree of reliability of annual nutrient flux estimates based on monthly sampling, i.e. the frequency of 80% of French water quality surveys since 1971. Estimates of relative errors in fluxes were,

therefore, targeted at this specific frequency in order to analyse long-term trends in fluxes at Villandry station from 1976 to 2000.
3. To optimize the sampling frequency when a particular level of precision is required.
4. To explain flux estimate errors according to the temporal behaviour of the concentrations and hydrological conditions, and establish the flux duration curves for these nutrients.

THE RIVER LOIRE CATCHMENT AND ORLÉANS STATION DATABASE

The Orléans station (36 970 km^2), 633 km from the source, is typical of the middle Loire. It drains 31 000 km^2 of the upper Loire and Allier catchments (of which 42% is forested, 21% is cultivated and 35% is pasture) and 5970 km^2 of the middle Loire (80% arable and pasture). Over 2 million people live in the drainage area. The population is mainly distributed near the Allier and Loire rivers (St Etienne, Clermont Ferrand, Nevers) and rarely spreads outside the valleys (population density <25 km^{-2}). The water quality station is situated upstream of the city of Orléans. The Loire is highly eutrophic here, with chlorophyll peaks exceeding 150 $\mu g\ l^{-1}$, daily dissolved oxygen variations up to 12 $mg\ l^{-1}$ and daily pH variations up to one unit (Crouzet, 1983; Moatar *et al*., 1999; Moatar *et al*., 2001). The hydrological regime of the Loire is nivo-pluvial and is characterized by (i) a summer low flow during two or three warm months, (ii) a winter high flow, generally from December to February with 1 or 2 weeks of high floods, and (iii) a secondary high flow period in spring related to the snow melt in the Massif Central.

Two nutrient data sets were used: (i) a pilot study at Orléans from 1981 to 1985 carried out by the Loire Bretagne water authority (AELB) with frequent sampling, i.e. a high number of analyses per year (125 to 264 for nitrate, average 182; 125 to 207 for orthophosphate, average 165; 71 to 135 for total-P, average 103); (ii) the 1986–99 regular water quality survey (Reseau National de Bassin, RNB) carried out jointly by the State Ministry of the Environment and the AELB, with monthly to bimonthly data from 1986 to 1994 and weekly data since 1995. In the Loire Bretagne basin, the water quality survey started in 1971 and was carried out at key stations, with 6 to 12 samples per year from 1971 to 1987 and 12 to 18 between 1987 to 1992, depending on the station, then 18 for all key stations after 1992.

Particulate phosphorus (particulate-P) was calculated as the difference between total-P measured in unfiltered water and orthophosphate phosphorus (orthophosphate-P). As such, the particulate-P estimate has a greater analytical error of around 15% (5% for orthophosphate-P and 10% for total-P).

During the 1981–85 period, the measurements for nitrate and orthophosphates were carried out either daily (50%) or every other day (40%). The sampling strategy for total-P used larger intervals: 2 days for 50% of measurements; 3 to 4 days for 40% of measurements. In most cases, when daily nitrate measurements were available for more than four consecutive days, variations over these periods were monotonic, as in October–November 1985 (Figure 1). Nitrate peaks can be observed over periods of 8–10 days without marked water discharge variations. Very short peaks (5 days), like the one observed in April 1985, are exceptional. Therefore, we believe that linear interpolation of the missing days is justified to complete the database at a daily frequency.

From these basic data we have thus reconstituted a daily reference set of nutrients at Orléans using linear interpolation between analysed samples. After careful screening of basic data we discarded some sampling years, such as 1983 for nitrate and 1985 for total-P and particulate-P, because high-frequency data were missing for some periods. For the other years the missing data periods did not exceed 10 days, usually during periods of stable flow, i.e. of relatively stable nutrient concentrations.

METHODOLOGICAL APPROACH

The full chain of data treatment for each of the four nutrients (nitrate-N, orthophosphate-P, total-P and particulate-P) is presented in Figure 2 with the following steps:

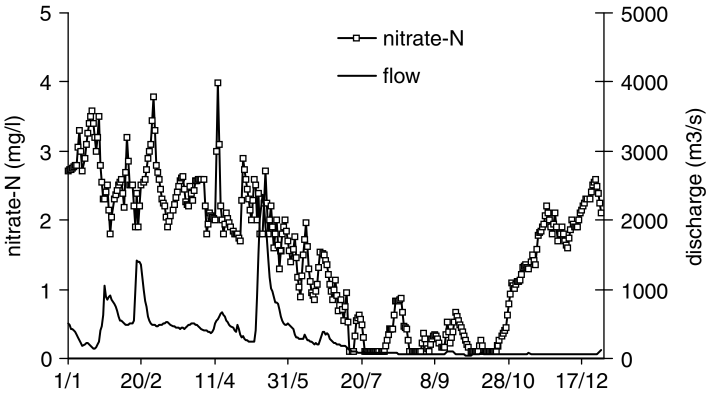

Figure 1. Evolution of nitrate concentrations and corresponding daily mean flow for the Loire at Orléans in 1985. Exceptionally, water discharge in November and December was regulated by upstream reservoirs

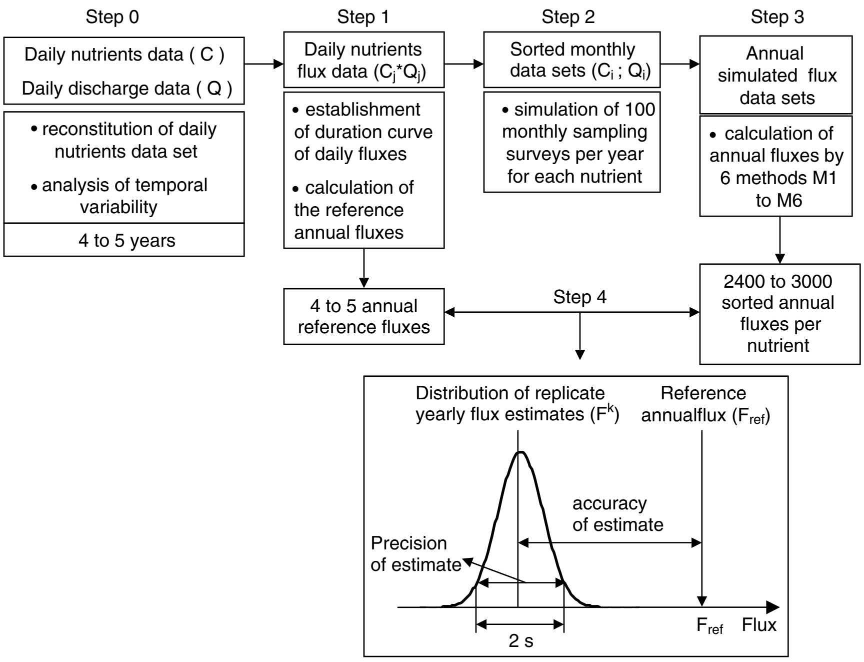

Figure 2. Flow chart of empirical testing of six calculation methods on sorted monthly data sets for each nutrient (NO_3^-, PO_4^{3-}, total-P, particulate-P)

Step 0 Reconstitution of daily concentrations of each nutrient by linear interpolation of sub-daily water quality surveys over 4 or 5 years (1981–85); analysis of the temporal variability of nutrients.

Step 1 Constitution of the daily nutrient flux data set and of the reference annual fluxes for 4 to 5 years based on Equation (1); establishing duration curves of daily fluxes.

Step 2 Simulation of 100 monthly sampling surveys per year (12 sorted samples × 100 replicates × 4 or 5 years, depending on the nutrient).

Step 3 Calculation of annual fluxes by six different methods on the simulated monthly surveys (100 replicates × 6 algorithms × 4 or 5 years).

Step 4 Comparison of calculated annual fluxes with the annual reference fluxes to estimate precision and accuracy in relation to calculation methods.

The temporal behaviour of nutrients and concentrations versus water discharge relationships (step 0), although not the main target of this study, was analysed in order to: (i) establish the origins (point or diffuse sources) of nutrients; (ii) test the influence of biological activity in this eutrophic river.

The duration curves (step 1) were determined from the daily nutrient flux data, e.g. the 5×365 daily fluxes were ranked in decreasing order then cumulated in order to determine the duration curves of fluxes (Walling 1977b, 1984; Meybeck *et al.*, 2003). The duration curves express the percentage of total flux, as calculated from daily fluxes within a given period, carried during 1%, 2%, 5%, 10% etc. of the elapsed time.

Generation of the monthly surveys (step 2) was based on the preliminary analysis of the existing RNB survey (1981–99), which showed that the samples were preferentially taken during the first 2 weeks of each month. The mean interval between two consecutive samples was 30 days with a standard deviation of only 4 days. The first day of simulated sampling was, therefore, generated in the first month by a normal law (mean 10 days, standard deviation 6 days). The sampling interval for the following months was determined by a normal law (mean 30 days, standard deviation 4 days).

The flux calculation methods are listed in Table I (step 3). All these methods, except method 6, have been discussed and investigated for several sampling intervals by Walling and Webb (1981, 1985) for the rivers Creedy and Exe (UK) to estimate suspended sediment load. These methods involve either interpolation (methods 1 to 5) or extrapolation algorithms (methods 6 and 7). Interpolation procedures essentially involve the assumption that the values of concentration or discharge obtained from instantaneous samples are representative of a much longer period of time. Method 7 uses an empirical relationship between C and Q of type $C = aQ^b$ (a rating curve) to predict unmeasured concentrations in Equation (1) at the desired short interval dt. This requires the log-transformation of concentration and discharge data prior to analysis (Horowitz, 2003). The conversion of results from log-space to arithmetic-space induces underestimations of both sediment and solute river fluxes by a factor increasing with the scatter around the rating curve (Ferguson, 1986). A correction factor derived from statistical arguments is proposed when sediment or solute rating curves are fitted by least-squares regression of logarithmically transformed data (Ferguson, 1986). In our case, the rating curves between nutrients and river discharge were poorly defined ($R^2 < 0{\cdot}3$) on 200 pairs of transformed variables, except for nitrate ($R^2 = 0{\cdot}5$) for which method 7 was adopted. The sorted monthly data sets (step 2) were used to analyse the concentration versus discharge relationship for nitrate for the 100 replicates for the whole period (4 years) and for two different seasons, i.e. summer (May to October) and winter (November to April).

In addition to Walling and Webb's (1981, 1985) approach, we introduced method 6, which assumes a linear relation between consecutive measured concentrations, to check its applicability to variables that display seasonal variability.

Replicated flux estimates were generated, then compared with the annual reference loads F_{ref} for each nutrient, to determine the relative errors for each simulation calculated as a percentage of the annual reference load (Step 4, Figure 2). For each chosen calculation method, the distribution of these relative errors ε provided measures of accuracy and precision. The mean of the relative errors $\bar{\varepsilon}$ was taken as a measure of accuracy, and the standard deviation s gave a measure of precision. We chose the 95% confidence level corresponding to the interval $[\bar{\varepsilon} - 2s; \bar{\varepsilon} + 2s]$. Different authors have shown an inverse relationship between accuracy and precision when comparing the estimates from several methods (Walling and Webb, 1981), and have proposed as evaluation criterion the root-mean-square error (RMSE), which combines bias and precision, calculated as follows (Dolan *et al.*, 1981):

$$\text{RMSE} = \sqrt{\bar{\varepsilon}^2 + s^2}$$

This criterion is used in this paper in addition to the two statistical concepts.

Table I. Flux estimation procedures

Method	Name	Numerical procedure
M1	Product of means of sampled C_i and Q_i	$\text{Flux} = K\left(\sum_{i=1}^{n}\frac{C_i}{n}\right)\left(\sum_{i=1}^{n}\frac{Q_i}{n}\right)$
M2	Mean of instantaneous fluxes $F_i = C_i * Q_i$	$\text{Flux} = K\sum_{i=1}^{n}\frac{C_iQ_i}{n}$
M3	Constant concentration hypothesis around sample	$\text{Flux} = K'\sum_{i=1}^{n}C_i\overline{Q_{i,i-1}}$
M4	Product of means of sampled C_i and annual discharge $\overline{Q}$	$\text{Flux} = K\overline{Q}\left(\sum_{i=1}^{n}\frac{C_i}{n}\right)$
M5	Flow-weighted mean concentration	$\text{Flux} = K\frac{\sum_{i=1}^{n}C_iQ_i}{\sum_{i=1}^{n}Q_i}\overline{Q}$
M6	Linear interpolation of C	$\text{Flux} = K''\sum_{j=1}^{365}C_j^{\text{int}}Q_j$
M7	Rating curve	$\text{Flux} = K'\sum_{j=1}^{365}C_j^{\text{ext}}Q_j$
K, K', K''	Conversion factors to account for the period of load estimation and measurement units	
C_i	Instantaneous concentration associated with individual samples (mg l^{-1})	
Q_i	Instantaneous discharge at time of sampling (m^3 s^{-1})	
Q_j	Daily discharge (m^3 s^{-1})	
$\overline{Q}$	Annual mean discharge, derived from a continuous flow record (m^3 s^{-1})	
$\overline{Q_{i,i-1}}$	Mean discharge for interval between samples i and $i-1$ (derived from a continuous flow record) (m^3 s^{-1})	
C_{int}	Daily concentration linearly interpolated between two measured samples	
C_{ext}	Daily concentration, extrapolated by a rating curve, if a significant relationship exists between concentration and discharge	
n	Number of chemical analyses	

RESULTS

Seasonality of nutrients

The seasonal variation of concentrations was established from the distribution of individual samples over the 1981–99 period, characterized by lower and upper deciles, and by the median of the four targeted nutrients (Figure 3c–f) and chlorophyll *a* (Figure 3b). The distribution of specific discharge (Figure 3a) was established from daily data for the same period.

Nitrate variations are highly seasonal (Figure 3c). They are nearly exhausted in August and maximum in December–January. This pattern is well known in this basin (CSEEL, 1984) and its causes are probably multiple. Firstly, soil nitrates are leached but they are slightly diluted for very high discharges (see below). Secondly, the lower summer level of nitrate at Orléans can be partially explained by a biological uptake of nitrate during the algal development period from April to October (Figure 3b). Theoretical nitrogen uptake may be based on chlorophyll levels, which are related to the algal organic carbon (algal particulate organic carbon (POC)/chlorophyll = 30 in the Loire; Meybeck *et al.*, 1988), and to a C/N ratio of 5·7 g g^{-1} in algal organic matter. In such conditions, uptake cannot exceed 0·8 mg l^{-1} for chlorophyll peaks at 150 μg l^{-1}, i.e. for 4·5 mg l^{-1} of algal POC. Moreover, as the seasonal variation of nitrate-N concentration is around 2·5 mg l^{-1} in relation to the median (Figure 3c), a bacterial denitrification process, probably in the riparian

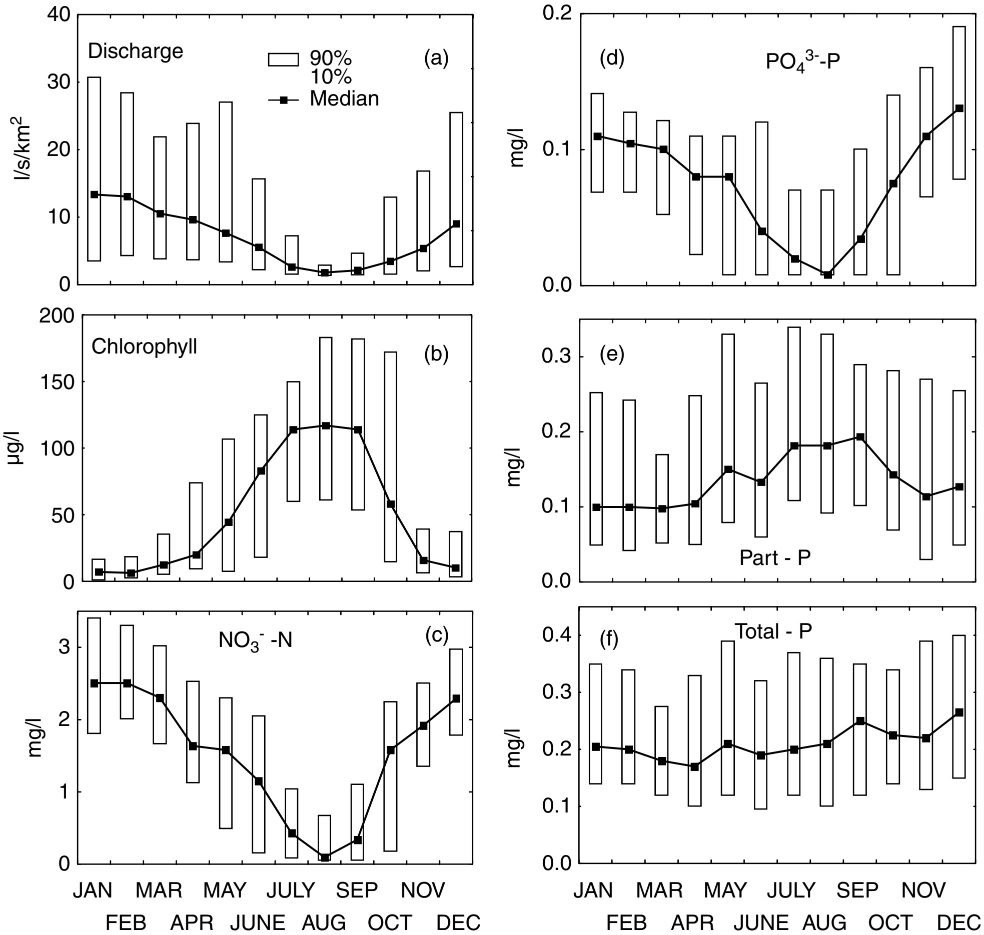

Figure 3. Seasonal variations (median, lower and upper deciles) of daily river attributes (1981–99): (a) specific discharge; (b) chlorophyll *a*; (c) $NO_3{}^-$-N; (d) $PO_4{}^{3-}$-P; (e) particulate-P; (f) total-P

alluvial plain, is also likely, particularly in the 150 km reach upstream of Orléans, as demonstrated in the neighbouring river Seine basin by Billen *et al.* (1998).

Conversely, the phosphate decrease in summer can be attributed to the biological uptake of phytoplankton: for plankton peaks at 150 µg l^{-1} chlorophyll *a*, the corresponding phosphorus uptake would be around 110 µg l^{-1} using a Redfield ratio of C106:P1 (mole/mole) in algal biomass, which is the equivalent seasonal variation of phosphates (Figure 3d). The particulate-P variations confirm such biological uptake, with a maximum observed from May to October (Figure 3e). The total-P pattern (Figure 3f) combines the orthophosphate-P and particulate-P variations; it remained almost stable throughout the year, even if its different constituents, i.e. orthophosphates, detrital phosphorus, phytoplankton phosphorus and waste-water particulate-P, were very variable.

Concentrations versus discharge relationships for nitrate

The general relationship between nitrate and water discharge using all 1981–85 data is very poor ($R^2 = 0{\cdot}17$; Figure 4a). When winter and summer periods are differentiated, two contrasting relationships are noted, with a summer increase with log $Q(R^2 = 0{\cdot}46)$ and winter stability (Figure 4b and c). Such relationships are also

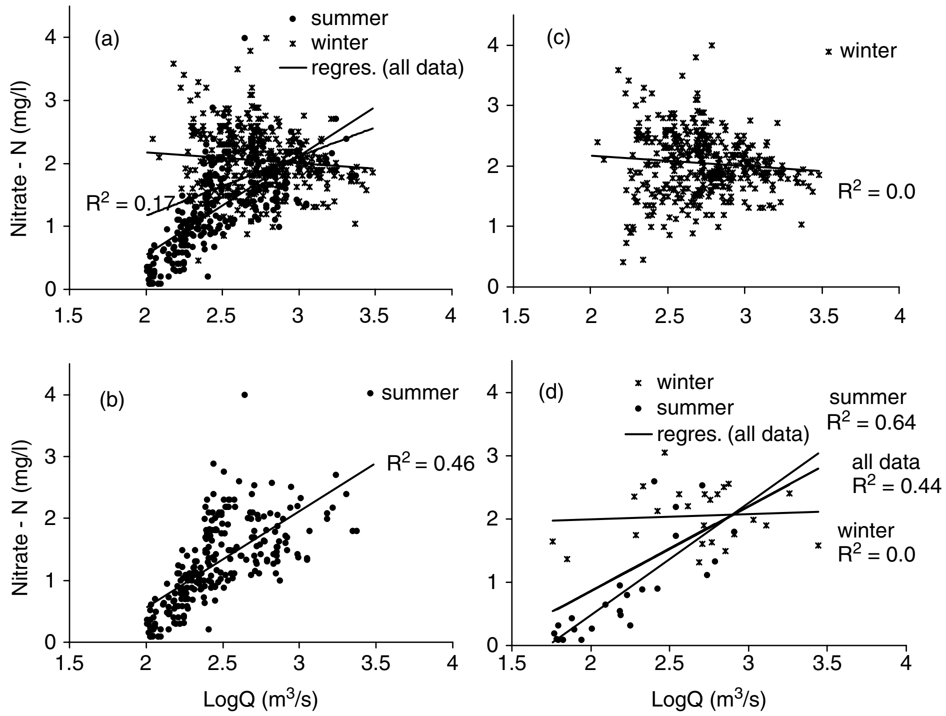

Figure 4. Relationships between nitrate-N and logarithm of discharge (log Q): (a) general correlation, all samples ($N = 651$); (b) summer correlation, all samples (May to October; $N = 243$); (c) winter correlation, all samples (November to April; $N = 408$); (d) example of monthly sorted data set for winter samples ($n = 24$), summer samples ($n = 24$) and whole year

found when the 100 individual monthly sorted data sets are examined (Figure 4d). The summer positive increase is always observed, even when based on only 24 samples over 4 years, with R^2 ranging from 0·52 to 0·88 depending on the particular data set. The winter stability of nitrate with Q is also generally noted. The combination of winter and summer in a single rating curve (R^2 ranging from 0·4 to 0·5 for the 100 sorted yearly correlations) leads to an underestimate of nitrate concentrations at high flows exceeding 1500 $m^3\ s^{-1}$, i.e. for 20% of river flows the nitrate concentration given by the rating curve exceeds 2·5 mg l^{-1}, whereas measured values do not exceed 2·0 mg l^{-1}.

Duration of fluxes

Flux duration curves established on high-frequency (at least daily) data are highly descriptive of the functioning of a given river basin at a given station. They depend on the hydrological regime, on the basin size and on the concentrations versus discharge relationship. For example, the percentage of annual TSS flux carried during 2% of the time (i.e. the top 18 daily ranked fluxes recorded in 5 years) ranges from 6·3% for the Mississippi to more than 90% for the Walla Walla river (Oregon) (Meybeck *et al.*, 2003). For diluted river-borne material for which the concentration decreases with Q, the duration curves are smoother than for the water discharges.

In the case of the Loire at Orléans, the fluxes carried during 2% of elapsed time are 10·6%, 13·7%, 12%, 16·8% and 11% for water, total-P, orthophosphates, particulate-P and nitrate respectively. For half of the elapsed time, the flux proportions are respectively 83%, 85%, 89%, 86% and 91%. Nutrient flux proportions carried 10% of the time are only slightly greater than the water fluxes, corresponding to a lack of a general relationship between concentration and water discharges or to a complex relationship combining the decrease and increase of nutrients with discharge, as shown above. When considering the percentage of time necessary to carry half of the flux, the Loire appears to be more 'irregular' than other French rivers: 50% of the water volume of the Loire was discharged in 19% of time for the period 1981–85, compared with 27·7% for the Seine, 21% for the Garonne and up to 36% for the Somme.

General comparison of flux estimation procedures

'Reference' nutrient fluxes F_{ref} for individual years resulting from the reconstitution of 365 daily fluxes are presented in Table II. The reference period is relatively wet if we compare these annual discharges with the mean annual flow at Orléans (364 $m^3\ s^{-1}$).

Box and whisker plots established on 400 (nitrate, total-P and particulate-P) to 500 (orthophosphates) flux estimate samples were used to show the range of errors in estimates (Figure 5). The difference is zero when the estimate of the annual load from monthly sampling is equal to the 'reference load' established from a daily flux set. The results show that the flux estimates differ significantly according to the method of calculation used and type of material (dissolved or particulate). Table III presents the mean errors $\bar{\varepsilon}$, standard deviations s and RMSEs of the replicate errors of orthophosphate flux estimates for 5 years, ranging from very wet ($Q_{1981}/Q_{\text{mean annual}} = 1{\cdot}5$) to medium dry ($Q_{1985}/Q_{\text{mean annual}} = 0{\cdot}85$). For the other nutrients, the criteria are presented for 1981 and for the subnormal year 1984 ($Q_{1984}/Q_{\text{mean annual}} = 0{\cdot}95$).

For all nutrients except particulate-P, methods M1, M2 and M3 produced the greatest errors in terms of RMSE, which ranged from 17 to 30%, whereas for methods M5 and M6 it ranged between 6% (M6 for nitrate) and 13% (M6 for particulate-P). Particulate-P showed a higher RMSE for all algorithms (Table III).

Method M4 produced variable RMSE scores: mediocre for nitrate (RMSE = 24%) and orthophosphate (RMSE = 19%), better for total-P and particulate-P (9% and 15% respectively). Methods M1 (product of means of sampled C and Q) and M2 (the mean of instantaneous fluxes) exhibited a very low degree of precision, because individual loads covered a wide range, including both under- and over-estimation. The standard deviation of the errors was between 15 and 24%, depending on the nutrient. These methods also had limited accuracy, because in most cases the mean of the errors presented non-zero values (nitrate: $\bar{\varepsilon} = -20\%$ for method M1; orthophosphates: $\bar{\varepsilon} = -15\%$ for M1 and 3% for M2; particulate-P: $\bar{\varepsilon} = -4\%$ for M2).

Method M3 (hypothesis of constant concentration around the sample) provided relatively precise estimates (standard deviation between 9% for nitrate and 18% for particulate-P), but fluxes were always underestimates (biases around −16%).

Method M4 (product of means of sampled C_i and annual discharge $\overline{Q}$) underestimated nitrate and orthophosphate at this station ($\bar{\varepsilon} = -22\%$ and $\bar{\varepsilon} = -16\%$), but provided better estimates for total-P and particulate-P (RMSE = 9% and 13% respectively).

Methods M5 (flow-weighted mean concentrations multiplied by the annual discharge) and M6 (linear interpolation of concentrations between actual analyses) gave very similar results and should be advocated for nitrate and orthophosphates: RMSE = 6·5% and 5·8% for nitrate and RMSE = 8·8% and 0·8% for orthophosphates respectively. For total-P, methods M6 (RMSE = 8·9%) and M4 (RMSE = 9%) should be advocated. For particulate-P, only method M4 should be applied.

Table II. Mean annual discharge and annual 'reference' nutrient flux F_{ref} based on reconstituted daily data sets at Orléans station

Year	Annual discharge ($m^3\ s^{-1}$)	NO_3^--N (t $year^{-1}$)	Total-P (t $year^{-1}$)	PO_4^{-3}-P (t $year^{-1}$)	Particulate-P (t $year^{-1}$)
1981	551	31 048	3729	1794	1924
1982	411	22 677	3597	1518	2073
1983	473	—	3850	1612	2237
1984	347	20 158	2728	1138	1588
1985	308	19 761	—	858	—

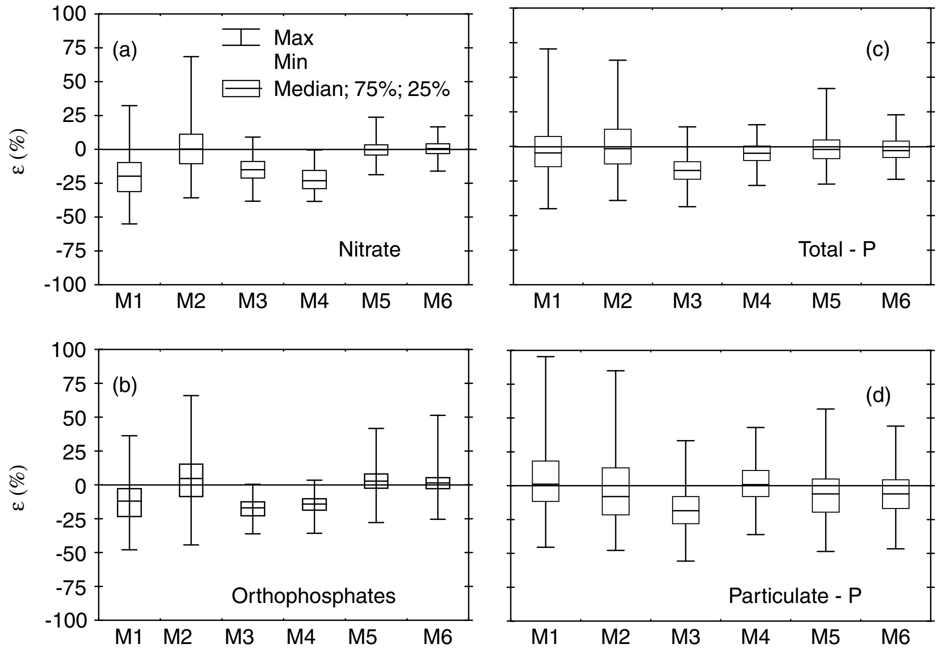

Figure 5. Comparison of the error range in annual nutrient load estimates with the true reference value (1981–85, simulated monthly sampling) based on six flux calculation methods (M1 to M6, see Table I): (a) nitrate-N; (b) orthophosphate-P; (c) total-P; (d) particulate-P

Method M7 (rating curve for winter and summer periods) produced precise ($s = 4\%$ for all years) but inaccurate flux estimates (Table IV). The bias of flux estimates ranged from -8% in 1985 to 30% in 1984.

DISCUSSION

Representativeness of flows associated with water quality measurements

For each simulated survey, the mean annual water discharge calculated from the monthly sampling data ($\overline{Q^*} = \sum_{i=1}^{12} Q_i/12$) can be compared with the actual recorded annual discharge $\overline{Q}$. Methods M1 and M2, as opposed to methods M3 to M6, take into account only the water discharge data at time of sampling, namely 12 measurements. The relative errors on load estimates ε by methods M1 and M2 are proportional to the bias between 'sampled' discharge and mean annual discharge, measured by $\overline{Q^*}/\overline{Q}$ (Figure 6). For methods M3 to M6 there is no relation between the relative errors ε and $\overline{Q^*}/\overline{Q}$.

For methods M1 and M2, the relative errors on fluxes are minimal when the sampling discharges are close to the annual mean ($\overline{Q^*}/\overline{Q} = 1{\cdot}0$). Conversely, the errors can reach $+60\%$ if $\overline{Q^*}/\overline{Q}$ is greater than 1·2 and -30% if $\overline{Q^*}/\overline{Q} < 0{\cdot}8$. Relative errors on fluxes made by methods M3 to M6, which make effective use of the daily discharge records, are not correlated to 'sampled discharges' biases.

Influence of wet and dry years on flux calculations

The year-to-year variations of estimated flux characteristics, in this case the mean $\bar{\varepsilon}$ and standard deviation s of relative errors, are less pronounced than the differences between flux estimate procedures (methods M1 to M6; Table III). In other words, a negative bias is observed in many years, wet or dry, as in orthophosphate fluxes measured by M3 or M5. When the errors are small, their means can be either positive or negative, but always limited, as in procedure M6.

Table III. Mean, standard deviation of relative errors and RMSE of 100 yearly flux estimates based on sorted monthly nitrate, orthophosphate, total−P and particulate-P samples (5 years for orthophosphates; two selected years for the others: dry 1984, wet 1981)

Year	M1			M2			M3			M4			M5			M6		
	$\bar{\varepsilon}$ (%)	s (%)	RMSE (%)	$\bar{\varepsilon}$ (%)	s (%)	RMSE (%)	$\bar{\varepsilon}$ (%)	s (%)	RMSE (%)	$\bar{\varepsilon}$ (%)	s (%)	RMSE (%)	$\bar{\varepsilon}$ (%)	s (%)	RMSE (%)	$\bar{\varepsilon}$ (%)	s (%)	RMSE (%)
Nitrate																		
1981	−11	12	16	−1	13	13	−16	6	17	−10	4	11	0	3	3	2	3	4
1984	−19	10	21	3	13	13	−17	10	19	−22	5	23	−2	6	7	−3	6	7
1981–85	−20	15	26	2	19	19	−15	9	17	−22	9	24	0	7	7	0	6	6
Orthophosphate																		
1981	−13	13	18	4	16	18	−18	6	19	−12	6	14	4	6	7	3	6	6
1982	−12	20	23	9	27	29	−23	8	25	−17	8	19	5	13	13	6	16	17
1983	−19	14	24	0	17	17	−16	6	17	−18	4	18	2	8	8	−1	6	6
1984	−5	12	13	7	13	16	−15	5	16	−10	5	11	1	4	5	1	4	5
1985	−24	22	33	−7	33	34	−17	20	27	−25	12	28	−8	23	24	−10	20	23
1981–85	−15	18	23	3	23	23	−17	12	21	−16	9	19	1	13	13	0	13	13
Total-P																		
1981	−6	14	15	−1	18	18	−23	8	25	−5	9	10	−1	10	10	1	9	9
1984	−1	14	14	6	16	17	−15	7	16	−6	6	9	0	8	8	−2	7	7
1981–85	−3	17	18	0	20	20	−17	9	20	−5	7	9	−2	10	10	−2	8	9
Particulate-P																		
1981	1	18	18	−5	24	26	−28	13	42	2	14	15	−5	18	19	0	15	15
1984	2	19	19	5	22	22	−15	12	25	−3	11	13	0	15	15	−4	14	16
1981–85	4	22	22	−4	24	26	−16	18	30	2	13	13	−5	17	19	−5	16	18

Table IV. Mean $\bar{\varepsilon}$, standard deviation s of relative errors and RMSE of 100 yearly nitrate flux estimates by method M7 (rating curve for winter and summer periods)

	1981	1982	1984	1985	1981–85
$\bar{\varepsilon}$ (%)	16	3	30	−8	10
s (%)	4	4	4	4	4
RMSE (%)	16	5	30	8	11

When comparing the very wet year 1981 and the subnormal year 1984, the performances of the flux procedures are still very comparable in terms of bias and precision. The variability of the flux estimates produced by methods M1 to M6 can also be analysed by plotting their statistical distribution. In Figure 7, we have selected the distribution of total-P flux estimates F^k (normalized by the reference flux F_{ref}) made by the most satisfactory method (M4 and M6) for two contrasting years, the wet year 1981 and the subnormal year 1984.

The linear interpolation of concentrations (M6) gives a generally symmetrical distribution during the wet and dry years. Method M4 (product of means of sampled C_i and annual discharge $\overline{Q}$) may produce an asymmetrical distribution, with slight underestimations for both contrasted years.

Most appropriate flux estimate method

The general performance of the flux estimate procedures is shown in Figure 8 for the four targeted nutrients. The figure plots the normal distribution represented by the appropriate values of mean and standard deviation of replicate nutrient load errors (Walling and Webb, 1981).

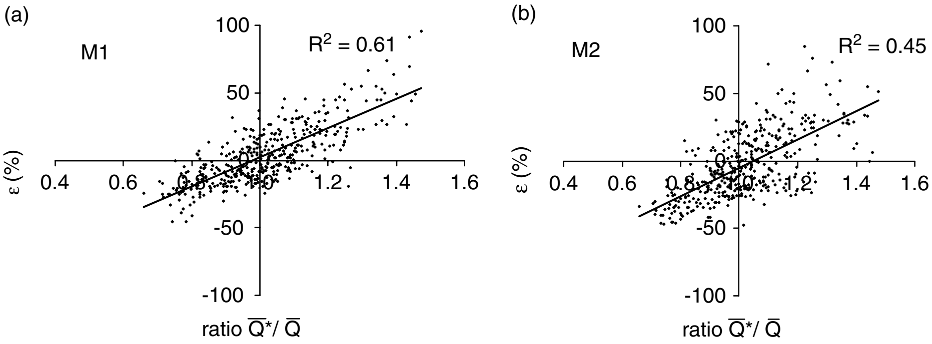

Figure 6. Errors of particulate-P flux estimates by methods M1 and M2 versus ratios between mean 'sampled' discharges and the annual mean discharge $\overline{Q^*}\Big/\overline{Q}$

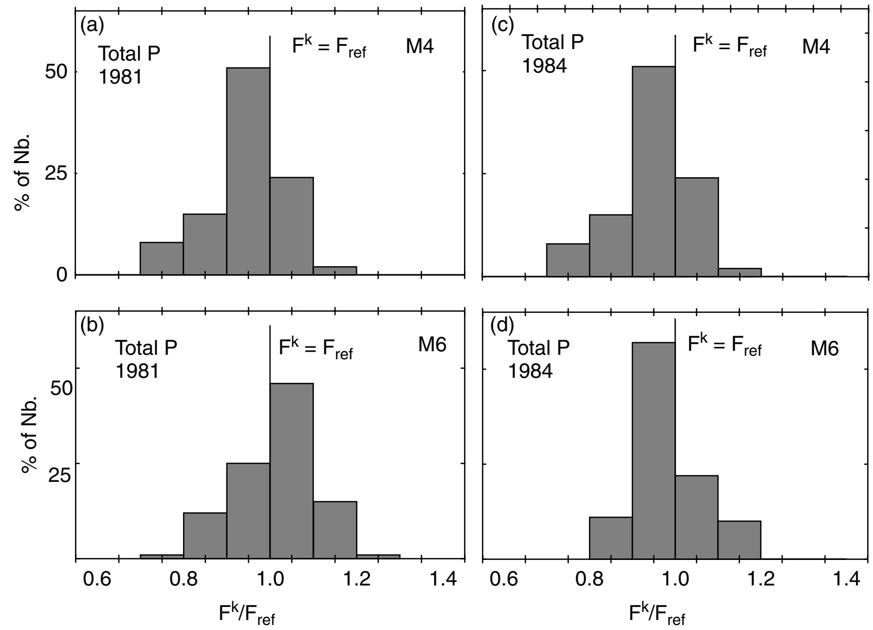

Figure 7. Distribution of 100 replicate yearly total phosphorus flux estimates by methods M6 and M4 based on sorted monthly data sets for the wet year 1981 (left) and the normal year 1984 (right). (a) Method M4, 1981; (b) method M6, 1981; (c) method M4, 1984; (d) method M6, 1984. Flux values are normalized to reference fluxes (Table III) established with 356 daily values (F^k/F_{ref})

Methods M6 (linear interpolation of C_i) and M5 (flow-weighted mean concentration) provide very similar results with non-bias and minimum dispersion, and are preferable for nitrate and orthophosphates (Figure 8a and b). The time variability of these nutrients is essentially governed by their seasonal fluctuations, due to chemical and biological processes during summer. In such cases, the linear interpolation (M6) with a monthly interval is the best applicable method, with non-bias and minimum dispersion. For the monthly sampling interval, the precision (confidence of 95%) of annual nitrate and orthophosphate fluxes obtained by the two appropriate methods are 13% and 26% respectively.

Methods M6 and M4 (product of means of sampled C_i and annual discharge) are preferable for total-P, despite the slight bias. The precision is around 17%. For particulate-P, the most accurate and precise fluxes are produced by method M4 (bias around 2%; precision about 26%).

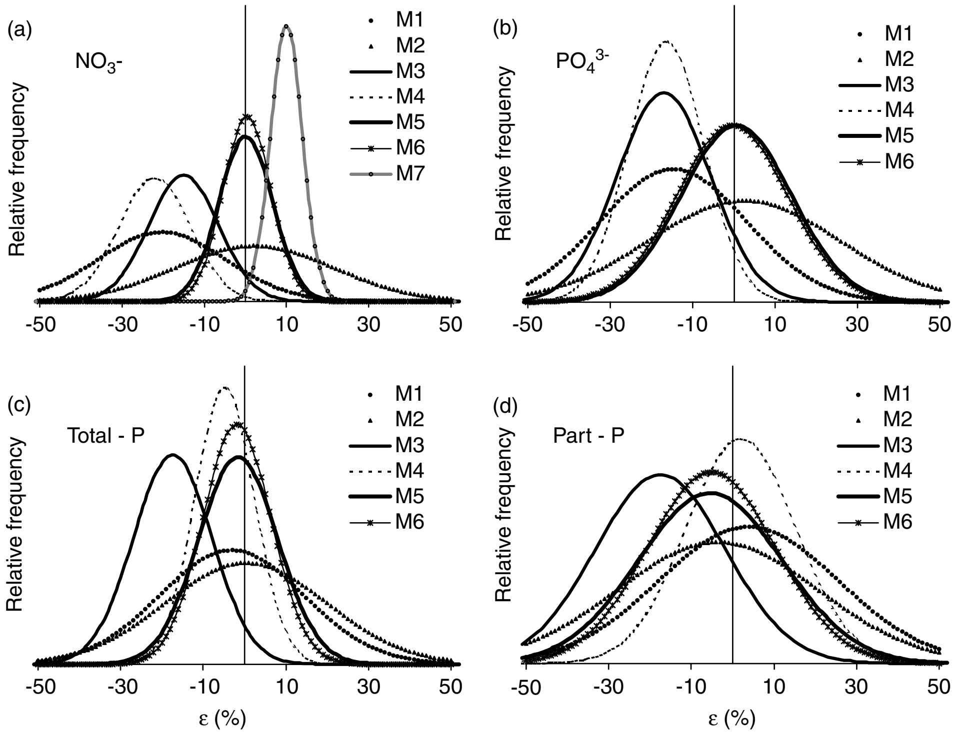

Figure 8. Idealized distribution of replicate nutrient load errors: (a) nitrate; (b) orthophosphate; (c) total-P; (d) particulate-P

The effect of the sampling interval was analysed to evaluate yearly fluxes using the appropriate methods for each nutrient. The variation of flux estimate bias and precision for 1 year (1981) was analysed by decreasing sampling intervals to 3 days. The bias shows little variation when the sampling interval decreases, whereas the precision improves in an approximately linear manner. The frequency of nutrient surveys required to obtain an annual nutrient flux with 10% precision is around 15 days for nitrate, 10 days for orthophosphates and total-P, and about 5 days for particulate-P.

Reconstitution of past nutrient fluxes from regular water quality surveys at Villandry and long-term trend analysis

In most cases, the analysis of water quality data for long-term trends is based on the hypothesis that data have been collected over a period of years in a consistent and reliable manner. Methods involved in detecting and estimating the magnitude of temporal trends depend on the type of trend hypothesis, e.g. step versus monotonic, and also on the concentration or flux variability (Hirsch *et al.*, 1991). In general, concentration or flux data do not have a normal distribution, and transformation of the data is generally used before trend analysis (Lemke, 1991; Worrall and Burt, 1999). Trend detection in fluxes from infrequent sampling of pollutants requires knowledge of the best possible load estimation method and the related precision.

Such flux reconstitution was carried out at the Villandry station (42 130 km^2), 139 km downstream of Orléans, from data gathered by the French national water quality network survey. Sampling was monthly prior to 1987, and bimonthly after 1988 during the high flow from November to April.

As fluxes are highly dependent on annual discharge, trend analysis here has been carried out on the average concentration derived from annual yields versus annual discharges for two different periods (Figure 9a and b). The errors in flux estimates are plotted for each year, depending on the current sampling frequency. The mean concentration over the period is the slope of the linear regression. For the periods 1976–87 and 1988–99,

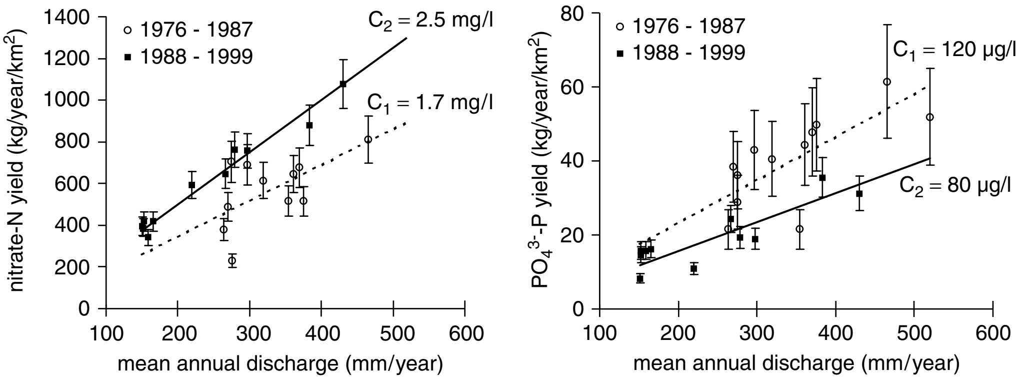

Figure 9. Long-term evolution of nutrient yields, calculated by method M6 from the regular but non-homogeneous frequency of the RNB survey at Villandry: (a) nitrate yields versus annual discharge; (b) orthophosphate yields versus annual discharge

there was an inverse relationship between nitrate and phosphorus trends: nitrate concentration increased by 44% between the two periods while orthophosphate concentration decreased by 33%.

CONCLUSIONS AND OUTLOOK

In the Loire at Orléans, relatively small day-to-day variations in nutrients are found. At this station, on the basis of accuracy and precision analyses, methods M5 (flow-weighted mean concentration) and M6 (linear interpolation of concentrations) are shown to be better than most other methods tested, especially for nitrate and orthophosphates. Other rivers with similar characteristics, i.e. in a medium-sized eutrophic catchment, are also likely to be amenable to this type of estimation. Method M6 gives good results in a monitoring programme with a regular sampling frequency and when nutrient concentrations display seasonal variability over the year. This method is particularly recommended for nitrate when linear interpolation between two measurements reasonably mimics the seasonality. A similar approach based on the fit of the seasonality by harmonic analysis could be used.

With regard to the monthly sampling interval, the precision (confidence level of 95%) of annual nutrient fluxes obtained by the appropriate methods is 13% for nitrates, 20% for total-P, 26% for orthophosphates and 34% for particulate-P. As the number of simulated samples increases, the results of the estimation methods considered in this study converge towards the actual mean flux. The frequency of water quality surveys required to obtain an annual nutrient flux with 10% precision is around 15 days for nitrate, 10 days for orthophosphates and total-P, and about 5 days for particulate-P.

The results of this study also indicate that it is possible to supply flux estimates and to identify temporal and spatial trends in a basin using the level of effort associated with a routine programme. However, it is highly recommended that the flux value be associated with the precision of the estimate, especially for spatial and temporal comparison of river flux estimates (Littlewood, 1992).

Further work is required to generalize this study and to provide indicative levels of accuracy and precision of flux estimates for each constituent in relation to hydrological and concentration variability (e.g. based on the serial correlation structure in the data), particularly for smaller river basins, in which water quality, like TSS, is usually more variable. In addition, it is necessary to evaluate resultant errors in both measurement and flux estimates.

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