Whole-stream phosphorus cycling: Testing methods to assess the effect of saturation of sorption capacity on nutrient uptake length measurements

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ABSTRACT

The cycling rate of nutrients such as phosphorus (P) is a fundamental parameter in stream ecology. In whole-stream ecosystem experiments, cycling rates are often assessed using continuous short-term nutrient addition studies. While several simplifying assumptions are generally recognised, these are rarely, if ever, fully tested under field conditions. One principal assumption is that uptake (sorption) processes do not become saturated during periods of nutrient addition, which is perhaps questionable from laboratory studies of soluble reactive phosphorus (SRP) sorption kinetics. Three approaches were developed and tested, which bridged the gap between laboratory-based net (sum of uptake and release) sorption kinetics and whole-stream assessments of P uptake. These were applied to a short-term (three times mean travel time of water in the studied reach) whole-stream multiple-rate P addition. The results were then tested independently with a whole-stream long-term (15 times mean travel time) SRP addition. The net sorption kinetics were not altered during the short-term addition with low SRP additions, 9–$16 \, \mu g \, L^{-1}$ (two to three times the ambient concentration). Although this may not be the case at higher added concentrations (as possibly hinted at five times the ambient concentration), the long-term addition showed no change in P uptake length with a P addition ($39 \, \mu g \, L^{-1}$) 16 times higher than the ambient concentration.

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1. Introduction

The phosphorus cycling rate is a fundamental parameter in aquatic ecology (Raven, 1992; Borchardt, 1996; Dodds, 2003). Two schools of thought have been developed to assess phosphate dynamics in streams at the interface between the river bed and water column. Both strive to determine the P retention capacity of the stream bed under different environmental and human pressures, which is important to predict potential downstream impacts.

The first approach is based on laboratory net sorption (uptake) kinetic studies of river bed sediment (House et al.,

1995a, b). Various models have been used to determine the uptake kinetics (House et al., 1995a, b; House and Denison, 2002). The second approach calculates the nutrient uptake length, which approximates to the average downstream distance travelled by a P atom, from river bed release to recapture (Newbold et al., 1981, 1983; Webster and Valett, 2006). The nutrient uptake length (m) can easily be converted into uptake rate (e.g. $mg \, P \, m^{-2} \, min^{-1}$, Webster and Valett, 2006).

Despite that, there has been little overlap between the two approaches, possibly because the former uses systems that are closed (batch bottles or recirculating flume), while the

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latter is essentially field based (at the stream reach scale). This makes the inter-comparison of results difficult. However, House et al. (1995b) provided a mechanism that allowed some interlinking through combining a net sorption kinetic equation (Elovich) with the negative exponential equation from which is derived the nutrient uptake length.

Both methods are applicable under stable low flow conditions, in small streams, where nutrient transport in particulate forms and precipitation reactions are negligible (cf. Newbold et al., 1983; Mulholland et al., 1985; Fox, 1989; House et al., 1995a; Neal, 2001). Both methods were derived from first principles (Atkinson et al., 1971; Stream Solute Workshop, 1990) and are extensively used. Both methods are based on exchange rate processes (rather than thermodynamic mechanistic understanding) and make no distinction between biotic and abiotic uptake (= sorption).

One measure of in-stream nutrient uptake length has been derived from continuous *in-situ* nutrient addition experiments where a conservative tracer is also included (Webster and Valett, 2006). Water samples are collected above, and at various locations below the point of tracer injection. Typically, small stream reaches take only a few hours for equilibrium conditions to become established. The uptake rate of the nutrient is deduced relative to the conservative tracer, which requires certain simplifying assumptions (Stream Solute Workshop, 1990; Webster and Ehrman, 1996), but these are rarely tested.

One key assumption is that the uptake processes do not become saturated during the nutrient addition (Stream Solute Workshop, 1990; Webster and Ehrman, 1996). However, the validity of this assumption can be questioned from two perspectives: the underestimation of ambient nutrient uptake rate (or flux) by nutrient addition studies compared to isotopic tracer studies (e.g. Mulholland et al., 2002) and published laboratory studies on P sorption kinetics (e.g. House et al., 1995a). A soluble reactive phosphorus (SRP) uptake kinetic study using undisturbed river sediment in a laboratory recirculating flume has shown that fast saturation of the sediment P sorption capacity occurred within the first 5 h after addition of P (House et al., 1995a). However, this kinetic study was run with a relatively high initial concentration of SRP addition (ca. $600 \mu g \, P \, L^{-1}$). Hence it remains to test more explicitly whether saturation of the sorption capacity occurs during whole-stream nutrient addition studies.

The present study extends recent methodological developments, including the nutrient ambient uptake length from multiple-rate P addition (Payn et al., 2005), using the Elovich equation, to test the extent to which net sorption kinetics are altered during a typical (three times mean travel time of the water in the studied reach) SRP addition. Firstly, the theoretical context is presented from which three potential solutions are suggested to test the assumption of saturation of the sorption capacity of the stream reach. Secondly, the theoretical developments are applied to short-term multiple-rate SRP addition studies in a small stream draining an upland-moorland catchment area. Thirdly, the kinetics of SRP sorption over a long-term (15 times mean travel time) SRP addition are reported as an independent test and implications of the work presented.

2. Theory

2.1. Nutrient uptake length

Under base flow conditions, in natural (or least impacted) small streams, it is reasonable to assume that there is a steady-state P concentration, where P uptake and release rates by the stream bed are balanced. This is conceptually equivalent to the zero equilibrium phosphate concentration (EPC_0), the solution concentration where the net flux of phosphorus between solid and solution phases is zero (Taylor and Kunishi, 1971; House and Denison, 2000). This dynamic equilibrium is maintained through a combination of biotic and abiotic processes. Under constant downstream flux of nutrients with time and distance the ambient nutrient uptake length, S_W (m), is

$$S_W = \frac{Q C_{AMB}}{w U_{AMB}} \qquad (1)$$

where Q is discharge ($m^3 \, min^{-1}$), w is average stream width (m), C_{AMB} is the ambient nutrient concentration of the stream ($mg \, m^{-3}$) and U_{AMB} is the ambient uptake rate ($mg \, m^{-2} \, min^{-1}$, Newbold et al., 1981). The nutrient uptake length is generally determined empirically from the negative exponential equation:

$$C_{(x)} = C_{(0)} \exp(-kx) \qquad (2)$$

where $C_{(x)}$ is the added nutrient concentration ($mg \, m^{-3}$) at a distance x (m) downstream of a point source of nutrient, $C_{(0)}$ is the added nutrient concentration ($mg \, m^{-3}$) at the injection point (top of the mixing zone) and k (m^{-1}) is the rate constant, as follows:

$$S_W = \frac{1}{k} \qquad (3)$$

2.2. Linking uptake rate to concentration

The relationship between uptake and concentration of a limiting nutrient is frequently described by a rectangular hyperbolic function mathematically equivalent to the Michaelis–Menten model of enzyme kinetics (Borchardt, 1996; Payn et al., 2005):

$$U = \frac{U_{MAX} C}{C_{HALF} + C} \qquad (4)$$

where U is gross uptake rate ($mg \, m^{-2} \, min^{-1}$), C is water column nutrient concentration, U_{MAX} is the maximum uptake rate ($mg \, m^{-2} \, min^{-1}$) capacity of the stream and C_{HALF} the concentration ($mg \, L^{-1}$) at which half the maximum gross uptake rate is realised.

2.3. Ambient uptake length from multiple-rate phosphorus addition

The nutrient uptake length has been measured using isotopic tracer studies (Ball and Hooper, 1963; Newbold et al., 1983) or more frequently nutrient addition studies (Webster and Ehrman, 1996). However, nutrient addition studies have been shown to overestimate the ambient uptake length and underestimate the ambient uptake rate (Mulholland et al.,

2002). Recently, Payn et al. (2005) suggested a new method to estimate the ambient uptake length using short-term (several hours) multiple-rate nutrient additions. Nutrient addition uptake lengths, $S_{W(ADD)}$, are plotted against added nutrient concentrations (geometric mean, C_{ADD}). The ambient uptake length, S_W, is then extrapolated to the negative ambient concentration, $-C_{AMB}$. Finally, Payn et al. (2005) derived the following equation to link added nutrient concentrations to nutrient uptake lengths:

$$S_{W(ADD)} = \frac{Q(C_{HALF} + C_{AMB})^2}{wU_{MAX}C_{HALF}} + C_{ADD}\left[\frac{Q(C_{HALF} + C_{AMB})}{wU_{MAX}C_{HALF}}\right]$$
$$\text{with } C_{ADD} \neq 0 \tag{5}$$

This is assuming that the release of nutrient is not affected by slightly increased nutrient concentrations, and that uptake rate can be represented by the Michaelis–Menten equation. The two unknown constants, C_{HALF} and U_{MAX}, parameters of the Michaelis–Menten equation, can be found numerically using a non-linear regression model.

2.4. Sorption kinetics

The interpretation of kinetic data for phosphate exchange in mixed systems (e.g. sediment and water phases) has frequently been described by the Elovich equation (e.g. Atkinson et al., 1970; Pavlatou and Polyzopoulos, 1988; House et al., 1995a, b):

$$\frac{dU_{NET}}{dt} = a\,\exp(-bU_{NET}) \tag{6}$$

where U_{NET} is the net uptake ($\mathrm{mg\,m^{-2}}$), t is the time (min), a is the initial uptake rate ($\mathrm{mg\,m^{-2}\,min^{-1}}$) and b the rate constant ($\mathrm{m^2\,mg^{-1}}$). With the condition that $U = 0$ at $t = 0$, this integrates (Allen and Scaife, 1966)

$$U_{NET} = \frac{1}{b}\ln(1 + abt) \tag{7}$$

2.5. Linking the Elovich equation with nutrient uptake length

The negative exponential equation (Eq. (2)) and the integrated form of the Elovich equation (Eq. (7)) can be related with stream depth, h (m), as follows:

$$U_{NET} = hC_{(x)} \tag{8}$$

equivalent to

$$h = \frac{(1/b)\ln(1 + abt)}{C_{(0)}\exp(-kx)} \tag{9}$$

which can be rearranged as follows:

$$hbC_{(0)} = \ln(1 + abt)\exp(kx) \tag{10}$$

The expansion of the exponential and logarithmic functions (with the condition that $abt \leqslant 1$) of Eq. (10) leads to the approximation

$$hbC_{(0)} = \left[abt - \frac{(abt)^2}{2} + \frac{(abt)^3}{3} - \frac{(abt)^4}{4}\right]$$
$$\times \left[1 + \frac{kx}{1!} + \frac{(kx)^2}{2!} + \frac{(kx)^3}{3!} + \frac{(kx)^4}{4!}\right] \tag{11}$$

Now, when

$$hbC_{(0)} \to 0 \tag{12}$$

we have

$$\left[abt - \frac{(abt)^2}{2} + \frac{(abt)^3}{3} - \frac{(abt)^4}{4}\right]\left[1 + \frac{kx}{1!} + \frac{(kx)^2}{2!} + \frac{(kx)^3}{3!} + \frac{(kx)^4}{4!}\right]$$
$$= f(abt)f(kx) \to 0 \tag{13}$$

Since $0 \leqslant f(abt) \leqslant \ln 2$ and $1 \leqslant f(kx) < \infty$, we must have $f(abt) \to 0$, $abt \to 0$ and $f(kx) \to 1$, $kx \to 0$. Hence we have the following approximation:

$$abt = kx. \tag{14}$$

Hence, with the condition that $abt \leqslant 1$, we have the following approximations (House et al., 1995b):

$$h = \frac{1}{bC_{(0)}} \tag{15}$$

$$k = \frac{abt}{x} = \frac{ab}{u} \tag{16}$$

with u being the mean water velocity ($\mathrm{m\,min^{-1}}$) and $C_{(0)}$ the initial (added) nutrient concentration. In practice, however, $C_{(0)}$ of the negative exponential equation (Eq. (2)) differs from the initial amount of P added to the stream reach, $C_{(TOP)}$, due to P uptake within the mixing zone. In Eq. (15) $C_{(0)}$ should therefore, for practical use, be substituted by $C_{(TOP)}$. Note also that the derivation of Eqs. (15) and (16) as presented above, in order to retrace the inexact wording of House et al. (1995b), is cumbersome. The expansion of the exponential and logarithmic functions is in fact unnecessary to the logical reasoning presented above and therefore the additional constraint $abt \leqslant 1$ not needed.

From Eq. (16), House et al. (1995b) noted that the SRP uptake length is interpreted in the Elovich equation as a function of the initial uptake rate a ($\mathrm{mg\,m^{-2}\,min^{-1}}$), the rate constant b ($\mathrm{m^2\,mg^{-1}}$) and water velocity u ($\mathrm{m\,min^{-1}}$). The product ab is therefore approximating the dynamic uptake rate λ_C (see Stream Solute Workshop, 1990; Webster and Valett, 2006). The nutrient uptake length can be converted to a mass transfer coefficient, now called vertical uptake velocity (v_f, Webster and Valett, 2006), at which the nutrients move from the water column to the stream bed after standardisation of the uptake length by stream water velocity and depth (see Webster and Valett, 2006). These conversions are useful to compare different types of stream systems.

2.6. Time for space (distance) substitution in nutrient addition experiments

Nutrient is added continuously to the stream together with a conservative tracer (e.g., NaCl). Once a steady-state concentration of the conservative tracer has been achieved at the lowest sampling point of the test stream reach, water samples are collected at fixed distances (x) downstream from the point of nutrient addition to determine the nutrient concentration profile, $C_{(x)}$. The conservative tracer study allows the determination of the mean travel time τ (min), and knowing the length of the study reach, L (m), the mean travel time per metre ($\mathrm{min\,m^{-1}}$). It is therefore possible to express the concentration of nutrient $C_{(x)}$ as a function of

time, $C_{(t)}$. This assumes a constant flow velocity along the test stream profile, which is reasonable if water samples are picked up at regular intervals (e.g., at a spatial frequency of ~10 times the stream width, w (m), which is usually adequate to include the physical heterogeneity of the riffle-pool system). Otherwise additional cross-section area measurements between sampling points would allow the average mean travel time between points to be assessed more accurately.

2.7. Modelling the observed net sorption by the stream reach: three solutions

Solution 1—One way to calculate the observed (total) uptake rate, U (mg m^{-2} min^{-1}), is to use the Michaelis–Menten equation (4), with constants determined by the multiple-rate nutrient addition from Eq. (5) and observed P concentrations, $C_{AMB}+C_{(t)}$. The constant ambient uptake rate, U_{AMB} (mg m^{-2} min^{-1}), can be determined using Eq. (1) with S_W. Hence we can deduce the net uptake rate, U_{NET} (mg m^{-2} min^{-1}), from

$$U = U_{AMB} + U_{NET} \qquad (17)$$

The net nutrient uptake rate, U_{NET} (mg m^{-2} min^{-1}), of the stream reach can be integrated over the $1, ..., i, ..., n$ time intervals, Δt (min), sampled along the river reach as follows to obtain the net nutrient uptake flux (mg m^{-2}):

$$U_{NET} = \sum_{i=1}^{n} \frac{\Delta C_i Q \Delta t_i}{\Delta A} \qquad (18)$$

with ΔC_i (mg m^{-3}) being the change in nutrient concentration over Δt_i and ΔA the area of the river bed (m^2) covered during Δt_i. This is essentially the whole-stream mass balance approach suggested by the Stream Solute Workshop (1990, p. 108). The net nutrient uptake rate (mg m^{-2} min^{-1}) is then regressed against the nutrient uptake flux (mg m^{-2}) with a negative exponential function to determine the parameters a and b of the Elovich equation (Eq. (6)). It is then possible to calculate dU_{NET}/dt and U_{NET}, from Eqs. (6) and (7), respectively, for any time elapsed since the nutrient addition started.

Solution 2—Calculate the initial P concentration added to the stream reach, $C_{(TOP)}$, from the negative exponential equation. Then calculate the Elovich parameters a and b from Eqs. (15) and (16) using $C_{(TOP)}$. Finally calculate the net nutrient uptake flux U_{NET} (mg m^{-2}) with Eq. (7).

Solution 3—From the set of observed net uptake U_{NET} from Eq. (18) at time t, it is possible to find a numerical solution for a and b using Eq. (7) (can be solved with the non-linear regression model of S-Plus 6.2 Professional or Solver in Excel). dU_{NET}/dt and U_{NET} can then be calculated for any time t using Eqs. (6) and (7).

2.8. Kinetics of the net nutrient retention

The net nutrient retention, $R_{(t)}$, at time t, for the stream reach can be calculated as follows:

$$R_{(t)} = \frac{U_{NET} L w}{C_{TOP} Q t} \qquad (19)$$

with U_{NET} being the net uptake flux (mg m^{-2}), L the reach length (m), w the reach width (m), C_{TOP} the nutrient

concentration at the top of the reach (mg m^{-3}), Q the discharge (m^3 min^{-1}) and t the time elapsed since the beginning of nutrient addition (min).

2.9. Predicted stream water concentration

The stream water concentration, $C_{(t)}$, as a function of time, for the stream reach can be calculated as follows:

$$C_{(t)} = C_{TOP}(1 - R_{(t)}) \qquad (20)$$

2.10. Kinetics of the nutrient uptake length

In order to check the values of the constants a and b, an approximated nutrient uptake length, S_W, can be calculated from Eqs. (3) and (15) as follows:

$$S_W = \frac{u}{ab} \qquad (21)$$

and checked against the ambient uptake length extrapolated to the negative ambient concentration. The kinetics of the nutrient uptake length, $S_{W(ADD)}$ (m), can easily be calculated using $C_{(t)}$ (mg m^{-3}) and U_{NET} (mg m^{-2}) to solve Eq. (1) for any time t.

3. Material and methods

3.1. Catchment area

The study area was located within the Glensaugh Research Station of the Macaulay Institute, north-east Scotland (long. 2°33′W, lat. 57°55′N). The catchment area of the studied stream (Cairn Burn) is 0.9 km^2 within a 265–450 m altitude range. Annual average precipitation is 1040 mm and evapotranspiration 300 mm. The area lies just to the north of the Highland Boundary Fault, with soils of the Strichen Association developed on glacial drifts. At the top of the catchment the soils are mainly hill peat (2 m deep on average), whilst at lower altitudes freely drained humus iron podzols predominate. The stream drains incised valleys of rounded hilltops. Small surface water flushes on the main hill slope feed the main stream. The catchment is used for hill farming: mixed sheep and cattle. The vegetation cover is predominantly grass and heather with rushes growing in the flushes and bracken on the hill slope along the stream. The management of the land includes the burning of the heather (10–12% of surface area yearly target). Part of the catchment was used to run productivity experiments for grazing animals in the late 1970s and early 1980s (calcium carbonate, nitrogen and phosphorus amendments). The Cairn Burn hydro-chemistry, under summer stable flows, is characterised by low concentrations of nitrate (80–140 μg N L^{-1}) and soluble reactive P (SRP, 2–5 μg P L^{-1}), dissolved organic carbon (2–5 mg L^{-1}) and circum-neutral pH (6.5–7.3 units). SRP concentrations from inflows of surface water flushes in the wider catchment area including the Birnie Burn and Cairn Burn (1.76 km^2) averaged ($\pm$95% interval confidence) 8 ± 2 μg P L^{-1} in the summer.

3.2. Phosphorus additions and chemical analyses

A multiple-rate P addition was run on October 2, 2005, under stable flow conditions (measured at a flume situated 138 m downstream of the studied reach). A 50 L carboy was filled with 36 L of stream water, 3.5 kg of NaCl and 11.4 g of P as KH_2PO_4. Three injection rates of the solution were run using a Watson Marlow 504S/RL peristaltic pump.

Conductivity was monitored below the mixing zone (28 m), at the top and bottom of the studied stream reach (67 m long) with multiparameter sondes (YSI600XLM, Yellow Springs, Ohio). When conductivity had reached a new plateau after each addition, water samples were collected upstream of the injection point to determine the ambient P concentration, and along the stream reach (at 0, 5, 15, 25, 35, 45, 55, 65 and 67 m).

Water samples were filtered through a pre-rinsed 0.45 μm cellulose nitrate filter as soon as possible after collection using a hand-held vacuum pump. The samples were kept cool (4–10 °C) and analysed the following day for SRP by colorimetry (blue—molybdenum) with a Skalar SAN++ autoanalyser (Skalar, Breda, The Netherlands). The detection limit was $1 \mu g P L^{-1}$ (Y. Cook, unpublished data). The added SRP concentrations along the stream reach were obtained by subtracting the ambient (background) concentration.

4. Results and discussion

4.1. Stream parameters

During the multiple-rate P addition, ambient (background) discharge and specific electric conductivity (at 25 °C) were 4.3 (± 0.6) $L s^{-1}$ and 138 μS cm^{-1}, respectively. The averaged SRP ambient concentration was 4.7 (± 0.3) $\mu g P L^{-1}$. Mean travel time (18 min), mean velocity (0.06 m s^{-1}), mean depth (0.07 m) and lateral inflows (5%) were deduced from discharge, stream width (1 m) and conductivity measurements at the top and bottom of the studied stream reach (Fig. 1). The effect of lateral inflows (mostly from surface water flushes) was
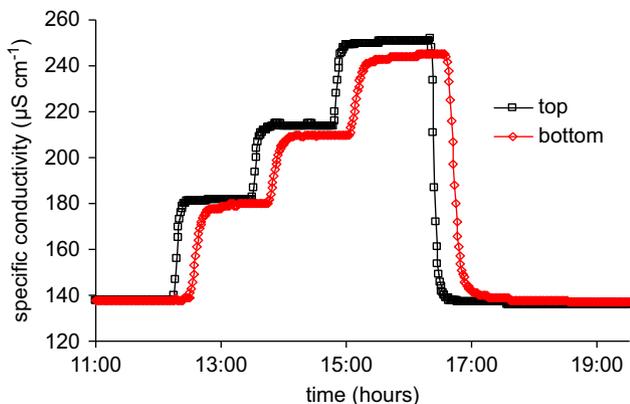
neglected for the purpose of this study because errors in SRP concentrations due to dilution effect were small (<5%).

4.2. Calculation of the Michaelis–Menten parameters

The normalised SRP concentration was plotted against distance (Fig. 2) and the negative exponential equation (Eq. (2)) was fitted to the data for three P additions ($r^2 = 0.93$–0.98, $P < 0.01$) to determine the P uptake lengths ($S_{W ADD}$) using Eq. (3). The geometric means (C_{ADD}) of the three additions were 9(± 1), 16(± 1) and 26(± 1) $\mu g P L^{-1}$, and $S_{W ADD}$ were 96 (± 11), 98 (± 5) and 108 (± 5) m, respectively.

The uptake length ($S_{W ADD}$) was then plotted against the geometric mean of the added SRP concentration (C_{ADD}), and the ambient uptake length (S_W) was extrapolated by linear regression ($r^2 = 0.93$, $P = 0.17$) to the negative ambient SRP concentration ($-C_{AMB}$), as shown in Fig. 3. S_W was 86(± 27) m. $S_{W ADD}$ were therefore overestimated by 12%, 14% and 26%, respectively, a relatively small overestimate compared to
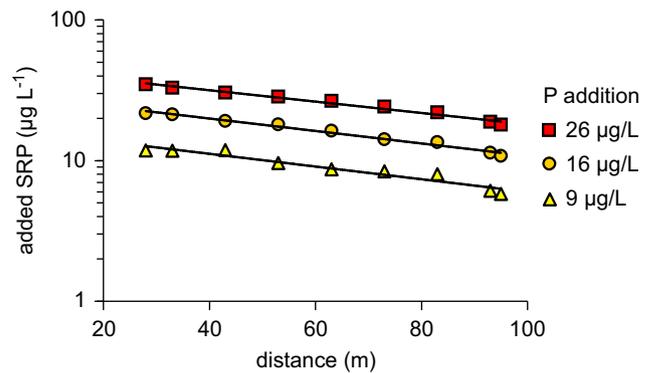

Fig. 2 – Added SRP concentrations along the stream reach at steady-state concentration of the conservative tracer for the three concentrations of SRP addition (geometric mean).
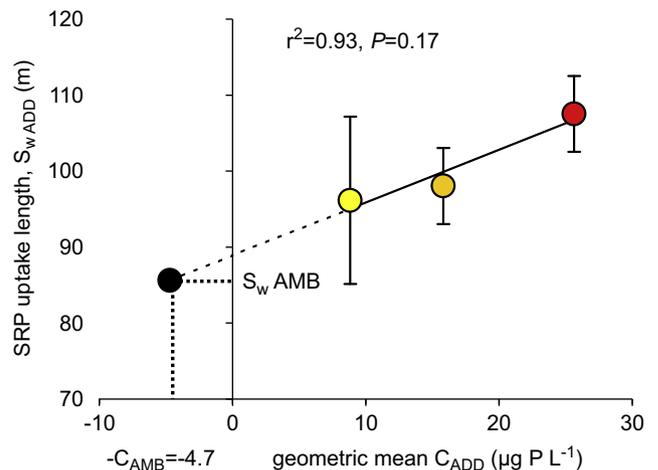

Fig. 3 – Extrapolation of the ambient uptake length at minus the ambient SRP concentration, from uptake lengths calculated from three SRP additions and plotted against the geometric mean of the study reach SRP added concentrations.

Fig. 1 – In-stream change in conductivity due to the multiple-rate addition of sodium chloride (conservative tracer).

other studies (Mulholland et al., 2002; Payn et al., 2005; Earl et al., 2007) probably due to the low C_{ADD}. The errors associated with the calculations were also relatively small due to the exceptional quality of the fit of Eq. (2) ($r^2 = 0.93$–0.98) for such low SRP additions (C_{ADD} 9–26 μg P L^{-1}) (cf. Earl et al., 2007; Hanafi et al., 2007).

The ambient uptake rate (U_{AMB}) could then be calculated using Eq. (1). U_{AMB} was 0.0142 (± 0.0042) mg P m^{-2} min^{-1}. The uptake rates under the three additions were 0.0127 (± 0.0029), 0.0124 (± 0.0021) and 0.0113 (± 0.0018) mg P m^{-2} min^{-1}, respectively. These uptake rates were therefore underestimated by 11%, 13% and 20%, respectively.

A non-linear regression model using S-plus 6.2 Professional was run to determine the two unknown parameters (C_{HALF} and U_{MAX}) of the Michaelis–Menten equation (Eq. (5); Fig. 4). C_{HALF} was 123 (± 40) μg L^{-1} and U_{MAX} 0.386 (± 0.103) mg P m^{-2} min^{-1}. The C_{AMB}:C_{HALF} ratio was only 0.04.

While abiotic and biotic processes influence P sorption, it is very likely that P was a limiting factor to stream metabolic activity for three reasons: the nutrient uptake lengths were relatively short (cf. Newbold et al., 1983; Mulholland et al., 1985; Marti et al., 2004), the ambient concentration (C_{AMB}) of the Cairn Burn was far below the half-saturation concentration (C_{HALF}), and the ambient uptake rate (U_{AMB}) was <4% of the maximum uptake rate. Nutrient limitation is important because it is one of the assumptions of the Michaelis–Menten model (Borchardt, 1996) and so a condition for the multiple-rate nutrient addition studies to perform well (Earl et al., 2007). This is the first estimation of the Michaelis–Menten parameters of P for a whole-stream reach. Further studies are required to assess the stream efficiency of P uptake, as suggested for N uptake in Payn et al. (2005). In streams with higher SRP concentrations, this approach will work as long as detectable sorption occurs. Whether this sorption is biological or not does not invalidate the Michaelis–Menten approach because similar rectangular hyperbolic functions are used for abiotic processes (e.g. Langmuir equation, House et al., 1995b).
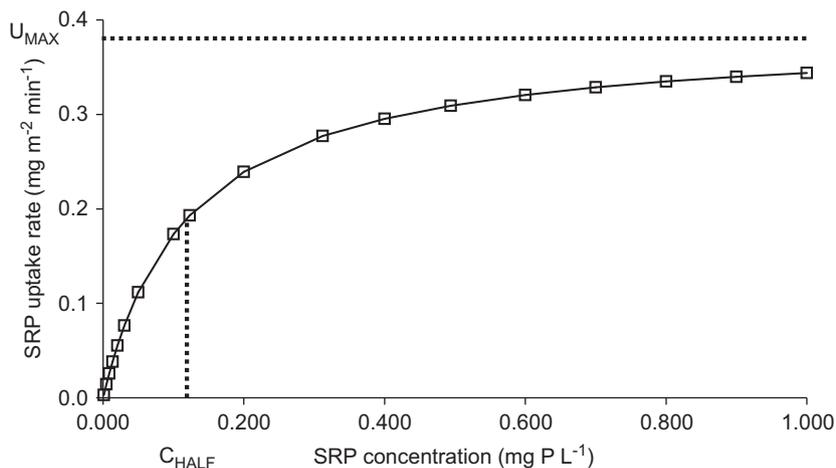

Fig. 4 – Gross uptake rates as a function of SRP concentrations using the Michaelis–Menten equation.
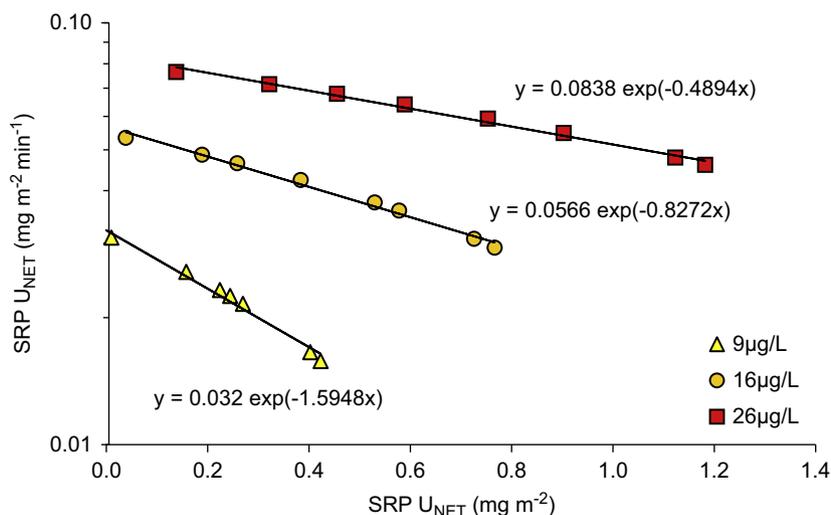

Fig. 5 – Net uptake rate as a function of net uptake flux for the three SRP additions. An exponential function was fitted to the data points to find the parameters of the Elovich equation. For example, for $C_{ADD} = 16$ μg P L^{-1}, $a = 0.0566$ (± 0.0008) mg P m^{-2} min^{-1} and $b = 0.8272$ (± 0.0360) m^2 mg^{-1}.

4.3. Modelling the observed net sorption of P by the stream reach

Solution 1—The observed net uptake rate (U_{NET}, $mg\,m^{-2}\,min^{-1}$), for each data point along the stream reach, was then calculated (from Eq. (10)) and plotted against the observed net uptake flux (U_{NET}, $mg\,m^{-2}$, Eq. (11)). An exponential function was fitted to the data ($R^2 = 0.98$–0.99, $P < 0.01$) to determine the parameters (a, b) of the Elovich equation (Eq. (6)) for the three SRP additions (Fig. 5). Uncertainties associated with a and b did not exceed 2% and 5% of their values, respectively. The fit of the Elovich model is further illustrated as a function of time in Fig. 6. The values of the net uptake rates were similar to the *ex-situ* study (recirculating flume) by House et al. (1995a). The calculated nutrient uptake length from the three additions using Eq. (21) were 73 (± 6), 79 (± 6) and 91 (± 7) m, respectively, in close agreement with the ambient uptake length $S_W = 86(\pm 27)$ m determined by the multiple-rate nutrient addition.

Solution 2—The results obtained from applying Eqs. (15) and (16) to parameterise Eq. (7) were qualitatively the same as solution 1, but the fit was less good (Fig. 6).

Solution 3—The parameters of the Elovich equation (Eq. (7)) were found numerically using the non-linear regression model of S-Plus. The results painted a different picture: the parameter b (curvature) was negative for the two lowest concentrations of P added to the stream. In order to remediate to this unlikely result, another numerical solution was sought using Solver with the constraint $b > 0$ ($b > 0.0001$ was used in Solver). Essentially, the net uptake rate ($mg\,m^{-2}\,min^{-1}$) was constant within the observed 18 min, although perhaps less so as the added P increased (Fig. 6).

4.4. Sorption kinetics of P by the stream reach

Solution 1—The Elovich model allowed extrapolation of the sorption kinetics over a 4-h long nutrient addition experiment typically used to determine nutrient uptake length of a stream reach (Fig. 7). It suggested that the net uptake rate ($mg\,m^{-2}\,min^{-1}$) fell very quickly within the first hour and this was reflected in the slowdown of net uptake ($mg\,m^{-2}$) over time. The SRP retention efficiency was lower at higher concentrations at the beginning, converging relatively quickly (within an hour) to a similar value. The stream reach SRP concentrations over time mirrored the retention capacity of the stream, showing stability after 1 h of P addition. This extrapolation relied, however, on the first 18 min of observation, and, as hinted above, may not represent the reality on this occasion (see Section 4.6. below). The same applied for solution 2.

Solution 3—The results portrayed a different picture (Fig. 8). Over 4 h, there was no change in nutrient uptake rate ($mg\,m^{-2}\,min^{-1}$) at the two lowest P additions, but some saturation of uptake ($mg\,m^{-2}$) might have occurred at the highest P added concentration.

4.5. Long-term phosphorus addition

Another P addition ($C_{ADD} = 39 \pm 2\,\mu g\,L^{-1}$), under similar flow conditions ($11.2 \pm 1\,L\,s^{-1}$), was run in the same stream reach
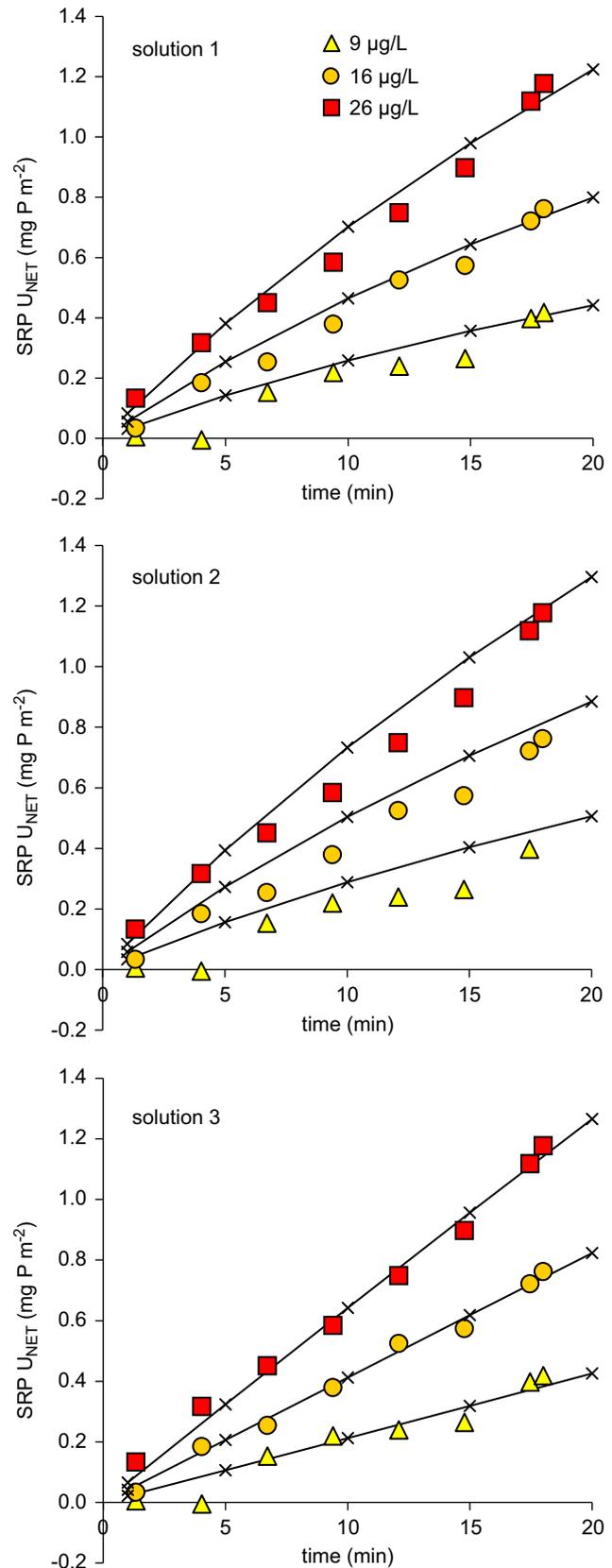
Fig. 6 – Results of three solutions to model uptake flux of SRP as a function of time for the three concentration additions. Symbols represent the observed net uptake flux and lines the modelled net uptake flux.
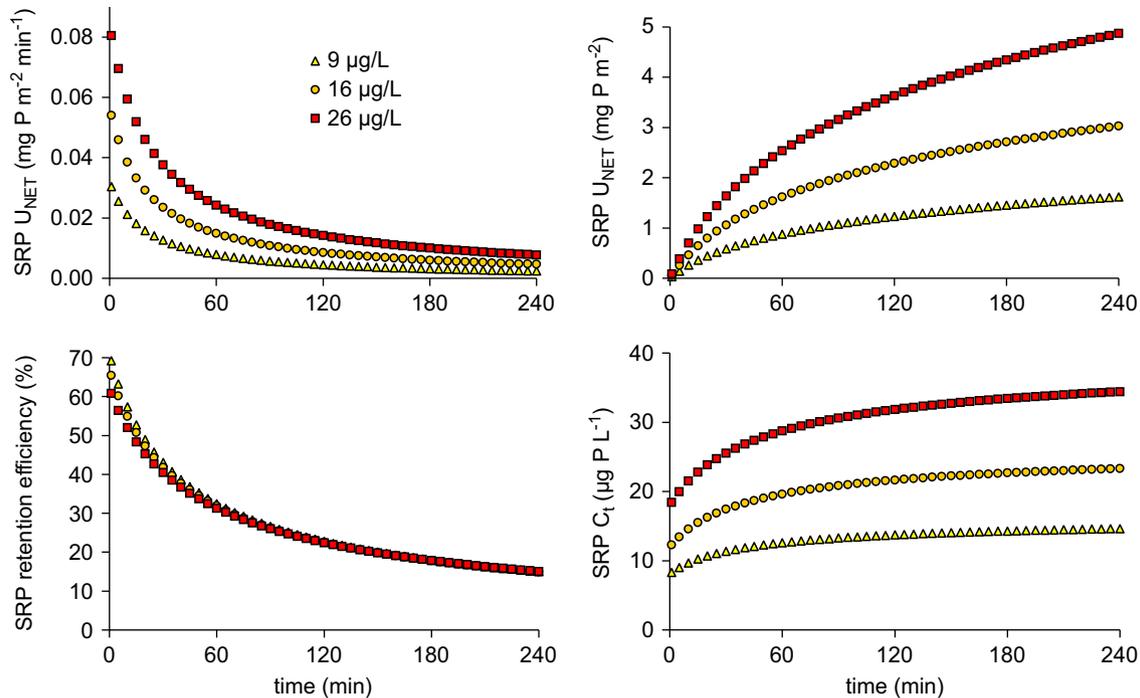
Fig. 7 – Four-hour extrapolation of SRP kinetics (net uptake rate, net uptake flux, retention and concentration), for the three SRP additions, using solution 1.
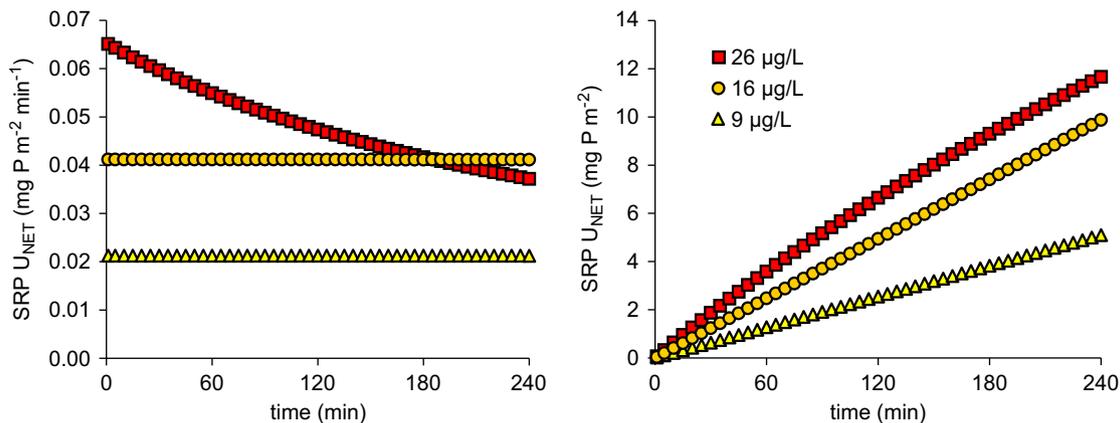

Fig. 8 – Four-hour extrapolation of SRP kinetics (net uptake rate and net uptake flux), for the three SRP additions, using solution 3.
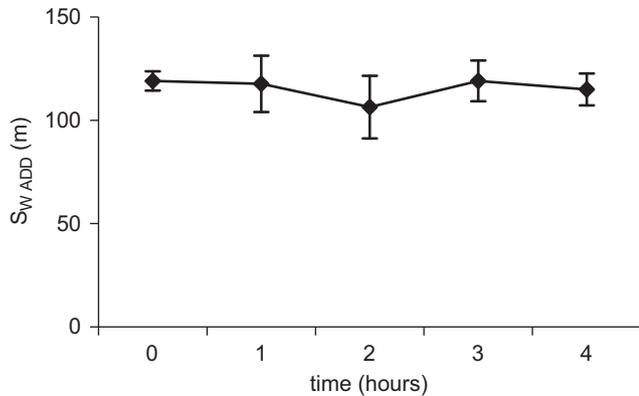
on September 5, 2007 and water samples were picked up as soon as the steady-state concentration of conservative tracer was reached ($t = 0$) and then every hour for 4 h. The SRP ambient concentration was $2.4(\pm 0.6)\,\mu g\,P\,L^{-1}$. This independent test showed (Fig. 9) that the nutrient uptake length did not change over the 4 additional hours of P addition, despite a P addition 16 times the ambient concentration.

4.6. Implications

Three solutions were presented to assess the kinetics of P in whole-stream reach. These solutions may apply to other nutrients (or pollutants) with similar behaviour. While the theoretical considerations may be generally useful, it was not

possible, in this case, to extrapolate the results beyond the observations. This was because the observed data only spanned the linear portion of the sorption isotherm. It is not wise to fit a non-linear model empirically unless some curvature starts appearing. In order to get the expected curvature, either saturation of the system needs to happen faster (e.g. by increasing significantly the concentration of the added nutrient) or the nutrient addition needs to be run over a longer time period (or longer stream reach length).

Comparison between *in-situ* (this study) and *ex-situ* (e.g. House et al., 1995a) P uptake kinetics are not straightforward. While the *ex-situ* EPC$_0$ approach, as usually done under batch conditions, may be valid for suspended solids (Froelich, 1988), it is unlikely to be comparable to *in-situ* whole-stream

Fig. 9 – Change in nutrient uptake length ($S_{W\ ADD}$) over time with a continuous SRP addition ($C_{ADD} = 39\,\mu g\,L^{-1}$), as soon as a steady-state concentration of conservative tracer was reached ($t = 0$), and then every hour for 4 h.

nutrient cycling, in small systems. The EPC_0 approach is probably more adequate, however, in large river systems and estuaries with high suspended sediments or phytoplankton concentrations. Recirculating flume experiments (e.g. House et al., 1995b) and *in-situ* DET gel probes (Jarvie et al., in press) may be more promising to assess nutrient exchange with benthic sediments in large river systems where nutrient addition is impractical. This has obvious management implications since in the UK it is the EPC_0 approach that has gained momentum (e.g. Jarvie et al., 2005), in contrast to in-stream nutrient cycling studies elsewhere (e.g. Marti et al., 2004; Gücker and Pusch, 2006; Newbold et al., 2006). Further work is needed to quantify the relative importance of the biota and to assess how these two approaches compare.

5. Conclusions

Overall, these results suggest that the assumption of constant uptake rate (no saturation of the sorption capacity, cf. Stream Solute Workshop, 1990, p. 107; Webster and Ehrman, 1996, p. 157) during nutrient cycling studies is reasonable, at least as long as the concentrations of nutrients added are kept as low as possible.

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