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Abstract

Soil phosphorus (P) quantity–intensity (q–i) relationships, based on common extraction methods, may potentially be used to estimate the risk of P loss in overland flow and subsurface drainage water. Some workers have used nonlinear q–i relationships to derive thresholds in soil test P (STP; a quantity factor) above which the risk of P loss increases, while others find linear relationships and no threshold. We present here a simple modelling exercise (based on Langmuir adsorption theory) along with data from literature to explain the behaviour of q–i relationships, and to give an explanation for this apparent discrepancy.

The data indicate that q–i relationships are dependent upon the soil to solution ratio of the P intensity parameter, adsorption capacity (Q_{max}) and strength (K) of the soil, and the total range in STP. In turn, this affects the calculation of a threshold in STP. The q–i relationship tends towards linearity under conditions of a narrow total range of STP and/or when using a wide soil to solution ratio for estimating the P intensity parameter. Under such conditions, a threshold is difficult to detect, and uncertain.

We conclude that the sensitivity of thresholds to experimental conditions and soils needs to be considered if thresholds are to be successful in environmental management to decrease P loss to surface waters.
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1. Introduction

Soil phosphorus (P) contents of intensively managed agricultural soils in e.g. Europe and the USA have increased in the course of the 20th century, as the result of heavy P applications via fertiliser and animal manure exceeding the withdrawal of P by harvested crops (e.g. Breeuwsma et al., 1995; Pautler and Sims, 2000). This build-up of soil P can increase the potential for P loss to surface waters via hydrological pathways such as overland flow and subsurface drainage water, contributing to P enrichment of surface waters and eutrophication (Sharpley et al., 1994; Sims et al., 1998).

Various methods have been proposed to estimate the potential P loss from P enriched soils. For example, McDowell and Sharpley (2001) used water and 0.01 M $CaCl_2$ extractable P to approximate P in overland flow and subsurface drainage, respectively. These and other authors (e.g. Hesketh and Brookes, 2000) have shown that such data can be coupled with measures of soil test P (STP; e.g. Mehlich-3 or Olsen extractable P), and can be fitted to a split-line model to calculate a change point or

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Nomenclature

a_1	slope of the linear relationship for values of q below the CP in the split-line model	DPS	degree of phosphorus saturation (%)
		F_{max}	total P sorption maximum ($mg\,P\,kg^{-1}$)
a_2	slope of the linear relationship after the CP in the split-line model	g	mass of soil (kg)
		i	intensity ($mg\,P\,l^{-1}$)
Δa	difference between a_2 and a_1 in the split-line model	K	constant Langmuir adsorption isotherm ($l\,mg^{-1}$)
α	ratio $F_{max}/[Fe + Al]$-ox	q	quantity ($mg\,P\,kg^{-1}$)
b	intercept of the split-line model	Q	amount of P adsorbed to the soil ($mg\,P\,kg^{-1}$)
β	ratio $Q_{max}/[Fe + Al]$-ox	Q_{max}	P adsorption maximum ($mg\,P\,kg^{-1}$)
C	concentration (intensity) of P desorbed in solution ($mg\,P\,l^{-1}$)	T	total amount of inorganic reversibly adsorbed P (mg P)
CP	change point or threshold ($mg\,P\,kg^{-1}$)	v	volume of extractant (l)

threshold in STP. The split-line model separates the relationship between STP and P loss into two sections on either side of the threshold, whereby soils in the section above the threshold exhibit an increased potential for P loss compared to the one below. Others (e.g. Heckrath et al., 1995) have demonstrated a threshold in STP for P loss via tile drainage. These thresholds have been derived with the purpose to find a critical level in STP, above which the potential of P loss increases, to be used for environmental management (e.g. McDowell et al., 2001a).

A method, recently developed in The Netherlands, compares the percentage or degree of P saturation (DPS) of the soil profile between the soil surface and the mean highest groundwater level, with the dissolved P concentration in soil solution leaching from the soil profile on the long-term (van der Zee et al., 1990). Based on model calculations using average measured P sorption and desorption characteristics of Dutch sandy soils, a relationship was derived between DPS and the P equilibrium concentration in soil solution. At 25% saturation of the soil with P (25% DPS), the P concentration in soil solution leaching from the soil profile corresponds to 0.1 mg dissolved $P\,l^{-1}$ (van der Zee et al., 1990). The value of 0.1 $mg\,P\,l^{-1}$ has been set as the Dutch limit for inorganic P in surface waters to prevent eutrophication and associated adverse effects (TCB, 1990). Above 25% DPS, the dissolved P concentration in the soil increases nonlinearly with DPS (Schoumans and Groenendijk, 2000). Indeed, experimental data often demonstrate nonlinear relationships between DPS and water extractable P (e.g. Lookman, 1995; Chardon and van Faassen, 1999; Koopmans et al., 2001).

McDowell et al. (2001a) applied the split-line model to laboratory extraction data of 0.01 M $CaCl_2$ extractable P (soil to solution ratio of 1 to 5 w:v) versus DPS in soils from New Zealand, the UK and USA. Thresholds

occurred at DPS values ranging from 25% to 34%, and corresponded to P concentrations in $CaCl_2$ extracts that were comparable to the dissolved P concentration in soil solution found by van der Zee et al. (1990) at 25% DPS. This method also applies to P loss via subsurface flow (Lookman, 1995).

The examples above have a commonality; they relate quantity (q; STP or DPS) to intensity (i; P in overland or subsurface flow or the approximation thereof, i.e., water or 0.01 M $CaCl_2$ extractable P) in a nonlinear manner. In contrast, many other examples show a linear relationship between STP or DPS and P loss in overland flow or 0.01 M $CaCl_2$ extractable soil P, and as a consequence, no threshold (e.g. Sharpley, 1995; Pote et al., 1996; Pautler and Sims, 2000). This is puzzling, but methodology (soil to solution ratio of the P intensity parameter and rainfall intensity) and soil chemical characteristics (soil type) and conditions (land use and range of STP) were different in the various studies. For example, a narrow soil to solution ratio (i.e., a low suspended sediment concentration) in overland flow exhibited a nonlinear q–i relationship, while a wide soil to solution ratio exhibited a linear relationship (McDowell and Sharpley, 2001). Furthermore, apparent linearity of data can simply be caused by not testing soils of sufficiently wide range in STP to show a nonlinear relationship (McDowell et al., 2001a). So far, a coherent explanation for these divergent results does not exist to our knowledge. A simple modelling exercise, based on the Langmuir adsorption isotherm, may explain such an apparent discrepancy. Thus, the primary objective of this study is to explore with theory and data from literature, the variation in q–i relationships as influenced by methodology, soil chemical characteristics and soil P levels. A secondary objective is to rationalise the existence of thresholds in STP, and to discuss the applicability and limitations of thresholds, and thus, place their calculation in perspective.

2. Materials and methods

2.1. Theory

The overall sorption reaction of inorganic P in soil may be simplified to consist of a fast reaction (reversible adsorption on surface sites), and a slow one (diffusion into soil aggregates followed by precipitation or sorption inside the aggregate) (e.g. van der Zee and van Riemsdijk, 1988). Phosphorus lost in overland flow and subsurface drainage water is significantly correlated only to the rapidly desorbable P pool, as revealed by recent data using radioactive ^{33}P (McDowell et al., 2001b). In our study, as an approximation, only reversibly adsorbed P is considered to be involved in the q–i relationships explored here.

Dispersing a known amount of soil (g; kg soil) containing a known amount of adsorbed P (T; mg P) in a known volume of solution (v; l) results in the establishment of an equilibrium within hours between the amount of P adsorbed to the soil (Q; mg P kg^{-1}) and the amount of P in solution (C; mg P l^{-1}), described by:

$$T = gQ + vC \tag{1}$$

The Langmuir adsorption isotherm can be used to describe reversible adsorption of P (van der Zee et al., 1988):

$$Q = \frac{Q_{max}KC}{1 + KC} \tag{2}$$

where Q_{max} is the adsorption maximum (mg P kg^{-1}) and K is a constant (l mg^{-1}) describing the affinity of the soil for P, or adsorption strength; Q_{max} and K are soil properties defined by the chemical characteristics of the soil. Substituting Eq. (2) in Eq. (1) gives:

$$T = g\frac{Q_{max}KC}{1 + KC} + vC \tag{3}$$

Eq. (3) can be solved for C to yield Eq. (4) (see Appendix A):

$$C = \frac{-(gQ_{max}K + v - TK) + \sqrt{(gQ_{max}K + v - TK)^2 - 4(vK)(-T)}}{2(vK)} \tag{4}$$

For both adsorption and desorption processes, the Langmuir isotherm is linear at small amounts of T and thus the increase of C with T is linear at low values of T. As T increases and Q approaches Q_{max}, the Langmuir isotherm becomes nonlinear, and the relationship between C and T changes from linear to nonlinear. As T increases further, $Q \approx Q_{max}$ and any additional P remains in solution; the Langmuir isotherm becomes linear again, and likewise, the increase of C with T. This

follows from Eq. (1), the slope of the C versus T relationship equals $1/v$ as $Q \approx Q_{max}$ and, thus, depends on the soil to solution ratio; widening this ratio decreases the slope.

Using Eq. (4), we analysed the behaviour of q–i relationships, i.e., C versus T, as a function of soil to solution ratio (g to v) at set values of Q_{max} and K. Next, we analysed the effects of varying Q_{max} and K at a set soil to solution ratio for a range of T. We used the split-line model (Eq. (9)), described by McDowell et al. (2001a), to calculate thresholds in the q–i relationships.

2.2. Elaboration

We used laboratory extraction data of Schoumans et al. (1991) and Chardon (unpublished) to obtain relevant ranges of values of Q_{max} and K. Soil samples were collected from the plough layer (0–30 cm) of 151 sites representative for intensively managed agricultural sandy soils in The Netherlands. These data sets contained the following parameters: soil density, organic matter, water extractable P at a soil to solution ratio of 1 to 60 v:v (Pw; Sissingh, 1971), ammonium-oxalate extractable P (P-ox) and Fe and Al ([Fe + Al]-ox), and P extractable with iron-oxide (FeO) impregnated filter paper (Pi-test; Sissingh, 1983). Furthermore, the data sets contained the pH-KCl (Schoumans et al., 1991) and the pH-H$_2$O (Chardon, unpublished).

We calculated DPS (%) according to van der Zee et al. (1990):

$$DPS = \frac{P\text{-ox}}{\alpha[Fe + Al]\text{-ox}}100 \tag{5}$$

where P-ox and [Fe + Al]-ox are expressed in mmol kg^{-1}; $\alpha = 0.5$ denotes the saturation factor, i.e., sorption strength of [Fe + Al]-ox for P. The value of α was calculated as the ratio between P-ox and [Fe + Al]-ox from a set of sandy soil samples pre-saturated with P in a laboratory experiment.

In sandy soils, Q_{max} depends upon the ammonium-oxalate extractable Fe and Al contents. The value of Q_{max} can be calculated from:

$$Q_{max} = \beta[Fe + Al]\text{-ox}31 \tag{6}$$

where $\beta = 0.135$, Fe and Al are expressed in mmol kg^{-1}, and 31 represents the atomic weight of P to obtain Q_{max} in mg P kg^{-1} (van der Zee et al., 1988). The value of β was calculated as the ratio between the amount of reversibly adsorbed P, as estimated by FeO impregnated filter paper, and [Fe + Al]-ox from a set of sandy soil samples pre-saturated with P in a laboratory experiment. Iron-oxide impregnated filter paper functions as an infinite sink for P, and maintains a negligible P concentration in suspension facilitating continuous

desorption of reversibly adsorbed P (van der Zee et al., 1987).

We estimated K from P desorption in a Pw extract by solving Eq. (3) for K (see Appendix B):

$$K = \frac{T - vC}{gQ_{max}C + vC^2 - TC} \tag{7}$$

We assumed equilibrium between P adsorbed to the soil and P measured in the Pw extract after 22 h of pre-equilibrating and 1 h of shaking at 20 °C. Usually, the Pw value, used as STP in P fertiliser recommendation for arable land in The Netherlands, is expressed in $mg\,P_2O_5\,l^{-1}$ of soil. To obtain K, we expressed Pw in $mg\,P\,kg^{-1}$ using soil density.

To assess the amount of reversibly adsorbed P (T), van der Zee et al. (1988) used FeO impregnated filter paper. We derived values of T from the data of the Pi-test.

2.3. Calculation of thresholds

Thresholds in the q–i relationships were calculated using a split-line model describing two linear relationships on either side of the threshold (McDowell et al., 2001a). Below the threshold, i varies with q according to:

$$i = a_1q + b \tag{8}$$

and above the threshold according to:

$$i = a_1q + \Delta a(q - CP) + b \tag{9}$$

where i is intensity ($mg\,P\,l^{-1}$), q is quantity ($mg\,P\,kg^{-1}$), CP is the threshold (or change point), a_1 is the slope of the linear relationship for values of q below the CP, Δa is the difference in slopes above the threshold compared to a_1, and b is the intercept. The four parameters (a_1, Δa, CP and b) were estimated using the method of maximum likelihood (analogous to the least-squares method) in Genstat 5, release 4.1. The slope of the linear relationship after the threshold a_2 was calculated as $a_2 = a_1 + \Delta a$. A low ratio of a_2 to a_1 is indicative of a small change in the increase of i with q after the threshold, or in other words, the relationship between q and i tends to become linear. When the ratio of a_2 to a_1 is 1, then the relationship between q and i is linear by definition. Hence, when the ratio of a_2 to a_1 is low, a threshold is difficult to detect and uncertain.

3. Results and discussion

3.1. Soil characteristics

The 151 soil samples represent the wide range in soil conditions found in intensively managed agricultural sandy soils in The Netherlands. The samples provide a

Table 1
Measured data of organic matter (OM), pH, Pw, Pi-test, P-ox, [Fe + Al]-ox and DPS of the 151 soil samples from The Netherlands (Schoumans et al., 1991; Chardon, unpublished), and estimated values of Q_{max} and K calculated according to Eq. (6) and Eq. (7) in this study

Parameter	Range	Mean	Standard deviation
OM (%)	2.1–15.5	5.2	±2.0
pH-KCl[a]	3.7–6.2	4.7	±0.5
pH-H_2O[b]	5.3–6.8	6.2	±0.3
Pw ($mg\,P\,kg^{-1}$)	2–65	16	±13
Pi-test ($mg\,P\,kg^{-1}$)	11–313	92	±67
P-ox ($mg\,P\,kg^{-1}$)	115–1211	485	±213
[Fe + Al]-ox ($mmol\,kg^{-1}$)	25–185	70	±23
DPS[c] (%)	16–100	46	±17
Q_{max} ($mg\,P\,kg^{-1}$)	103–775	292	±97
K ($l\,mg^{-1}$)	0.1–6.2	1.5	±1.1

[a] Schoumans et al. (1991); $n = 67$.
[b] Chardon (unpublished); $n = 84$.
[c] DPS was calculated according to Eq. (5). The DPS is calculated here for soil samples from the 0–30 cm layer only, while van der Zee et al. (1990) apply the DPS to the soil profile between the soil surface and the mean highest groundwater level.

wide range in soil P levels (Pw, Pi-test extractable P, P-ox and DPS) and soil chemical characteristics (organic matter, pH, [Fe + Al]-ox, Q_{max} and K) (Schoumans et al., 1991; Chardon, unpublished). The range, mean and standard deviation of these parameters are presented in Table 1. The pH-KCl of the soil samples taken from the study of Schoumans et al. (1991) was a little lower than the pH-H_2O in the study of Chardon (unpublished). Because the pH of the soil samples selected is higher than the point of zero net charge, the pH in a high ionic strength medium (KCl) is lower than the pH in a low ionic strength medium (water) (McBride, 1994). Amounts of Pw and Pi-test extractable P were, on average, 3.4% and 19.5% of P-ox, respectively. Approximately 80% of the samples had Q_{max} and K values that ranged from 150 to 500 $mg\,P\,kg^{-1}$ and from 0.3 to 3.3 $l\,mg^{-1}$, respectively. These results are similar to data presented by van der Zee et al. (1988).

3.2. Influence of soil to solution ratio on q–i relationship

Fig. 1 shows the relationship between quantity (as T/g to give $mg\,P\,kg^{-1}$ soil) and intensity (C in $mg\,P\,l^{-1}$) calculated for soil to solution ratios of 1:0.3, 1:5, 1:10 and 1:50 (g to ml) for a soil of $Q_{max} = 300\ mg\,P\,kg^{-1}$ and $K = 1.5\ l\,mg^{-1}$. According to Eq. (4), C may increase with T to infinity. However, P will precipitate as the concentration of P in soil solution exceeds the solubility product of the solid phase determining the solubility of P in soil. In acidic to neutral soils, heavily enriched
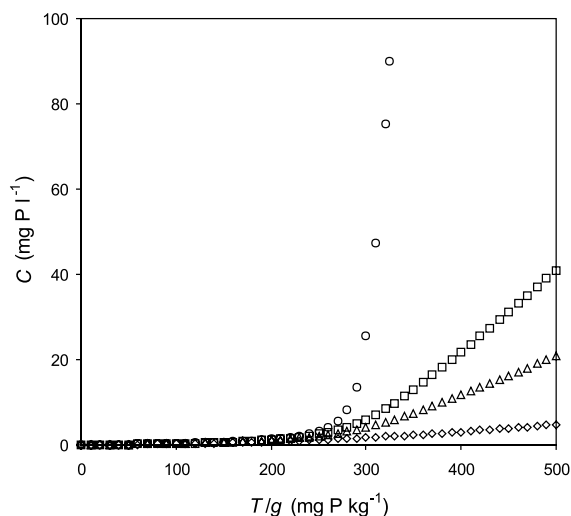
Fig. 1. Modelled data of the phosphorus intensity (C) versus P quantity (T/g) at four different soil to solution ratios calculated using Eq. (4) (($\bigcirc$): 1:0.3; ($\square$): 1:5; ($\triangle$): 1:10; ($\diamondsuit$): 1:50; $Q_{max} = 300$ mg P kg^{-1} and $K = 1.5$ l mg^{-1}).

with P, Ca– and Mg–P compounds may exist as metastable solid phases. An extreme example of a P enriched soil was described by Dantzman et al. (1983). They investigated a site which had been used as a feedlot for 15 years and showed that P accumulated as Ca–P. Nair et al. (1995), Sharpley and Smith (1995) and Lookman et al. (1997) also observed accumulation of Ca–P on sites that received large amounts of animal manure. Also, de Haan and van Riemsdijk (1986) found indications for the existence of brushite (CaHPO$_4 \cdot$2H$_2$O) in heavily pig manured sandy soils. They measured a maximum P concentration of approximately 90 mg P l^{-1}, and therefore, in Fig. 1, we showed C in the 1:0.3 extract up to this P concentration.

The P concentration in the 1:0.3 extract shows a strong increase with T/g, and a large change in slope, but as the soil to solution ratio of the P intensity pa-

rameter widens, this increase lessens, and the slope of the relationship between T/g and C changes less (Fig. 1). Thus, at a wide soil to solution ratio, the relationship between T/g and C tends to become linear.

To calculate a threshold in these q–i relationships, we applied the split-line model (McDowell et al., 2001a; Eq. (9)), assuming that T/g ranges from 0 to 325 mg P kg^{-1} ($T/g = 325$ mg P kg^{-1} corresponds to $C = 90$ mg P l^{-1} in the 1:0.3 extract). In the 1:0.3 extract, a clear threshold is evident, however, as the soil to solution ratio widens, the threshold and the ratio of a_2 to a_1 decreased (Table 2). Decreasing the T/g range, used for calculating the threshold, from 0–325 to 0–150 mg P kg^{-1} has the same effect; the threshold and the ratio of a_2 to a_1 decreased (Table 2). In both cases, the corresponding Q and C values decreased as well. Summarising, at a wider soil to solution ratio and/or a decreasing T/g range, the increase of C with T/g becomes smaller and the slope of the relationship between T/g and C changes less (Fig. 1), and as a result, the threshold calculated by the split-line model decreases.

Clearly, q–i relationships calculated are highly dependent upon the soil to solution ratio used for determining the P intensity parameter and the total range in STP. As a result, the threshold, calculated by the split-line model, and the corresponding C value, are also affected by experimental conditions and soil selection. At a wide soil to solution ratio and/or a narrow total range in STP, the relationship between T/g and C tends towards linearity, and thus, a threshold may be difficult to detect.

3.3. Influence of soil chemical characteristics on q–i relationship

Fig. 2 shows the relationships between T/g and C for a soil to solution ratio of 1:0.3, $Q_{max} = 150$ and 500 mg P kg^{-1}, and $K = 0.3$ and 3.3 l mg^{-1}. Similar to Fig. 1, C is shown up to a maximum of 90 mg P l^{-1}. Increasing Q_{max} and/or K has the effect of increasing the range in

Table 2
Modelled data of the threshold in T/g, calculated from the split-line model (Eq. (9)), the corresponding amount of P adsorbed (Q) and P equilibrium concentration (C), and the ratio of a_2 to a_1 calculated at different soil to solution ratios for a soil of $Q_{max} = 300$ mg P kg^{-1} and $K = 1.5$ l mg^{-1} (Fig. 1). T/g ranged from 0–325 to 0–150 mg P kg^{-1}, respectively

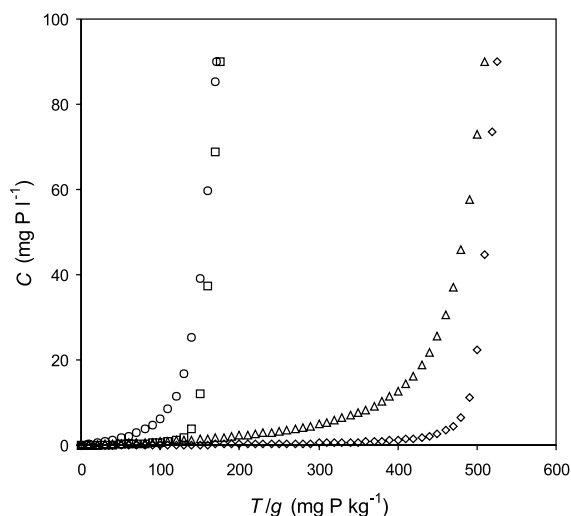| Soil to solution ratio	T/g (mg P kg^{-1})	Threshold in T/g (mg P kg^{-1})	Q (mg P kg^{-1})	C (mg P l^{-1})	a_2 to a_1 ratio
1:0.3	0–325	293	288	16.1	110.3
1:5	0–325	246	234	2.4	11.4
1:10	0–325	227	211	1.6	7.1
1:50	0–325	187	152	0.7	2.7
1:0.3	0–150	87	87	0.3	2.1
1:5	0–150	87	86	0.3	2.0
1:10	0–150	87	84	0.3	2.0
1:50	0–150	85	74	0.2	1.6

Fig. 2. Modelled data of the phosphorus intensity (C) in a 1:0.3 extract versus P quantity (T/g) at two different P adsorption maxima (Q_{max}) and strengths (K) calculated using Eq. (4) (($\bigcirc$): $Q_{max} = 150$ mg P kg^{-1} and $K = 0.3$ l mg^{-1}; ($\square$): $Q_{max} = 150$ mg P kg^{-1} and $K = 3.3$ l mg^{-1}; ($\triangle$): $Q_{max} = 500$ mg P kg^{-1} and $K = 0.3$ l mg^{-1}; ($\diamond$): $Q_{max} = 500$ mg P kg^{-1} and $K = 3.3$ l mg^{-1}).

T/g before the slope of the relationship between T/g and C changes. Applying the split-line model to the data presented in Fig. 2 shows that at higher values of either Q_{max} or K, both the threshold and the ratio of a_2 to a_1 increase (Table 3). Conversely, widening the soil to solution ratio of the P intensity parameter to 1:50 caused the threshold and the ratio of a_2 to a_1 to decrease (Table 3).

Thus, in theory, q–i relationships are highly dependent upon Q_{max} and K of the soil. As a result, the threshold and the corresponding C value are also affected by the selection of soils. For example, in sandy soils with a low adsorption strength, the threshold may be difficult to detect, especially at a wide soil to solution ratio used for determining the P intensity parameter.

3.4. Examples in the literature

Many examples exist in the literature to demonstrate our theory. In a study by Hesketh and Brookes (2000), Olsen P was related to P loss in subsurface drainage waters from experimental columns containing soils of different P contents. They noted a threshold in Olsen P, above which P loss in subsurface drainage waters increased. This was mimicked by a plot of P extracted by 0.01 M CaCl$_2$ versus Olsen P (Fig. 3, adapted from Hesketh and Brookes (2000)). Widening the soil to solution ratio of the 0.01 M CaCl$_2$ extraction method caused the slope of the relationship between Olsen P and 0.01 M CaCl$_2$ extractable P above the threshold to de-
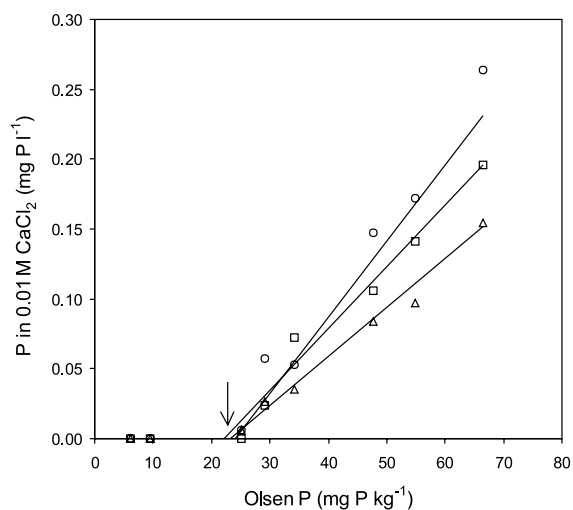

Fig. 3. Measured data of the P concentration in a 0.01 M CaCl$_2$ extract at three different soil to solution ratios versus Olsen P in experimental columns containing soils from different plots of Saxmundham (UK). Arrow indicates the thresholds (($\bigcirc$): 1:5; ($\square$): 1:10; ($\triangle$): 1:20) (adapted from Hesketh and Brookes (2000)).

Table 3
Modelled data of the threshold in T/g, calculated from the split-line model (Eq. (9)), and ratio of a_2 to a_1 calculated at a soil to solution ratio of 1:0.3 (Fig. 2) and 1:50 for different values of Q_{max} (150 or 500 mg P kg^{-1}) and K (0.3 and 3.3 l mg^{-1}). T/g ranged from 0 mg P kg^{-1} to the value required to obtain $C = 90$ mg P l^{-1} in the 1:0.3 extract

Q_{max} (mg P kg^{-1})	K (l mg^{-1})	Soil to solution ratio	T/g (mg P kg^{-1})	Threshold in T/g (mg P kg^{-1})	Q (mg P kg^{-1})	C (mg P l^{-1})	a_2 to a_1 ratio
150	0.3	1:0.3	0–172	135	129	20.6	20.0
150	3.3	1:0.3	0–177	147	145	8.2	169.6
500	0.3	1:0.3	0–509	444	437	23.0	30.6
500	3.3	1:0.3	0–525	493	489	13.8	323.7
150	0.3	1:50	0–172	84	35	1.0	1.2
150	3.3	1:50	0–177	105	85	0.4	3.1
500	0.3	1:50	0–509	264	175	1.8	1.6
500	3.3	1:50	0–525	358	329	0.6	5.4

crease. They used this phenomenon to explain why plots of Olsen P from topsoils of the Broadbalk Continuous Wheat experiment (Rothamsted, Harpenden, UK) versus the P concentration in subsurface drainage waters yielded by approximation the same thresholds, but different slopes of the relationships between Olsen P and the P concentration in drainage waters, for rainfall events with a different intensity. The different volume of rainfall caused the soil to solution ratio to change and, thus, the slope of the q–i relationship. These results agree with our data presented in Fig. 1 and Table 2.

The importance of the soil to solution ratio was also suggested in a study by McDowell and Sharpley (2001). In Fig. 4, the dissolved P concentration in overland flow, generated from air-dried soil packed in boxes in response to a rainfall event of 65 mm h^{-1}, is plotted against Mehlich-3 P (a measure of STP) (Pennsylvania soils, USA) and Olsen P (Devon soils, UK), respectively

(adapted from McDowell and Sharpley (2001)). At the beginning of the event (i.e., the first 250 ml of overland flow), the dissolved P concentration increased in a nonlinear manner with both Mehlich-3 P and Olsen P, and in both relationships, a threshold was detected. In contrast, at the remainder of the event, a linear relationship between both Mehlich-3 P and Olsen P and the dissolved P concentration was suggested. This transition was attributed to the slaking and dispersion of soil in overland flow at the beginning of the event resulting in a larger amount of soil suspended in solution, and hence yielding a comparatively narrow soil to solution ratio. This was confirmed by measuring the suspended sediment concentration in a subsample of all overland flow combined, which contained <10% of the suspended sediment concentration in the first 250 ml.

Others (e.g. Sharpley, 1995; Pote et al., 1996) have suggested linear relationships between STP and P in
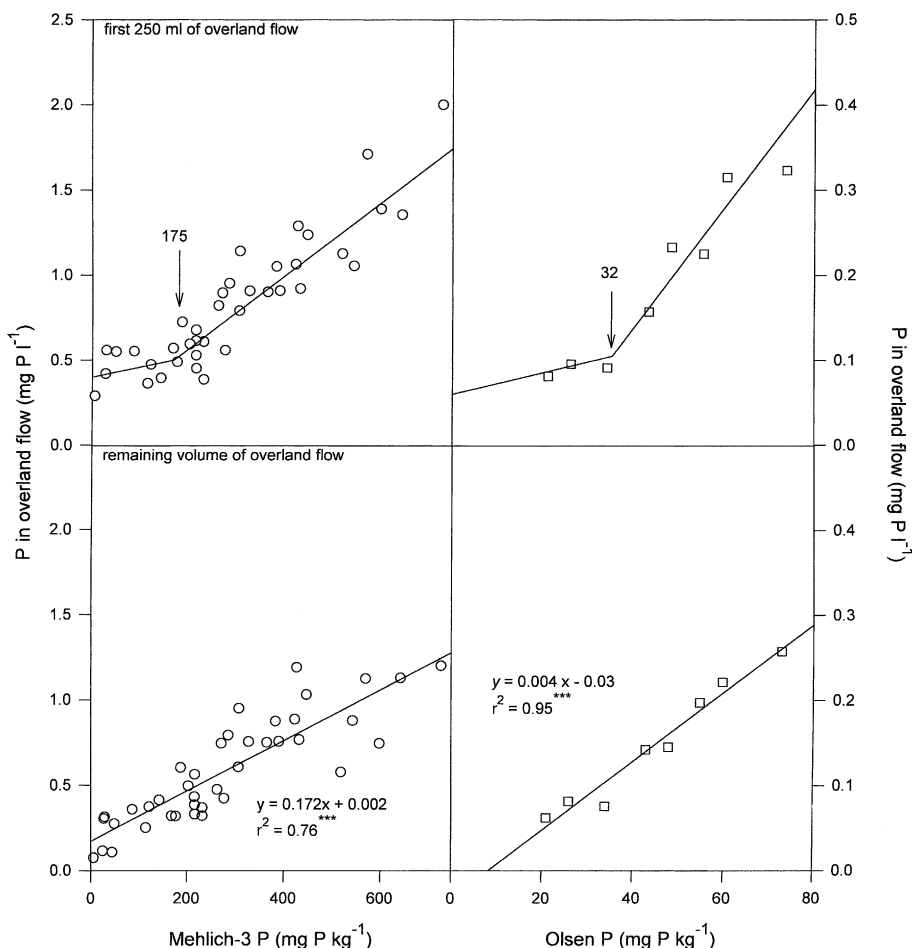

Fig. 4. Measured data of the P concentration in the first 250 ml of overland flow and the remaining volume of overland flow versus Mehlich-3 P and Olsen P for selected soils from Pennsylvania (USA; (○)) and Devon (UK; (□)), respectively. Arrows indicate the thresholds (adapted from McDowell and Sharpley (2001)) (∗∗∗ indicates significance at $P < 0.001$).

overland flow. As a result, there was no threshold. The reasons for these contradictory results may be two-fold. Firstly, the range of STP tested may not have been sufficiently wide to detect a clear threshold and secondly, the experimental conditions may have differed, i.e., the soil to solution ratio is too wide. For example, the rainfall intensity of 25.4 mm h^{-1} used in the study by Sharpley (1995) is much less than the intensity used by McDowell and Sharpley (2001), resulting in less loss of soil. Furthermore, the soils used by Sharpley (1995) were pre-wetted, negating the effect of slaking and the increased soil loss this would have caused. Little soil loss was also likely in the study by Pote et al. (1996) where plots were covered by a thick Fescue sward.

3.5. Application

In flat areas with a high groundwater level, subsurface flow is an important transport route for P loss from soil (e.g. Sims et al., 1998). For most subsurface flow situations, we expect a nonlinear relationship between STP and the P concentration in solution, since compared with overland flow, much soil comes into contact with solution, yielding a narrow soil to solution ratio. In a study by Heckrath et al. (1995), a nonlinear relationship was noted even when transport was mediated by preferential flow through large macroporous cracks in the subsoil, and little contact with the soil occurred compared to matrix flow. In areas where overland flow predominates, nonlinear relationships will be likely, where conditions favour erosion of much sediment into solution during high-intensity rainfall events, and a high soil adsorption strength. However, we hypothesise that there must be a wide range in STP values, whatever the predominant hydrological pathway for P loss.

Clearly, q–i relationships depend upon the soil to solution ratio of the P intensity parameter, adsorption capacity and strength of the soil, and total range in STP. As a result, the threshold in STP calculated by the split-line model is also affected by experimental conditions and by the selection of soils, i.e., the total range of STP and Q_{max} and K. Hence, thresholds derived from q–i relationships cannot be used in environmental management without considering their sensitivity to experimental conditions and soils. Furthermore, the P concentration in solution corresponding to the threshold depends on experimental conditions, soil chemical characteristics and total range in STP. As a consequence, in some cases, the P concentration at STP values lower than the threshold still can be considerably high (e.g. see Fig. 4, $<0.5 \text{ mg P l}^{-1}$ for the Pennsylvania soils), and can exceed the critical P concentration mentioned for triggering eutrophication effects in surface waters, i.e., 0.015–$0.030 \text{ mg total P l}^{-1}$ (USEPA, 1994). Clearly, this P concentration should also be considered before using

thresholds for mitigating P loss from soil to surface waters in practice.

4. Conclusions

Experimental relationships between soil P quantity (e.g. STP or % DPS) and P intensity (e.g. P extracted by water or dilute $CaCl_2$ or P lost in overland or subsurface flow) are often nonlinear, and yield a threshold. However, in some cases, these q–i relationships are linear, and there is no threshold. Based on our exploration of q–i relationships, we conclude that under conditions of a narrow total range in P quantity being tested, and/or a wide soil to solution ratio of the P intensity parameter, q–i relationships tend towards linearity. Under such conditions, a threshold is difficult to detect and uncertain.

What is clear is that q–i relationships are highly dependent upon experimental conditions, soil chemical characteristics and total range in STP. This should be considered when calculating thresholds from these relationships to be used for environmental management.

Appendix A. Derivation of *C* from mass balance

The amount of P extracted can be calculated at a set of values of g, v, Q_{max} and K for a range of T by solving for C in Eq. (3):

$$(1 + KC)(T) = \left(g \frac{Q_{max}KC}{1 + KC} \right)(1 + KC) + (vC) + (1 + KC) \tag{A.1}$$

yielding:

$$(T) + (TK)C = (gQ_{max}K)C + (v)C + (vK)C^2 \tag{A.2}$$

Eq. (A.2) can be written as:

$$(vK)C^2 + (gQ_{max}K + v - TK)C + (-T) = 0 \tag{A.3}$$

and solved using a quadratic equation of C:

$$C_{1,2} = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \tag{A.4}$$

Eq. (A.4) gives two solutions of which one solution is negative. Obviously, a negative value of C does not exist. We used the positive solution, i.e., Eq. (4).

Appendix B. Derivation of *K* from mass balance

Adsorption strength of the soil for P can be estimated at a set of values of T, g, v, Q_{max} and C by solving for K

in Eq. (3) leading to Eq. (A.1). Eq. (A.1) can be written as:

$$(T) + (TC)K = (gQ_{max}C)K + (vC) + (vC^2)K \qquad \text{(B.1)}$$

which can be solved for K according to Eq. (7).

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