

## Evaluation of base solutions to determine equilibrium phosphorus concentrations (EPC<sub>0</sub>) in stream sediments\*\*

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**A b s t r a c t.** The equilibrium phosphorus (P) concentration (EPC<sub>0</sub>) is used to identify sediments as sinks or sources of P in impacted waterways. It is determined by incubating the sediment with base solutions spiked with graduated amounts of P. This base solution should be stream water, but its chemistry changes with time and makes comparing sediments sampled at different times of the year impossible. We compared EPC<sub>0</sub> values determined using five base solutions, for a range of sediments and compared these with values obtained using stream water. For EPC<sub>0</sub> values < 0.5 mg P l<sup>-1</sup>, 0.0005M CaCl<sub>2</sub> was the best predictor of stream EPC<sub>0</sub> values ( $y=1.01x+0.01$ ;  $R^2 = 0.55$ ,  $P<0.05$ ), followed by tap water ( $y=1.23x+0.02$ ;  $R^2=0.55$ ,  $P<0.05$ ). Both solutions had Ca concentrations similar to the mean stream water Ca concentration of 21 mg l<sup>-1</sup>. The commonly used 0.01M CaCl<sub>2</sub> solution resulted in EPC<sub>0</sub> values much lower than stream water EPC<sub>0</sub> values, overestimating the sediment capacity to remove P from overlying water. Therefore it is recommended that stream water Ca concentrations are measured before deciding on an appropriate base solution from which to derive EPC<sub>0</sub> values.

**K e y w o r d s:** phosphorus, sediment, erosion, equilibrium phosphorus concentration

### INTRODUCTION

Phosphorus (P) and nitrogen (N) are the two main nutrients limiting algal growth in freshwater ecosystems. Phosphorus entering waterways may originate from diffuse sources such as agriculture and point sources such as waste water treatment facilities. In-stream physical, chemical and biological processes further affect P concentrations (Green *et al.*, 1978). Bed sediments are central to in-stream processes that affect P concentrations in stream flow. These sedi-

ments are derived from local parent material and deposited particulates eroded from surrounding land uses during different flow regimes (Kändler and Seidler, 2009). The ability of bed sediment to influence P at baseflow, when most interaction between sediment and the water column occurs, can be estimated by determining the equilibrium phosphorus concentration (EPC<sub>0</sub>). These measurements of stream water and sediments identify whether the sediments are likely to act as sinks or sources of P. For instance, when dissolved (filtered <0.45 μm) reactive P (DRP) in overlying water is greater than the EPC<sub>0</sub> of the sediment, the sediment will theoretically remove DRP from the water column, and the opposite is true when DRP < EPC<sub>0</sub>. It is therefore important that the EPC<sub>0</sub> is determined accurately so that the ability of the stream to buffer sporadic inputs of P can be better understood. Such inputs could include cattle dung in areas where streams are not fenced off, or a point source discharge of industrial or municipal wastewater. The EPC<sub>0</sub> of sediments may also explain why elevated P concentrations may persist when point source inputs cease.

The EPC<sub>0</sub> is calculated by incubating a known mass of sediment with base solutions (or background matrix) spiked with P, but the exact method used varies. Many authors have shown that using dried or fresh sediments, different size fractions of sediment and sampling depths all influence determination of the EPC<sub>0</sub> (Baldwin *et al.*, 2000; Klotz, 1988), but most agree that fresh sediment that has been sieved < 2 mm represents the most reactive fraction of sediment under natural conditions. However, many different base solutions have been used containing salts such as CaCl<sub>2</sub> or KCl in varying concentrations. Klotz (1988) demonstrated a wide range in EPC<sub>0</sub> values measured for the same sediment using

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base solutions with different calcium concentrations (0–400 mg Ca l<sup>-1</sup>). Calcium chloride concentrations used in the literature range from 0.0005 to 0.01M (Table 1), which are believed to reflect the water's natural chemistry, although few authors supply measurements of the sample water chemistry. These differences make comparing studies difficult and also have the potential to influence conclusions about sorption or desorption of P from sediments.

If the main criterion for the selection of the most appropriate base solution is to have an ionic strength that mimics stream water, logic would dictate that the base solution should be stream water. However, stream water may not be best suited for routine use since getting two stream solutions from the same site that are exactly the same is difficult, even if taken only a day apart. It is likely that the flow regime will have changed (depending on stream size) and along with it the ionic strength and concentration of sediment, entrained P and microbes. Lastly, there may also be difficulty in transporting sufficient amounts of stream water back to the lab.

Hence, the objective of this study was to determine if EPC<sub>0</sub> values established in any one of six different base solutions (stream water, 0.01M KCl, 0.01M CaCl<sub>2</sub>, 0.0005M CaCl<sub>2</sub>, distilled and tap water) that are commonly used are able to replicate EPC<sub>0</sub> values in stream water taken under baseflow conditions at a number of sites with contrasting land use, parent material and flow regimes.

#### MATERIALS AND METHODS

Sediment sampling sites were located in the South Island of New Zealand, primarily around the city of Dunedin (45° 52'S, 170° 30'E), with one additional site 100 km north (N. Otago) and one site 250 km to the west (Hauroko). The sites sampled represented a variety of stream orders, catchment sizes, land use and geology that is common in this region (Table 2). The predominant land use in this area is pasture grazed by sheep and beef cattle, with forestry and some urban areas also represented. Two of the catchments were

**Table 1.** Base solutions (or background matrices) used for equilibrium phosphorus concentration (EPC<sub>0</sub>) determination by different authors

Base solution	References
0.01M CaCl <sub>2</sub>	Kunishi <i>et al.</i> , 1972; McCallister and Logan, 1978; Nair <i>et al.</i> , 1984; Stutter and Lumsdon, 2008; White and Beckett, 1964
0.0005M CaCl <sub>2</sub>	Klotz, 1988
0.01M KCl	Gimsing and Borggaard, 2001; Lair <i>et al.</i> , 2009; Reddy <i>et al.</i> , 1998
Tap water	James and Larson, 2008
Deionized water	Koski-Vahala and Hartikainen, 2001; McDaniel <i>et al.</i> , 2009; Ryden <i>et al.</i> , 1972; Sharpley <i>et al.</i> , 1981
Stream water	McDaniel <i>et al.</i> , 2009; Popova <i>et al.</i> , 2006; Smith <i>et al.</i> , 2006

**Table 2.** Characteristics of the sampled stream sites

Site	Land use	Stream order (Hortonian)	Geology	Soil (USDA taxonomy)
Native	Native bush	1	Schist	Dystrochrept
INV	Sheep, deer and beef	1	Volcanic	Fragichrept
Riccarton	Forestry, urban, sheep and beef	4	Sedimentary	Fluvent
Rail R	Forestry and pasture	3	Schist, sedimentary in valley	Ustochrept
Owhiro	Urban and pasture	3	Schist and sedimentary	Ustochrept
Brockville	Sheep, bush and some urban	1	Volcanic	Dystrochrept
N. Otago	Sheep	4	Sedimentary including limestone and sandstone	Rendolls
Abbotts	Urban and pasture	3	Schist and sedimentary	Dystrochrept
Hauroko	Native bush	2	Granite	Orthod

covered in native bush vegetation (Native and Hauroko) and one catchment was subject to historic wastewater treatment discharge (Riccarton). The underlying geology is generally made up of schist and volcanic basalt on the hills, and sedimentary rocks (including sandstone and limestone) in the plains and valleys. Records indicated that average annual rainfalls at the Dunedin, N. Otago and Hauroko sites were 850, 625 and 1200 mm  $y^{-1}$ , respectively.

Sediment samples were taken during baseflow conditions in the summer when the sediments would most likely be in equilibrium with the overlying water. Sediment samples from the 0–4 cm depth were collected with a plastic scoop. Approximately 10 l of stream water was also collected at each site for use as base solution and for later analysis (see below).

Once back in the lab, sediments were wet-sieved through a 2 mm sieve, centrifuged for 15 min at  $1100 \times g$  and the supernatant discarded to make a dewatered slurry. This slurry was kept refrigerated until analysis (within 6 days). A subsample of sediment slurry was oven dried ( $105^{\circ}\text{C}$ ) for 24 h to determine moisture content and calculate dry weight equivalents. Sediment retained on a 2 mm sieve was dried, and expressed as a percentage of the total sediment sampled.

Sediment pH was determined on fresh sediments using a 1:10 sediment-water suspension. Particle size fractionation was performed on dried sediments using the dry sieving method of Sheldrick and Wang (1993) for sediments  $> 63 \mu\text{m}$ , and wet sieving for sediments  $< 63 \mu\text{m}$ . Total P concentrations in sediment samples ( $\text{TP}_{\text{sed}}$ ) were measured by *aqua regia* digestion according to the method of Crosland *et al.* (1995). Analysis of total C and N was performed using an elemental analyser (Elementar Vario-Max CN). Concentrations of total P, C and N were measured on dried (oven,  $105^{\circ}\text{C} \geq 24\text{h}$ ) sediments.

Measurements of pH were made on site with a portable HI 9812 pH/EC/TDS meter (Hanna Instruments). In addition, the dissolved oxygen (DO) concentration of streambed sediments was measured in situ at 6 cm depth with a DO6 dissolved oxygen palm-top meter (Eutech/Oakton Instruments). Suspended sediment was determined after passing a known volume of liquid sample through a  $0.7 \mu\text{m}$  glass-fibre filter paper and weighing the oven-dried residue. Dissolved reactive P (DRP) was determined on filtered ( $< 0.45 \mu\text{m}$ ) water samples by the colorimetric method of Watanabe and Olsen (1965). The remaining nutrient concentrations were measured using ICP-OES.

One gram (dry mass equivalent) of slurry was measured into a 30 ml centrifuge tube and 20 ml of base solution added. Fresh sediments were used because drying of sediment has been shown to increase adsorption capacity (Klotz, 1988). The addition of chloroform, toluene or other reagents to minimize the effect of biota was avoided to ensure that the concentration of P measured in the sediment-slurry was not artificially increased (Meyer, 1979).

Six base solutions (stream water,  $0.01\text{M KCl}$ ,  $0.01\text{M CaCl}_2$ ,  $0.0005\text{M CaCl}_2$ , deionized water (D.I.) and tap water) were used which contained initial P concentrations of 0, 0.5, 1, 2, 5, 10, 20, and 50  $\text{mg P l}^{-1}$  (as  $\text{KH}_2\text{PO}_4$ ). These base solutions (or background matrices) have been commonly used in the measurement of  $\text{EPC}_0$  in other studies (Table 1). The samples were then mixed 20 h using an end-over-end shaker. Samples were then centrifuged at  $3600 \times g$  for 10 min. An aliquot of the supernatant was used for determining phosphorus concentrations. Centrifugation did not always remove all of the fine material from a few of the samples. In these instances a replicate of the same sample and volume was measured in the spectrophotometer, but without molybdate-blue added, to serve as a blank.

At low P concentrations, there is typically a linear relationship between P sorbed or desorbed, ( $S^1$ ,  $\text{mg kg}^{-1}$ ) and the concentration of P in solution after equilibrium ( $C$ ,  $\text{mg l}^{-1}$ ) (House and Denison, 2000). This linear relationship was found only at one site (INV) and a linear isotherm was used to calculate  $\text{EPC}_0$  for that sediment. However, this was not the case for most of our measurements. Instead, the first four points of the sorption isotherm ie solutions  $< 2 \text{mg P l}^{-1}$  were used and the concentration of P ( $C$ ) was log transformed to obtain a linear relationship that fitted the data better than the commonly used Freundlich equation. The linear equation used was as follows:

$$S^1 = m \ln C + b.$$

$\text{EPC}_0$  was calculated as the concentration, where there was no adsorption or desorption of P, or where  $S^1 = 0$ . The terms  $m$  (slope) and  $b$  (y axis intercept) were obtained from the regression. Statistical analyses, including correlation and regression analyses, were carried out using GenStat (v. 11.1). Correlation probabilities were evaluated using a two-sided test different from zero. In all other analyses the standard error of the mean, and/or correlation coefficients and probabilities, are as specified in the text.

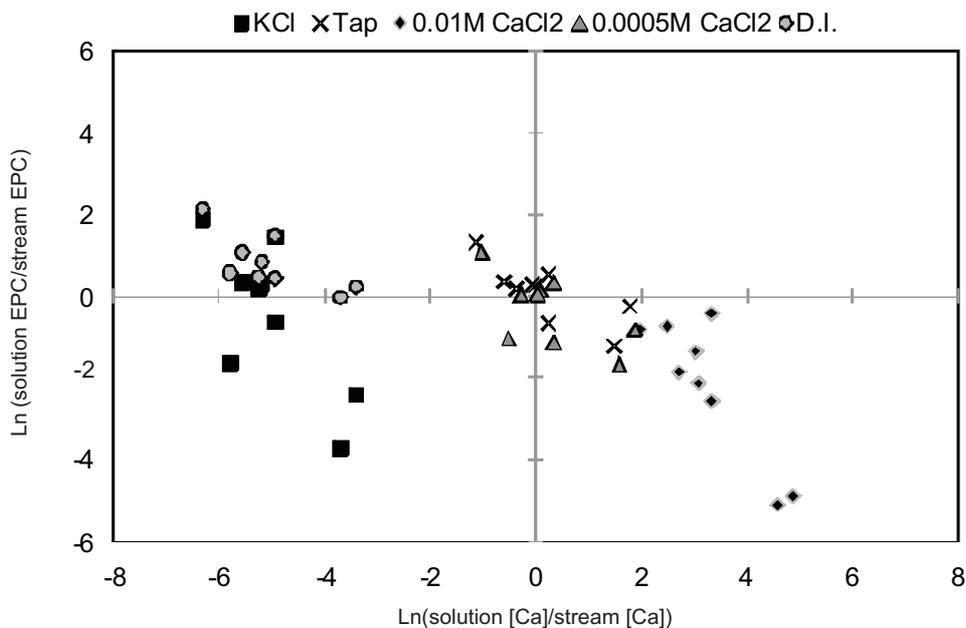
## RESULTS AND DISCUSSION

Equilibrium P concentrations measured using stream water ( $\text{EPC}_0^S$ ) ranged from 0.004 to 2.64  $\text{mg P l}^{-1}$ , illustrating the diverse nature of sites sampled (Table 3). A correlation analysis between  $\text{EPC}_0^S$  and stream water constituents showed  $\text{EPC}_0^S$  values were significantly related to the concentration of Ca in base solutions (log transformed;  $r = 0.74$ ,  $P < 0.05$ ), but not with any other constituent measured. Further analysis indicated that those solutions that best predicted stream water  $\text{EPC}_0^S$  values were solutions with Ca concentrations near that of stream waters. This is demonstrated in Fig. 1 as the relative difference between  $\text{EPC}_0$  measured with different base solutions and  $\text{EPC}_0^S$ , and the difference between base solution Ca concentration and stream Ca concentrations. The points closest to  $y = 0$  are the base solutions

**Table 3.** Equilibrium phosphorus concentrations ( $EPC_0$ ) measured using different base solutions

Site	Stream	KCl	Tap	0.01M CaCl <sub>2</sub>	0.0005M CaCl <sub>2</sub>	Deionized water
Abbotts	0.018 (0.002)	0.004 (0.002)	0.026 (0.001)	0.009 (0.001)	0.007 (0.000)	0.032 (0.003)
Brock	0.532 (0.015)	0.013 (0.005)	0.155 (0.017)	0.003 (0.002)	0.103 (0.010)	0.527 (0.025)
Hauroko	0.096 (0.008)	0.116 (0.011)	0.127 (0.013)	0.025 (0.003)	0.101 (0.027)	0.152 (0.017)
INV	2.639 (0.011)	0.247 (0.009)	2.007 (0.033)	0.020 (0.002)	1.157 (0.010)	3.328 (0.047)
Native	0.110 (0.024)	0.158 (0.010)	0.131 (0.013)	0.017 (0.006)	0.113 (0.009)	0.320 (0.013)
N. Otago	0.044 (0.005)	0.286 (0.012)	0.165 (0.007)	0.020 (0.008)	0.130 (0.021)	0.366 (0.015)
Owhiro	0.162 (0.019)	0.209 (0.017)	0.205 (0.006)	0.019 (0.003)	0.186 (0.017)	0.376 (0.036)
Rail	0.064 (0.020)	0.034 (0.005)	0.033 (0.014)	0.005 (0.000)	0.020 (0.003)	0.100 (0.010)
Riccarton	0.004 (0.002)	0.016 (0.004)	0.006 (0.004)	0.003 (0.001)	0.005 (0.003)	0.017 (0.006)

Numbers in parentheses are the standard errors of the linear regressions used to derive  $EPC_0$  concentrations.



**Fig. 1.** Comparison of  $EPC_0$  determined using with different solutions with the  $EPC_0$  measured using stream water, and of the calcium (Ca) concentrations in each solution compared with stream water Ca concentration. Those closer to the origin (0) are most closely associated with one another *ie* the points closest to  $y = 0$  are the base solutions with  $EPC_0$  values closest to the stream waters, and the points closest to  $x = 0$  are the base solutions with Ca concentrations closest to the stream waters.

with  $EPC_0$  values closest to the stream waters, and the points closest to  $x = 0$  are the base solutions with Ca concentrations closest to the stream waters at each site. This figure shows that  $EPC_0$  determined with either 0.0005M  $CaCl_2$  or tap water gave values similar to  $EPC_0^S$ . For  $EPC_0$  values  $< 0.5 \text{ mg P l}^{-1}$ , a solution of 0.0005M  $CaCl_2$  gave the best prediction of stream  $EPC_0$  values ( $y = 1.01x + 0.01$ ;  $R^2 = 0.55$ ,  $P < 0.05$ ) followed by tap water ( $y = 1.23x + 0.02$ ;  $R^2 = 0.55$ ,  $P < 0.05$ ). The tap water and dilute  $CaCl_2$  solutions had similar Ca concentrations, 18 and 20  $\text{mg Ca l}^{-1}$ , respectively, and were close to the average stream water Ca concentrations of 21  $\text{mg Ca l}^{-1}$  (Table 4).

forming (House and Denison, 2002), while organic C has been found to be poorly P sorptive and to bind P in labile humic-P complexes (McDowell and Sharpley, 2001). Both mechanisms function to enrich P in solution. Although no reason was given, Klotz (1988) also found a negative correlation between organic matter concentration and  $EPC_0$ . Contrary to other findings, no significant correlation was found for  $EPC_0^S$  and any of the particle sizes measured (McDowell *et al.*, 2003; Palmer-Felgate *et al.*, 2009).

Our data supports the premise that solutions using Ca are suitable for use in measuring  $EPC_0$  values in stream waters. Popova *et al.* (2006) used both  $CaCl_2$  solution and

**Table 4.** Some chemical and physical characteristics of stream water and sediment sampled

Site	Stream water								Sediment		
	pH <sub>H<sub>2</sub>O</sub>	DRP ( $\text{mg l}^{-1}$ )	SS ( $\text{g l}^{-1}$ )	Ca ( $\text{mg l}^{-1}$ )	Na ( $\text{mg l}^{-1}$ )	DO (%)	C ( $\text{g kg}^{-1}$ )	C:N	pH <sub>H<sub>2</sub>O</sub>	< 2 mm (%)	TP <sub>sed</sub> ( $\text{mg kg}^{-1}$ )
Native	8.0	0.054	1.39	26	14	68	5.4	53.5	7.4	62	259 (7)
Riccarton	9.0	0.003	2.69	14	13	-	3.4	11.1	7.7	4	243 (5)
Rail R	7.8	0.011	1.12	14	14	68	2.3	44.1	7.4	20	237 (24)
Brockville	8.0	0.007	2.01	4	6	80	17.7	47.9	7.2	15	875 (74)
Owhiro	7.7	0.076	5.10	18	19	16	1.6	65.9	7.3	32	238 (24)
INV	7.1	0.022	5.42	3	13	24	87.1	13.3	-	100	1311 (18)
N.Otago	7.7	0.010	1.92	55	26	87	1.9	18.8	7.8	15	392 (16)
Abbotts	5.2	0.003	2.51	33	28	23	6.8	20.1	5.7	9	1426 (209)
Hauroko	8.0	0.015	1.38	19	5	64	0.6	5.6	7.6	53	271 (6)

DRP – dissolved reactive phosphorus, SS – suspended sediment, Ca – calcium, Na – sodium, DO – dissolved oxygen (measured at 6 cm depth), C – carbon, C:N – carbon to nitrogen ratio, TP<sub>sed</sub> – total sediment less than 2 mm (<2mm) and total phosphorus. SEM – standard error of the mean is given in parenthesis after TP<sub>sed</sub> (n = 3).

Of the other solutions evaluated,  $EPC_0$  values determined using 0.01M  $CaCl_2$  were all less than  $EPC_0^S$  values and  $EPC_0$  values determined with deionized water were all much greater. This is due to the different ionic strengths of the solutions: those with greater ionic strength tend to suppress desorption (Barlow *et al.*, 2004). The KCl base solution had the greatest spread of the solutions used and KCl is sometimes preferred in alkaline soils to avoid the precipitation of Ca-P (Gimsing and Borggaard, 2001). However, unlike Ca, K is a monovalent cation and is more easily displaced than Ca (except where preferential adsorption to some vermiculites occurs) (Page *et al.*, 1967) thus affecting P sorption.

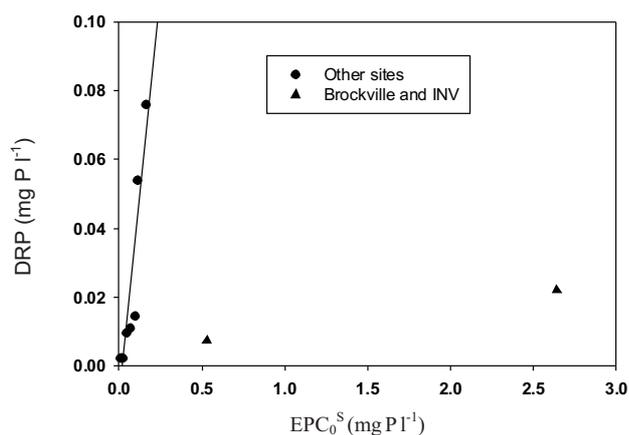
There were two sites where measured  $EPC_0$  values were at least three times greater than found for other sediments: INV and Brockville (Table 3). At these two sites,  $EPC_0^S$  concentrations were high ( $> 0.5 \text{ mg P l}^{-1}$ ), but coincided with the lowest Ca concentrations in stream water (3-4  $\text{mg Ca l}^{-1}$ ) and greatest sediment C concentration (17 and 87  $\text{g kg}^{-1}$ ). Low Ca concentrations decrease the likelihood of insoluble Ca-P

stream water as a background matrix and concluded that filtered stream water may be appropriate to use because using  $CaCl_2$  produced  $EPC_0$  values three times greater than when filtered stream water was used. However, they did not specify the concentration of  $CaCl_2$  used, only that it had an 'electrical conductivity similar to that of ambient stream water'. This emphasizes the need to determine the Ca concentration of stream water before choosing a suitable Ca-based base solution.

All sites were sampled at base flow conditions with the assumption that sediments would be at, or near, equilibrium with dissolved P concentrations in the stream. However, at all of the sampled sites  $EPC_0$  values were greater than DRP concentrations implying the sediments were acting as a P source. Many authors *eg* Klotz (1988) have used 0.01M  $CaCl_2$  as a base solution and found the opposite *ie*  $EPC_0 < \text{DRP}$ . However, we have shown that using 0.01M  $CaCl_2$  as a base solution decreases  $EPC_0$  values, perhaps lower than would be expected if stream water was used. In contrast, Haggard *et al.* (2007) used filtered stream water as a base

solution and found  $EPC_0 > DRP$ . In most of the sediments studied by Jarvie *et al.* (2005) and Palmer-Felgate *et al.* (2009),  $DRP$  was also greater than  $EPC_0$ . Unique sediment characteristics will affect measurements from site to site, but one conclusion that can be drawn from all these studies is that sediments are rarely in equilibrium with the water column. This raises a number of questions: firstly, how great an importance should we place on  $EPC$  values when equilibrium is rarely achieved in the field; or, secondly is the problem that the sampling and measurement techniques, as wide and varied as they are, do not adequately measure the true  $EPC_0$ ? For example, the Invermay site had the greatest  $EPC_0^S$  ( $2.64 \text{ mg P l}^{-1}$ ). However, monthly monitoring has shown that the maximum  $DRP$  measured at the site has not been  $> 0.04 \text{ mg DRP l}^{-1}$  in the last two years.

For additional insight into how sediments affect  $DRP$  concentrations we performed a linear regression, plotting  $DRP$  against  $EPC_0^S$  (Fig. 2). Excluding the INV and Brockville sites, there was a positive relationship between  $EPC_0^S$  and  $DRP$  concentration ( $DRP = 0.473 EPC_0^S - 0.009$ ;  $R^2 = 0.79$ ,  $P < 0.01$ ). The two excluded sites have  $EPC_0^S$  values much greater than stream water concentrations, and from this analysis it can be assumed that sediments were either not in equilibrium with the stream water (as suggested above for the INV site) or that these sediments play a minor role in regulating stream water P concentrations. Other studies have found stronger (Klotz, 1988, 1991; McDowell *et al.*, 2003; Palmer-Felgate *et al.*, 2009) or weaker (Haggard *et al.*, 2007; Jarvie *et al.*, 2005) relationships between  $EPC$  and  $DRP$  in stream water (or no relationships (House and



**Fig. 2.** Linear regression of dissolved reactive phosphorus ( $DRP$ ) and the equilibrium phosphorus concentration measured using stream water as a base solution ( $EPC_0^S$ ). The Brockville and INV sites are not included in the regression because stream water P concentration and sediment are not in equilibrium. Regression equation:  $DRP = 0.473 EPC_0^S - 0.009$ ;  $R^2 = 0.79$ ,  $P < 0.01$ .

Denison, 2002; Smith *et al.*, 2006)). It is thus difficult to draw conclusions between  $EPC$  and  $DRP$  when sampling methods and  $EPC_0$  determinations are so different and, in some cases, do not reflect stream conditions.

## CONCLUSIONS

1. The data show that the choice of method for determining  $EPC_0$  values has a marked effect on results and the utility of conclusions.

2. Using a standardized  $0.01M$   $CaCl_2$  solution, as proposed by Nair *et al.* (1984) and used by many others, resulted in lower  $EPC_0$  than if stream water was used. This would lead to overestimation of the sediment capacity to remove phosphorus from overlying water.

3. It is suggested that a more standardized method of sampling and analysis should be developed to allow comparison between studies, and even draw conclusions within studies as to the fluxes of phosphorus to and from sediments.

4. It is suggested that unless variation in stream water chemistry can be proven to be small when sampled, then it should become standard practice to measure stream water calcium concentration before deciding on an appropriate base solution from which to derive  $EPC_0$  values.

5. Our initial suggestion is to use a base solution of  $0.0005M$   $CaCl_2$  if the mean calcium concentration at base flow is  $5\text{--}55 \text{ mg l}^{-1}$  otherwise deionized water may be suitable for low ( $< 5 \text{ mg l}^{-1}$ ) calcium stream waters.

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