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Abstract:	Phosphorus (P) is the main reason many surficial water bodies in the UK are currently failing to meet the chemical standards set by the Water Framework Directive (WFD). This work focuses on the role of sediments in the upper reaches of the River Taw in the South West of the UK. Point and diffuse sources of P have been identified as well as a number of mitigation measures applied or planned to address the issues. However it is unknown what affect these sources have had on the river's sediments and how they will react to diminishing inputs of P into the water column in the future. The Diffusive Gradient in Thin-Films (DGT) method is utilised in situ to quantify and identify labile, potentially bioavailable P fluxes and potential storage mechanisms at sites of known diffuse and point P inputs. In the vicinity of a heavily contaminated point source, data present here shows that sediments are still acting as a sink. The proposed mechanism for this is the formation of a 'calcium cap' which provides a geochemical barrier between the sediment and overlying water to prevent loss of labile P. The strong correlation between calcium and total P under most circumstances supports this hypothesis. This conclusion provides some confidence that even though P concentrations in some sediments are significantly elevated, mobility between the sediment and overlying water is restricted. In the context of routine monitoring against WFD targets, the molybdenum blue method generally employed to determine soluble reactive phosphorus was shown to not be equivalent to the DGT labile P pool, especially at pristine or moderately point/diffuse influenced sites. This is likely due to desorption of weakly bound P from colloids, which is unavailable to DGT devices. These results have the potential to be scaled up to the full catchment or other catchments which exhibit similar physical and chemical sediment composition and provide a stronger foundation for management and target setting than current monitoring approaches.
Response to Reviewers:	Reviewers' comments: Reviewer #3: I find in general the paper is much improved giving a cleaner more

understandable paper. There are still a couple of points that need addressing though.

Figure 2. You seem to have not understood my point I made about the error bars, unless you carried out more than one repeat chemical analysis on the same eluent from each part of the DGT. You cannot use standard deviation as error bars on points in a figure that are not mean values. This is not scientifically or statistically sound. You can only do this on mean values. Therefore please remove your error bars on all figures except for that of Skaigh Wood.

Answer
Done.

L415: You refer to Figure 4 but you should be referring to Figure 3.

Answer
Done

L448-451 (clean document): You still do not explain how North Tawton can have R values greater than 1.

Answer
Clarification:

North Tawton and Washford Pyne represented point source industrial and agricultural influences respectively. The largest CDGT values were found at these sites indicating a large pool of SRP and the solid phase has a good ability to resupply the depleted porewater SRP concentrations, almost maintaining equilibrium, as described by a high value of R. However this interpretation is limited to CDGT values less than 800 ug/l as values above this concentration exceed the capacity of the device and will no longer accurately reflect DGT theorized uptake. This is evidenced by R values greater than 1 (figure 3) that correspond with the CDGT values above 800 ug/l (figure 2). R values above 1 occur when the device is no longer responding to DGT theory, in this case reliable capacity of the device has been exceeded. (Zhang et al., 1998). Ding (2010) calculated a capacity per centimeter of the DGT device to be 400 ug/l, our spatial resolution was 2 cm therefore above values of 800 ug/L the integrity of that portion of the device has been compromised.

Text changed to explain better.

L501-502: "The impact of dairy cattle using the site for drinking may explain higher levels of Ca present" Actually the opposite is present, at Washford Pyne there is lower Ca with P than the general correlation. Please change.

Answer
The impact of dairy cattle using the site as a drinking point helps explain higher P concentrations in comparison to the most undisturbed sites. Anthropogenic inputs of P at this site are unmatched by Ca unlike at the North Tawton site where Ca is released in tandem with phosphate in creamery effluent.

You say you have added the SRP pore water values to the paper but you have only added the mean values for the whole profile in Table 2. I still think it is needed to add these values for the whole depth profile in supplementary information.

Answer

There may be some confusion here – as described in the method section:
"Sediment porewaters were obtained by extracting 3 cores of consolidated bed material at each site using an 8 cm diameter plastic tube and plunger and placed into polythene bags prior to centrifugation at 3000 rpm for 15 minutes in a MSR Centaur 2 centrifuge. Due to the nature of the sediment each core was bulked into a single sample. The porewater was filtered using acid washed 25mm diameter Millipore cellulose acetate filters (0.45 µm) into acid washed polythene bottles. P was determined using the molybdenum blue method described above."
Therefore we have 3 core values, but nothing through depth because each core

needed to be bulked to get enough porewater to analyse. The porewater data, however, do provide us with valid information in which we drew our conclusions upon.

We have noted the limitations via the statement regarding use of DET:
"The deployment of both DGT and DET together would provide the most accurate and matching description of CDGT and SRP in situ. "

Determining riverine sediment storage mechanisms of biologically reactive phosphorus *in situ* using DGT

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Abstract

Phosphorus (P) is the main reason many surficial water bodies in the UK are currently failing to meet the chemical standards set by the Water Framework Directive (WFD). This work focuses on the role of sediments in the upper reaches of the River Taw in the South West of the UK. Point and diffuse sources of P have been identified as well as a number of mitigation measures applied or planned to address the issues. However it is unknown what affect these sources have had on the river's sediments and how they will react to diminishing inputs of P into the water column in the future. The Diffusive Gradient in Thin-Films (DGT) method is utilised *in situ* to quantify and identify labile, potentially bioavailable P fluxes and potential storage mechanisms at sites of known diffuse and point P inputs. In the vicinity of a heavily contaminated point source, data present here shows that sediments are still acting as a sink. The proposed mechanism for this is the formation of a 'calcium cap' which provides a geochemical barrier between the sediment and overlying water to prevent loss of labile P. The strong correlation between calcium and total P under most circumstances supports this hypothesis. This conclusion provides some confidence that even though P concentrations in some sediments are significantly elevated, mobility between the sediment and overlying water is restricted. In the context of routine monitoring against WFD targets, the molybdenum blue method generally employed to determine soluble reactive phosphorus was shown to not be equivalent to the DGT labile P pool, especially at pristine or moderately point/diffuse influenced sites. This is likely due to desorption of weakly bound P from colloids, which is unavailable to DGT devices. These results have the potential to be scaled up to the full catchment or other catchments which exhibit similar physical and chemical sediment composition and provide a stronger foundation for management and target setting than current monitoring approaches.

Keywords

DGT, phosphorus, freshwater, eutrophication, sediment storage mechanisms

1. Introduction

1.1 Background

Phosphorus (P) is an essential and commonly limiting nutrient in freshwater systems (Neal et al., 2002; Jarvie et al., 2002). Natural P cycles have been disrupted by increasing societal needs for food production and waste water disposal (Jarvie et al. 2008; Reynolds and Davies, 2007). Agriculture and sewage treatment works (STWs) are both established sources of phosphorus to surficial watercourses potentially causing environmentally detrimental effects, such as eutrophication. The effects of eutrophication are rooted mainly in ecological impacts such as decreased species biodiversity and abundance (Muscutt & Withers, 1996), however there are also consequences for humans via increased cost of water treatment, decreased amenity value of watercourses and in extreme cases, the production of toxic blue-green algae (Withers & Jarvie, 2008).

The European Water Framework Directive (WFD; EU, 2000) has set challenging targets for ecological quality, which have been transposed by the UK regulators into very low Environmental Quality Standards (EQS) for soluble reactive phosphorus (SRP) associated with moves to improve diatom ecology in impacted water bodies. Current P Environmental Quality Standard (EQS) failures in rivers throughout the UK are being addressed by a reduction of P in effluents discharged to rivers via industry and STWs, as well as potential diffuse sources addressed through advice and subsidies to farmers. The result will be a decrease of P entering rivers; however, the historic accumulation of P in sediments may potentially slow the recovery of rivers via repartitioning of P back into overlying waters. However, the likelihood of this occurring and the bioavailability of the P released into the overlying water have not been studied to any degree in rivers.

An understanding of sediment interactions and channel storage has the potential to provide a risk assessment for overall water quality, especially when reducing river P inputs because their reduction may not result in a drop in phosphate concentration or improved biological quality. Sediments may release P by resuspension or desorption to re-establish equilibrium with the water column (Van der Perk et al. 2007; Collins & McGonigle 2008). Whether this will occur or to what extent the released P may be considered available for diatom uptake is unknown, however it may potentially lead to a failure to achieve WFD objectives.

Phosphorus exists in many forms in freshwater systems: dissolved, colloidal, particulate or sorbed, inorganic and organic species (Worsfold et al., 2008). Dissolved P is considered a major part of the bioavailable pool, while the contribution of the other fractions is largely unknown. The major processes considered in this study that render phosphate biologically unavailable and therefore constitute sediment uptake are sorption and mineral precipitate reactions with aluminium, iron and calcium (Van der Perk et al., 2007). The opposite of these reactions, desorption/dissolution are the equivalent of sediment P release for the purpose of this study. The occurrence of these reactions is dependent on chemical abundance, available sorption sites and environmental conditions such as Eh and pH and can be reversed when conditions change (Reynolds & Davies, 2007). In many systems the presence of Fe provides an important precipitation reaction with P where at an Eh above +200 mV, Fe^{2+} will be oxidised to Fe^{3+} and

65　P will precipitate out of solution. The opposite reaction will occur under reducing conditions therefore dissolving Fe

66　complexes and releasing dissolved P back into solution (Monbet et al. 2010, Withers & Jarvie 2008).

67　The biological controls on P retention and mobilisation are important, however, these are not the focus of this

68　project. Sediments have been shown to act as sinks of P, immobilising and removing excess concentrations from a

69　system via the cycling mechanisms previously described, acting as somewhat of a 'self-cleansing' mechanism to

70　avoid P saturation in the water column (Jarvie et al., 2008). Svendsen (1995) found that P retention was occurring in

71　the summer when excess soluble reactive phosphorus (SRP) poses the greatest threat to ecosystem health through

72　the precipitation of phosphate with Ca, Al and Fe.

73　Mass balance P studies previously used to estimate P uptake and cycling are not precise and target the catchment as

74　whole (Bowes et al., 2001; Withers & Jarvie, 2008). The subject of this study, the River Taw, southwest UK, is

75　failing WFD phosphorus quality standards in certain areas, therefore a more specific understanding of P fluxes and

76　the processes controlling them is required. The standard method employed by the UK Environment Agency for

77　determining SRP is the 'molybdenum blue method' which is a colorimetric determination of phosphorus carried out

78　in 0.25M sulphuric acid (Reynolds & Davies 2007). However how much of this pool is truly bioavailable to

79　contribute to eutrophication is debatable, leading to over/underestimation (Jarvie et al., 2002).

80　*1.2 DGT Theory and Sediment P Channel Storage*

81　A method is available that can provide information about P sediment fluxes as well as the mechanisms which

82　govern sediment P cycling. This method involves the use of diffusive gradient in thin-films (DGT) which were

83　introduced in the mid-1990s by Davison & Zhang (1994) and have since gained significant recognition for

84　their comparability to bioavailability as well as their ability to produce *in situ* concentration profiles at a high

85　spatial resolution (Davison et al., 1999; Degryse et al. 2009; Zhang et al. 1995; Zhang et al. 2001).

86　A DGT device is a compilation of layers which together, act as a diffusive medium with a sink (an Fe-oxide

87　layer) where P is stored, invoking a diffusive driven resupply from the kinetically labile solid phase in

88　response to the concentration gradient formed in solution by the DGT (Davison et al., 1997). The diffusive

89　layer is an acrylamide gel coupled with an agarose-derived cross linker patented by DGT Research, UK which

90　enables simple diffusion of the desired solute across the membrane to the binding gel. The theory behind DGT

91　is extensively explained elsewhere (Zhang, 2004) however, deploying DGT in sediment is quite different than

92　deployments in water or homogenous slurries, requiring several adaptations to the theory in order to apply it to

93　sediments (see Davison et al. 2007; Harper et al., 1998; Zhang, 2004).

94　When deployed in sediments, DGT can be used to quantify either porewater SRP concentrations or the kinetic

95　labile resupply of P from sediment when porewater SRP has been depleted by the device. By removing the

96　dissolved P fraction a kinetically labile resupply from the other phases such as colloidal or sorbed fraction is

97　provoked. This is similar to how an organism would obtain P, depleting the available dissolved fraction then

98   stimulating a diffusive resupply from colloidal and sorbed fractions by 1st order equilibrium kinetics. The DGT

99   is capable of measuring an average resupply rate over a defined exposure period; the shorter the response time,

100   the greater ability of the sediment-bound P to partition between the solid and dissolved phase. This allows the

101   user to capture the potential solid phase contribution of low molecular weight, labile and potentially

102   bioavailable P, which can then be added to the original porewater SRP concentration using the DIFS model

103   (Harper et al., 2000) resulting in what has been termed effective concentration (C_E) (Zhang et al. 2004), an

104   estimate for the entirety of the bioavailable fraction in a system.

105   The concentration derived by the DGT provides an indication of the labile fraction by both the ability to

106   determine porewater SRP concentrations as well as the kinetic resupply from the solid labile phase determined

107   by, R (Harper et al. 1998). R is a number between 0-1 where 1 is a fully sustained resupply case and therefore

108   representative of the actual porewater labile P concentration, which would be rare in sediment porewaters as

109   they are poorly mixed. An R below 0.95 but greater than 0.1 is considered partially sustained, meaning that the

110   resupply from the solid labile phase is not great enough to match the original initially depleted porewaters

111   (Harper et al. 1999; Monbet et al. 2008). This is the most common case in sediments due lack of mixing,

112   whereas in well mixed waters a rapid resupply of P to the device after the local depletion of P occurs and

113   results in R> 0.95 and is classified as fully sustained (Harper et al. 1998; Monbet et al. 2008). The final R

114   scenario is deemed unsustained where R< 0.1 implying that there is little or no resupply from the labile solid

115   phase after porewater P concentration directly adjacent to the device is depleted (Zhang et al. 1998). Hence,

116   the larger the R value, the higher the potential risk of labile P being able to be released from porewater to

117   overlying water at a rate that may contribute to EQS failures and eutrophication. This is reflected in the

118   calculation of C_{DGT} which is a time averaged flux to a hypothetical infinite sink limited by diffusion over the

119   deployment time and why the C_{DGT} will be less than porewater P concentration measured as SRP using the

120   molybdenum blue method (Harper et al. 1998). This also provided the opportunity to compare porewater

121   reactive P measured via the DGT with that determined using the established molybdenum blue method.

122   The deployment of DGT devices in overlying water is more straightforward as there is no restriction on the

123   resupply of P (R = 1) and so DGTs immersed in river water can be used to estimate bioavailable phosphorus

124   present in the dissolved aqueous phase and therefore can complement data generated by DGT probes placed

125   into adjacent sediment.

126   DGT technology has the potential to gain important information pertaining to sediment P mechanisms and

127   processes greatly needed to increase knowledge and to assist in future P management within catchments

128   (Jarvie et al., 2005, 2008; Withers & Jarvie 2008; Palmer-Feldgate 2010). Therefore this study aims to quantify

129   potential channel stored P fluxes from sediment to water i.e. release and uptake interactions with the water

130   column by abiotic means.

2. Materials and Methods

2.1 Study Sites

The 1243 km^2 Taw catchment (Figure 1) is located in Devon, southwest UK. The Taw originates in the upland granites of Dartmoor and flows through mainly rural farmland until it reaches the Taw and Torridge estuary (EA, 2011). The catchment comprises of both low porosity and permeable soils and geology (EA, 2011) leading to low groundwater storage and river flows dominated by rainfall. Several rural sewage treatment works (STWs) discharge P into the river along its course and a large dairy processing plant also known to contain significant concentrations of P discharges effluent just upstream of North Tawton (Figure 1). An initial scoping study of the Taw took place during the winter of 2013 where suspended bottom sediment samples throughout the upstream sub-catchments of the Taw were analysed for total P by XRF. The total elemental concentrations of P were used to help guide site choice in this study to cover a range of representative environments within the study catchment (Table 1).

A large proportion of the upper Taw catchment main channel is currently failing WFD objectives with a classification of 'bad'. Two study sites were chosen within this portion of the Taw: a site above most anthropogenic P inputs in the headwaters near Dartmoor, Skaigh Wood assumed to be a near reference site of at least good ecological status, and a site at North Tawton subject to significant anthropogenic sources of P including agricultural inputs, some STW effluent and in particular, a creamery effluent containing elevated concentrations of P which has been discharged into the Taw since 1974. The other sites are found in two of the Taw sub-catchments, the River Dalch where the site at Washford Pyne is impacted by livestock accessing the stream to drink, as evidenced by their presence during sampling and heavily eroded river bank and the Little Dart River where two sites were selected; Creacombe which was considered a control site owing to its presence near the headwaters of the stream with few obvious P sources, and Chawleigh further down the catchment, downstream of a STW discharge, a known source of P (Comber et al., 2013). Both these sub catchments are only currently classified as 'moderate' in terms of WFD categorisation. This makes up a total 253 km^2 study area, with sampling locations shown in Figure 1.
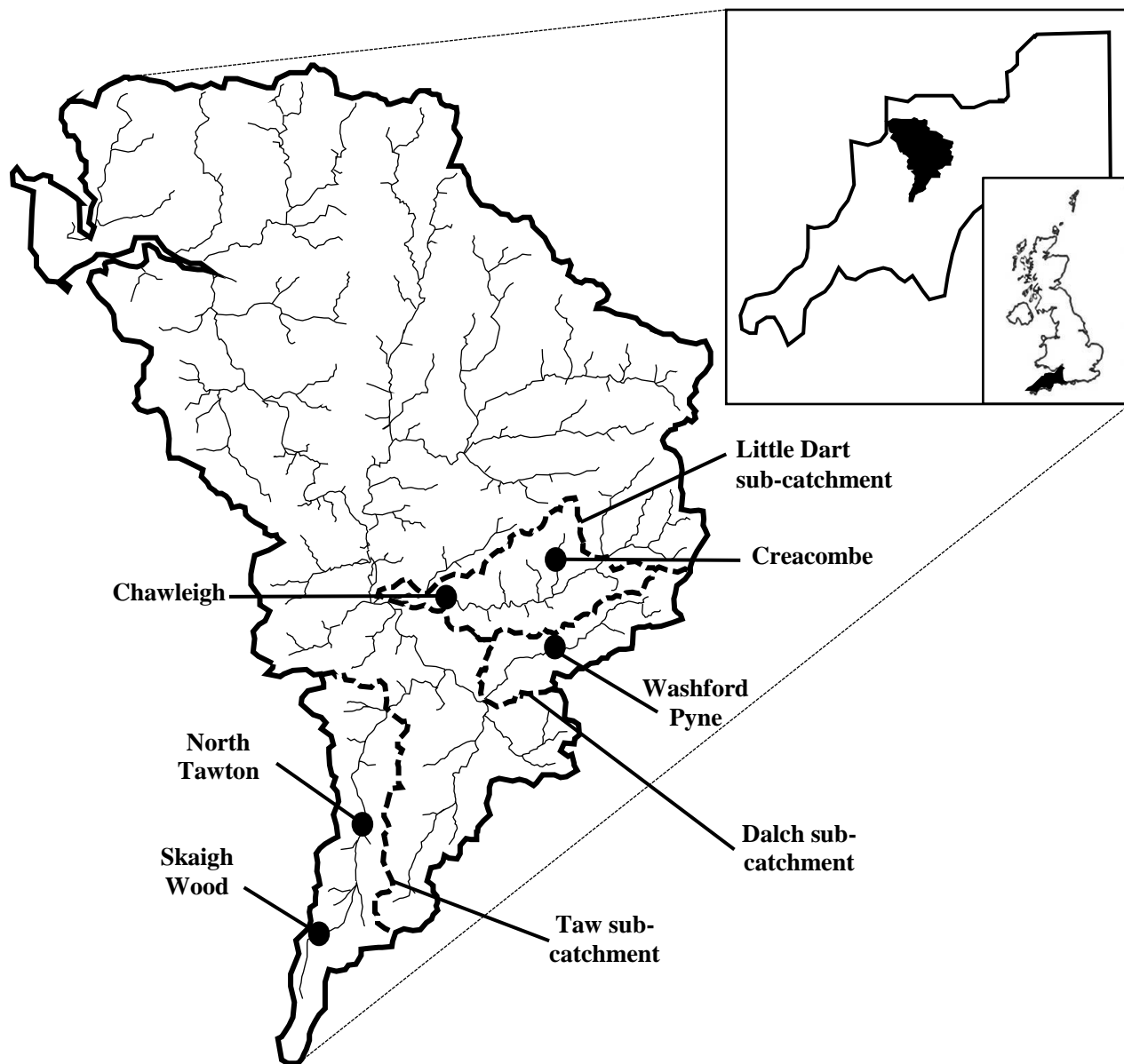
Fig. 1. A map displaying the location of the Taw catchment in the southwest of the UK. The three sub-catchments are designated by dotted lines and each of the 5 sample locations as designated by the black circles.

2.2 DGT Preparation and Deployment

Three DGT probes were deployed *in situ* within the sediment at each of the five identified sites in Figure 1. In addition three replicate DGT disks were also deployed under laboratory conditions for 24 hours within a discreet overlying water sample collected from each site to estimate bioavailable phosphorus present in the river water itself.

169 DGT probes for deployment in sediment were 15cm in length with a window width of 1.8cm, providing a

170 contact surface area with the sediment of 22.5 cm^2. Each probe was loaded with (i) an Fe-oxide gel with

171 approximately a 1 nm exclusion pore size, then layered with (ii) an agarose derived diffuse gel (0.78 mm

172 thick), patented by Lancaster University, and (iii) a protective Millipore membrane (0.45 µm), comprising a

173 diffusive layer thickness of 0.91 mm. Each layer was hand cut and loaded. Prior to deployment the probes were

174 stored at 4 °C and kept moist with 0.01M NaCl. Before deployment the probes were degassed by immersion in

175 MilliQ water and bubbled with a stream of nitrogen gas for at least 24 hours.

176 DGT disks used for measuring bioavailable P in unfiltered surface water collected from each site and exposed

177 to the DGT under laboratory conditions were 2.5 cm in diameter and contained the same materials as the

178 sediment probes and were handled in an identical way.

179 The DGT deployment time was determined through the placement of 3 DGT devices at the Washford Pyne and

180 North Tawton site. The deployment times ranged from 2 hours to 72 hours. The optimum time to deploy the

181 devices was 24 hours as it was both practical and fell within the linear portion of the P accumulation versus

182 time plot as reported elsewhere (Menzies et al. 2005; Zhang, 2003).

183 At all sites, three DGT devices were deployed for 24 hours on separate occasions during July 2013. The DGT

184 deployment data and site characteristics are listed in Table 1. Devices were spread across the riverine channel

185 where possible, however rocky conditions made it difficult to deploy the devices to the 15 cm depth required.

186 This limited not only site selection but also in some cases concentrated the DGT devices on one side of the

187 channel. The uppermost 2 cm of the DGT window was left above the sediment to interact with stream water

188 and comprises the sediment-water interface. Upon retrieval the DGTs were rinsed with MilliQ deionised water

189 and returned to the laboratory.

190 At each DGT deployment site, temperature and Eh were determined for the stream water and both the 5 cm

191 and 15 cm sediment depth. An Orion model 105 was used for temperature while a, Oakton pH 6+ meter was

192 used to determine Eh. A measurement for pH was not made due to the large range (2-10 pH) which Zhang

193 (1998) determined Fe-oxide gels could be used before performance is affected. The study sites were expected

194 to fall well within this range based on their geological and ecological parameters.

195 *2.3 DGT P Measurements*

196 On return to the laboratory, DGT probes were sliced with a clean scalpel to a 2 cm resolution before being

197 separately subject to the eluting acid, 10 ml of 0.25M sulphuric acid, while DGT disks kept their original

198 dimensions. The elution solutions were left overnight and analysed for phosphorus the next day. Phosphorus

199 eluted from the DGT gels was determined using the molybdenum blue method (Jarvie et al. 2002, He et al.,

200 2005). Aliquots (10ml) of acidified samples (0.25M sulphuric acid, Aristar grade or equivalent) were mixed

201   with 1.4ml of mixed reagent containing a 10:3:1 ratio of MilliQ deionised water (with a resistance of at least
202   18 MΩ·cm); ammonium molybdate (40g/l) and potassium antimonyl tartrate (2.8g/l) respectively. Finally
203   ascorbic acid (0.6ml of 17.6 g/l) was added and thoroughly mixed as described by Zhang (2003). The resultant
204   colour was determined after 20 minutes using a CECIL 1000 Series CE 1010 spectrometer at 880nm, with a
205   1cm cuvette. Calibration was carried out over 0 to 1500 µg-P/l using stock standards made up from laboratory
206   grade Trisodium phosphate. Calibration standards were confirmed against expected absorbance based on the
207   Beer-Lambert Law. All solutions were made up in MilliQ water. All sample bottles were plastic and
208   prewashed in 5% nitric acid then rinsed 3 times with MilliQ deionised water. The limit of detection (LOD)
209   based on standard deviation of 3x the method blank was subtracted from each absorbance before carrying out
210   further calculations. The LOD was estimated for each calibration batch. The average method limit of detection
211   across all analytical runs was 9 µg/L. Precision calculated as relative standard deviation (RSD) was 4.4% for 3
212   replicate determinations of DGT eluates and 3.6% for water samples. DGT blanks were determined to be less
213   than the limit of detection.

214   After concentrations were measured, the time averaged concentration was calculated, described as C_{DGT}
215   (Davison & Zhang 1994), which is representative of the concentration of P accumulated in the DGT supplied
216   by simple diffusion over the deployment time (Equation 1). It is based on Fick's law of diffusion and its
217   derivation and use is described elsewhere (Zhang, 2003).

218   $$C_{DGT} = C = \frac{M\Delta g}{DAt} \qquad [1]$$

219   C_{DGT} is representative of the porewater P concentration, and the labile resupply of P averaged over time (t),
220   area of the DGT window (A) and diffusion coefficient of P (D). The Δg term is representative of diffusive
221   layer thickness and (M) is the mass of P contained within the device calculated from equation 2. The mass of P
222   is the concentration of P is that is eluted from the Fe-oxide layer of the DGT when digested in acid.

223   $$M\ (\mu g) = Concentration\ of\ P\ (\mu g/l)x\ volume\ of\ eluent\ (l) \qquad [2]$$

224   C_{DGT} therefore represents a reactive P concentration similar to that which organisms accumulate nutrients by
225   diffusion as it takes into account porewater concentration as well as the available resupply from the labile solid
226   phase. Further analysis is required to obtain the actual bioavailability or effective concentration (C_E) such as
227   the DIFS model (Harper et al. 1999), however is beyond the scope of this study. In this case only the
228   calculation of R is required beyond C_{DGT} (Equation 3).

229   $$R = \frac{C_{DGT}}{C} \qquad [3]$$

230   Where (C) is the porewater concentration obtained from the molybdenum blue method.

8

231 *2.4 Sediment Bulk Geochemistry*

232 Channel-stored fine sediment was collected using a stilling well approach to isolate a part of the stream bed,
233 followed by sediment resuspension using a power drill with mixing attachment (Lambert and Walling, 1988).
234 The resultant water and resuspended sediment mix (typically mixing the first 5cm of sediment) was collected
235 in 2.5 L acid-washed plastic bottles, centrifuged, freeze-dried and homogenised. Resulting powders were
236 sieved to < 63 μm and packed into containers for X-Ray Fluorescence (XRF) analysis by energy dispersive X-
237 ray fluorescence (XRF) spectrometry using a Thermo Scientific Niton hand-held XRF analyser (model XL3t
238 950 He GOLDD+). The instrument is fitted with an X-ray tube with Ag anode target excitation source,
239 operating at voltages up to 50 kV and at beam currents up to 200 μA, and a geometrically optimised large area
240 drift detector. A CCD camera stores sample images and data are transferred via USB, Bluetooth or an RS-232
241 serial communicator using Thermo Scientific Niton data transfer (NDT) PC software. In the present study, the
242 instrument was placed in a bench top accessory stand for operation in the laboratory. Individual sediment
243 samples were packed into a sample holder with a thin film containing the sample. Overall measurement time
244 was between 185 and 245 seconds and spectra up to 18 keV were quantified using a parameter algorithm
245 configured for "mining" mode. The instrument detection limits, supplied by the manufacturer and in μg/g for a
246 SiO_2 matrix analysed for a period of 60 seconds, are as follows: Ba = 50; Cr = 25; Cu = 12; Pb = 4; Sn = 16;
247 Zn = 6. Triplicate measurements of a reference material that was certified for concentrations of Cr and Pb
248 (Niton PN 180-554, polyethylene impregnated with metals; Cr = 995 μg/g; Pb = 1002 μg/g) returned mean (±
249 one sd) concentrations of 1022 (± 51) μg/g and 922 (± 3.3) μg/g, respectively. (Note that the reference plastic
250 had not been amended with the remaining substances considered in this study).

251 The samples were analysed for a suite of major and minor element constituents (Mo, Nb, Zr, Sr, Rb, Bi, As,
252 Se, Au, Pb, W, Zn, Cu, Re, Ta, Hf, Ni, Co, Fe, Mn, Cr, V, Ti, Ca, K, Ba, Sb, Sn, Cd, Pd, Ag, Al, P, Si, Cl, S
253 and Mg).

254 *2.5 ICP-MS Sediment Metal Concentration Confirmation*

255 To confirm the XRF total P data, selected samples (approximately 5g each dry weight) across the full range of
256 concentrations measured by XRF were digested under hot reflux in concentrated nitric and sulphuric acid (5:1
257 ratio). The resulting solution was filtered and analysed for P by ICP-OES using a Thermo Scientific iCAP
258 7400 instrument following the standard operating procedures of the Plymouth University Analytical Research
259 Facility (ARF).

260 A comparison of the XRF with the acid-digestion ICP-MS data is provided in the results section.

261 *2.6 Sediment Porewater Sampling and Analysis*

262 Sediment porewaters were obtained by extracting 3 cores of consolidated bed material at each site using an 8

263 cm diameter plastic tube and plunger and placed into polythene bags prior to centrifugation at 3000 rpm for 15

264 minutes in a MSR Centaur 2 centrifuge. Due to the nature of the sediment each core was bulked into a single

265 sample. The porewater was filtered using acid washed 25mm diameter Millipore cellulose acetate filters (0.45

266 μm) into acid washed polythene bottles. P was determined using the molybdenum blue method described

267 above.

268 *2.7 Complimentary Surface Water Sampling and Analysis*

269 To support the sediment depth profile data and overlying water DGT measurements, complimentary surface

270 waters were collected on site and filtered using acid washed 25mm diameter 0.45 μm millipore cellulose

271 acetate filters into acid washed polythene bottles. SRP was determined using the molybdenum blue method

272 described above. In addition, a grab sample of stream water was also collected and three disk (25mm diameter

273 gels) DGTs were deployed in a stirred sample for 24 hours prior to P determination. This served as both a

274 comparison between DGT stream water P and SRP as well as giving an indication of conditions in the stream

275 water as a whole compared with the *in situ* DGT device.

276 **Table 1. Study site locations and characteristics.**

Site	Location (lat and long)	Notes
North Tawton 22/7/2013	50.799231, -3.9085227 Taw main channel	Sample taken where creamery effluent ditch meets the Taw main channel, highest suspended bottom sediment P of 4034 ±122 mg/kg.
Skaigh Wood 22/7/2013	50.7286, -3.93257 Taw main channel	Taw pristine headwaters, unusually high suspended bottom sediment P of 3324 ±1548 mg/kg.
Washford Pyne 8/7/2013	50.896, -3.692 River Dalch	Heavy agricultural influence, near cattle drinking point and surrounded by steep improved grasslands, suspended bottom sediment P of 3321± 1058 mg/kg.
Chawleigh 14/7/2013	50.9031, -3.8231 Little Dart River	Moderate agricultural influence and downstream of a rural STW discharge point, suspended bottom sediment P of 1478 ± 112 mg/kg.
Creacombe 14/7/2013	50.9600, -3.685 Little Dart River	Low agriculturally diffuse impacted site. Lowest sediment P observed, suspended bottom sediment P by XRF of 998 ± 112 mg/kg.

277

278

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3. Results

3.1 Bed Sediment Characteristics

XRF results (Table 2&3) indicate that North Tawton had a significant accumulation of P in bed sediment with concentrations decreasing towards the less heavily influenced sites with Creacombe containing the least. Interestingly the seemingly pristine headwater site, Skaigh Wood, had one of the highest XRF P concentrations. Here, none of the Eh measurements were negative reflecting the poorly consolidated sediment allowing significant entrainment of oxygen into the porewaters. . The sites with high sediment P loading at North Tawton and Washford Pyne exhibited anoxic conditions. The site at Chawleigh also exhibited anoxic conditions reflecting a combination of significant sediment accumulation and supply of organic matter and nutrients to promote biological activity.

Table 2. Sediment and stream water characteristics at each site (Confidence intervals were calculated from three times the standard deviation of three sample replicates).

	North Tawton	Washford Pyne	Chawleigh	Creacombe	Skaigh Wood
Sediment XRF total P (mg/Kg)	4034 ± 122	3321 ± 1058	1478 ± 112	998 ± 112	3324 ± 1548
Porewater SRP (µg/L)	1115 ± 60	267 ± 16	1657 ± 66	3477 ± 690	N/A
Stream water SRP (µg/L)	1396 ± 8	70 ± 4	5878 ± 810	33 ± 6	29 ± 3
Stream water C_{DGT} (µg/L)	311 ± 79	9 ± 2	141 ± 22	45 ± 10	10 ± 6
Sediment Eh 5 cm depth (mV)	-189	-114	-123	206	82
Sediment Eh 15 cm depth (mV)	-204	-163	-121	218	23
Stream water Eh (mv)	150	79	92	216	64

Excellent comparison (1:1 correlation) was achieved between XRF data for total P in the sediment versus that generated via aqua regia digested-ICP-MS determined P, supporting XRF as a rapid, accurate and precise measure of geochemical constituents of sediment.

Table 3. Additional sediment geochemistry at the sites sampled.

Sample	Whole sediment concentration by XRF (mg/Kg)				% composition		
	Fe	**Ca**	**Al**	**P**	**Sand**	**Silt**	**Clay**
North Tawton	53591	16128	41809	4034	7.0	91.7	1.2
Washford Pyne	47007	5400	39264	3321	10.3	87.7	2.0
Chawleigh	49533	4822	45136	1478	9.7	88.3	2.0
Creacombe	60743	3248	52983	998	5.3	92.7	1.9
Skaigh Woods	65400	14482	57639	3324	20.2	79.1	0.7

3.2 DGT Porewater Profiles

The porewater profiles presented (Figure 2) represent the three C_{DGT} replicates with depth at each site. Spatial variation is apparent at each site with the exception of Skaigh Wood which was averaged together to give a single profile due to the lack of significant differences (determined by an ANOVA; $p > 0.05$) between probe measurements for each depth segment. Spatial variation was expected due to the nature of unmixed sediments, however it clear that in most cases a similar trend through depth is seen.
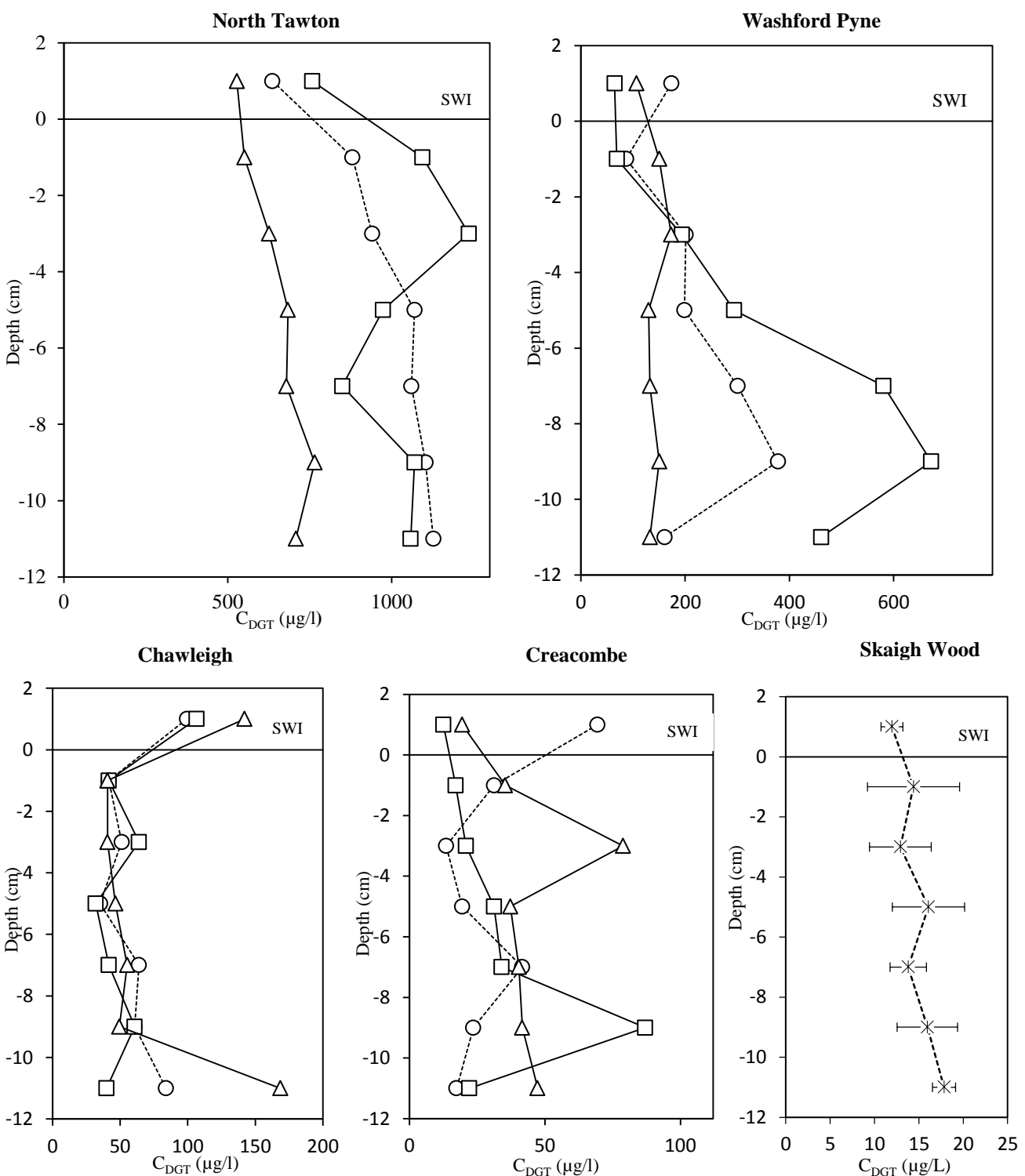
Note: The line at 0 cm depth represents the sediment-water interface (SWI), where 2 cm of the window is exposed to the stream water and the 12 cm below the SWI represent the C_{DGT} through depth.

Fig. 2. The above five graphs represent DGT devices at each site, while Skaigh Wood is the average of the three DGT devices (confidence interval = three times the standard deviation of the mean of three replicate determinations).
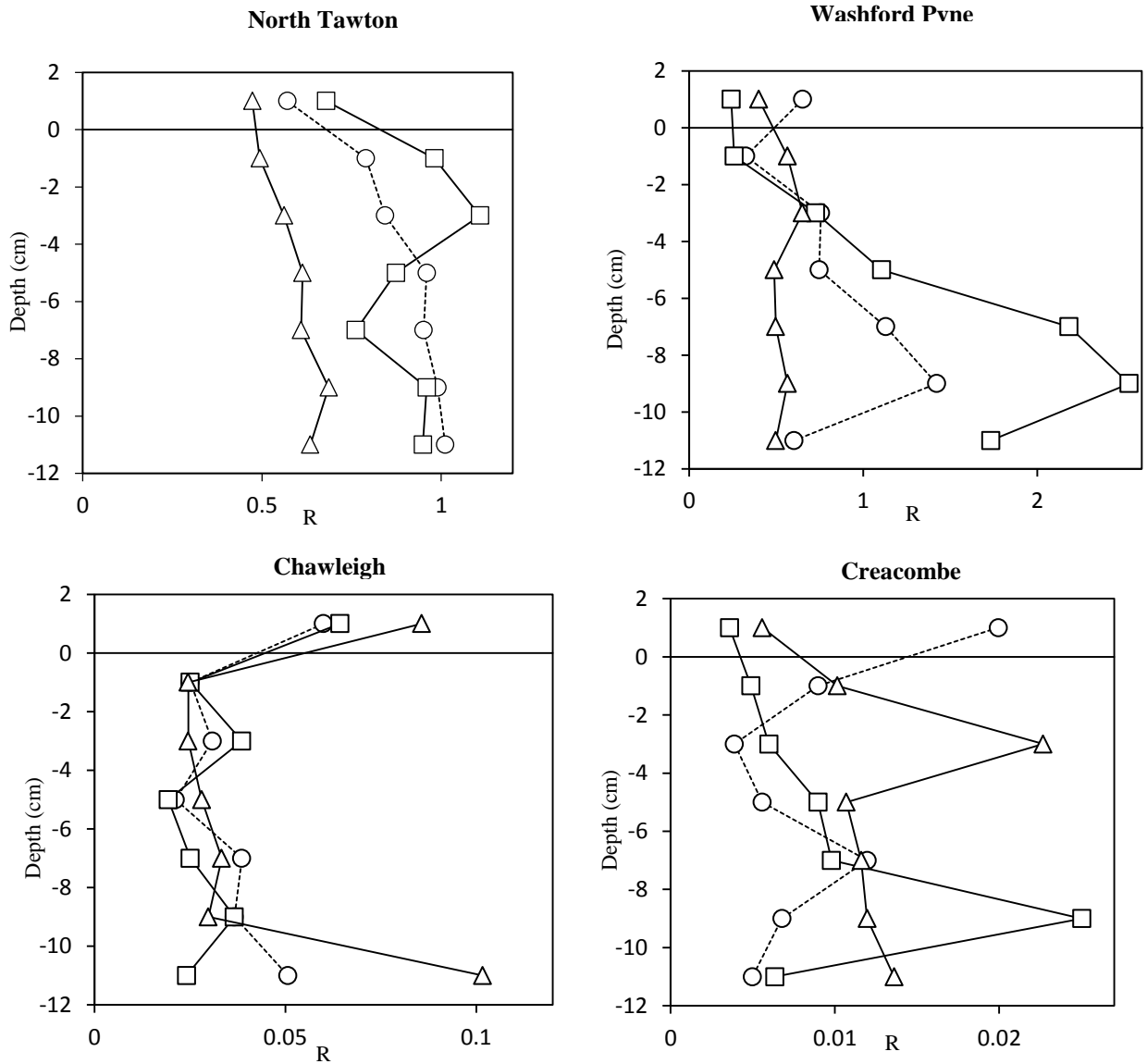
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338 Sites inferred to have less anthropogenic diffuse and point P influence (Creacombe and Skaigh Wood) had less
339 varied profiles with depth and C_{DGT} concentrations at the surface water interface (SWI) similar to the sediment.
340 North Tawton had an exaggerated profile with a greater concentration range than observed at other sites.
341 Washford Pyne had the second highest C_{DGT} and also an exaggerated difference in C_{DGT} throughout the
342 sediment depth. Chawleigh had a high SWI C_{DGT}, however through depth the concentration did not differ
343 greatly from Creacombe. Skaigh Wood had the lowest C_{DGT} but the second highest total P in the suspended
344 bottom sediment. This indicates that only a small portion of the total P found by XRF was available to the
345 DGT device.

346 *3.3 Comparison of R across sites*

347 C_{DGT} will theoretically be less than or equal to sediment porewater measured by another method due to its
348 selectivity and length of time left in the sediment. Therefore the ratio R (Equation 3) can be calculated and acts
349 as a standardized value for the magnitude of kinetic resupply of the solid labile phase for a given response time
350 both through depth and between sites (Figure 3).
351 In each case the lowest or second lowest concentrations of solid phase labile P in the sediment through depth
352 was the uppermost layer. Labile P also increased with sediment depth, however, the pattern is not the same at
353 each site. The values above 1 observed at the Washford Pyne and North Tawton site should be disregarded as
354 the capacity of the device has been exceeded and therefore not compliable withDGT theory (Ding et al., 2010).

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North Tawton

Washford Pvne

Chawleigh

Creacombe

Note: There is no profile for Skaigh Wood because a porewater sample could not be obtained.

Fig. 3.The calculated R values (0-1) through depth with 1 representing the fully sustained resupply case or most reactive and 0 being unsustained and no resupply from the solid phase resulting in little or no reactivity.

3.4 Relationship of P to Sediment Composition

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395　To assess possible interactions such as precipitation reactions and sorption to colloidal material, between total

396　sedimentary P and other elements, correlations with Al, Ca and Fe obtained via XRF were undertaken for the

397　channel stored fine sedimentary material (<0.63 µm) (Figures 4).

398

399　No significant correlation was observed between suspended bottom sediment P and Al (r=0.100, p=0.05)

400　or Fe (r=0.007, p=0.05), When total P was compared with total Ca, however, stronger correlations were

401　observed (r=0.652, p=0.05). The Ca correlation (r=0.988, p=0.05) was dramatically improved when the

402　Washford Pyne site was removed from the analysis (Figure 4) but similar improvements in Al and Fe

403　correlation were not observed.

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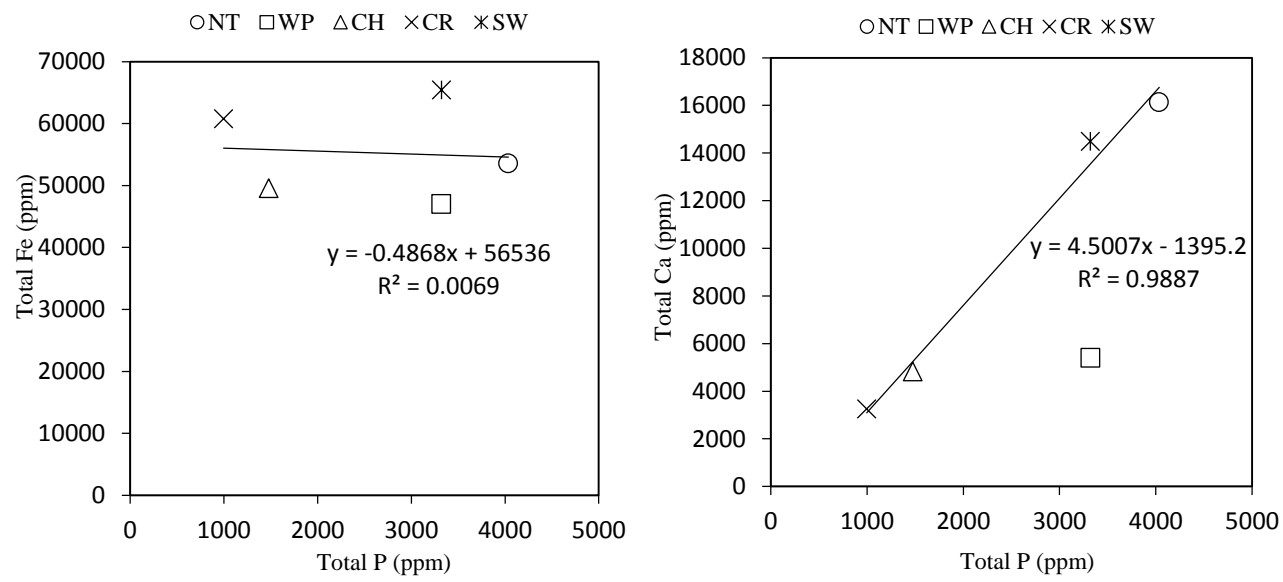
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406　**Fig. 4.The correlation between total P, Fe and Ca. Washford Pyne was omitted from the Ca**

407　**correlation analysis.**

408

4. Discussion

409

4.1 Sediment P Lability

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411   One of the simplest applications of DGT in sediments is to calculate an R value which is a ratio of C_{DGT} to

412   porewater concentration (measured by a separate method) that serves as a comparable measure of the ability of

413   the sediment to resupply porewater with labile P. The R value clearly and unsurprisingly differs between sites

414   of contrasting impacts, but also quite substantially through sediment depth within sites.

415

416   A clear trend was seen in the top 0-2 cm portion of each sediment profile where either the lowest or second

417   lowest R value were reported (Figure 3). A low R value is indicative of slow dissociation kinetics and therefore

418   can serve as an indication of the rate of desorption from the solid phase (Degryse et al. 2009). A drop in redox

419   was also observed with depth, which could increase the desorption of redox sensitive compounds, hence

420   increase reactivity (Degryse et al. 2009; Ding et al. 2010). Processes that produce SRP at depth such as the

421   liberation of P from decomposing organic matter or the desorption of P from ferric sorption sites in the

422   presence of anoxic conditions have a significant impact on the ability of sediments to act as a sink (Monbet et

423   al. 2008, 2010; Jarvie et al. 2008). A low R value in the upper layer compared with the deeper sediment

424   indicates that important chemical or biological processes are occurring that slow the sediment kinetics

425   regarding the potential release of labile P suggesting that a significant drop in P concentrations in the water

426   column is unlikely to result in as large a release of P due the reduction in surficial sediment reactivity. This

427   may be a consequence of the geochemistry limiting both the diffusion of labile P in and out of surficial

428   sediment, or there was simply more labile P at depth due to redox conditions and the breakdown of organic

429   matter (Palmer-Felgate et al. 2010).

430   The profiles all differed from each other at lower depths demonstrating the influence of spatial heterogeneity

431   between sites. Ding (2010) suggested that the downward increase in R was related to changes in the redox

432   state. Creacombe, the relatively low impacted headwater site had R values all equal to or lesser than 0.01,

433   which Harper (1999) deemed as a diffusion only case, R_{diff}. There is no resupply from the solid labile phase

434   resulting in little or no reactivity. The Chawleigh site had slightly larger R values than the Creacombe site, but

435   still mostly <0.1 so considered unsustained. The R values were slightly elevated compared with the control site

436   at Creacombe, possibly owing to the sediment being influenced by its location downstream of a phosphorus

437   source, namely a wastewater treatment works.

4.2 Sediment P Interaction With Other Elements

438

439   Previous studies have shown that the fate of sedimentary phosphorus may be controlled by other elements

440   present in the sediment such as aluminium, iron or calcium via precipitation reactions or formation of colloids

441   (Evans et al. 2004; Palmer-Feldgate et al. 2010; Reynolds & Davies 2001). No significant correlation was

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442 observed between suspended bottom sediment P and Al (r=0.100, p=0.05) or Fe (r=0.007, p=0.05), When total

443 P was compared with total Ca, however, stronger correlations were observed (r=0.652, p=0.05). The Ca

444 correlation (r=0.988, p=0.05) was dramatically improved when the Washford Pyne site was removed from the

445 analysis (Figure 4) but similar improvements in Al and Fe correlation were not observed. This implies that in

446 this system, total P is more closely associated with calcium in contrasts to finding of Jarvie et al. (2008) who

447 identified strong association with iron.

448

449 *4.3 Interpreting DGT Spatial Profiles*

450 North Tawton and Washford Pyne represented point source industrial and agricultural influences respectively.

451 The largest C_{DGT} values were found at these sites indicating a large pool of SRP and the solid phase has a good

452 ability to resupply the depleted porewater SRP concentrations, almost maintaining equilibrium, as described by

453 a high value of R. However this interpretation is limited to C_{DGT} values less than 800 **µ**g/L as values above this

454 concentration exceed the capacity of the device and will no longer accurately reflect DGT theorized uptake.

455 This is evidenced by R values greater than 1 (**F**igure 3) that correspond with the C_{DGT} values above 800 **µ**g/L

456 (**F**igure 2). R values above 1 occur when the device is no longer responding to DGT theory, in this case

457 reliable capacity of the device has been exceeded. (Zhang et al., 1998). Ding (2010) calculated a capacity per

458 centimeter of the DGT device to be 400 **µ**g/L, our spatial resolution was 2 cm therefore above values of 800

459 **µ**g/L the integrity of that portion of the device has been compromised. The shape of the C_{DGT} profile through

460 depth and magnitude of R can be compared with concentrations of elements suspected to be important in

461 phosphate cycling mechanisms as well as porewater and stream water concentrations, thereby determining on a

462 sub-catchment scale the important drivers in channel storage of phosphorus. The shape of the C_{DGT} profiles

463 through depth varied and provided an indication of differing channel storage mechanisms occurring. The North

464 Tawton C_{DGT} exhibited highest of all concentrations in the surface sediment and at the bottom of the sediment

465 profile concentrations exceeded 1000 µg/l. The cheese factory upstream of the sampling point has been

466 discharging P in its effluent for 40 years potentially explaining elevated total P concentrations above those

467 sites influenced by STW or agricultural inputs alone. The Washford Pyne site impacted by agricultural inputs

468 from livestock also exhibits elevated C_{DGT} compared with less impacted sites, but significantly lower than that

469 from North Tawton. For two of the three depth profiles, concentrations of labile P increase to a sediment depth

470 of 9 cm before decreasing at the final depth measured (11cm). The two most impacted sites at Washford Pyne

471 and North Tawton had relatively low porewater SRP concentrations compared with less impacted sites, but the

472 proportion of SRP which was labile (via C_{DGT} measurements) was high as indicated by the higher R values. An

473 explanation for this may be that both of these sites also have reducing sediment conditions throughout their

474 depth profiles. The total iron concentrations at both of the sites is high, and under sufficiently reducing

475 conditions a large proportion of the filterable phosphorus may be sufficiently labile to be captured by the DGT.

476 Under less reducing conditions, as at the other sites, the forms of iron and phosphorus present may be forming

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477   colloids which although filterable (as detected by filtration through 0.45 μm) are sufficiently large to be unable

478   to pass through the DGT membrane (Palmer-Felgate et al., 2010). This would increase SRP through depth and

479   this is supported by increasing C_{DGT} with depth in both profiles.

480   The reduction of iron leads to the assumption that the anoxic condition are what is driving highly labile P

481   concentrations (at least in anoxic sediments), but when stream water SRP is considered, a more complicated

482   situation arises. The overlying water SRP at the North Tawton site was approximately 200 μg/L more than the

483   porewater SRP, but at the Washford Pyne site the overlying water SRP, 70 μg/L, was lower than both the

484   porewater SRP and C_{DGT}, 276 and 102 μg/L respectively. This presents an odd contrast when considering the

485   reduction of Fe under anoxic conditions should be causing an increase in sediment SRP in comparison to the

486   oxic stream water. A laboratory DGT device was deployed in the stream water at Washford Pyne resulting in a

487   C_{DGT} of 9 μg/L, much lower than the *in situ* SWI C_{DGT} of 115 μg/L. The low concentration of SRP and low

488   C_{DGT} in stream water in comparison with the high SWI measurement indicates that Washford Pyne sediment

489   was likely acting as a source of SRP to the water column at the time of sampling. There is likely P loss by

490   means of diffusion at the SWI which is potentially why the C_{DGT} is much higher there than the water column

491   as a whole. The shape of the Washford Pyne profile suggests that C_{DGT} concentrations are relatively low at the

492   surface of the sediment compared with further down the profile. This shape may be the result of a reduction of

493   an 'oxic cap' due to negative Eh values, which control labile P concentrations by means of Fe adsorption and

494   precipitation under aerobic conditions described elsewhere (Jarvie et al. 2008; Withers & Jarvie, 2008; Palmer-

495   Felgate et al. 2010).

496   Even though high Fe and anoxic conditions were observed at the North Tawton site, the above mechanism

497   does not explain the C_{DGT} depth gradient observed there. The SWI C_{DGT} was much lower than 0-2 cm C_{DGT}

498   sediment concentration and the SWI C_{DGT} was also lower than the SRP measured in the stream water, the

499   opposite of Washford Pyne. The shape of the concentration profile at North Tawton in tandem with the SWI

500   C_{DGT} and water column SRP indicates that North Tawton was potentially acting as a sink for P. The proposed

501   reason for retention of P in sediments at North Tawton is a 'calcium cap' where co-precipitation of calcium

502   with phosphorus renders phosphate non labile via the formation of insoluble calcium phosphate minerals.

503   Assuming simple $Ca_3(PO_4)_2$ precipitation, an excess of Ca in the North Tawton sediment can be hypothesised

504   to permit precipitation. In contrast, concentrations at Washford Pyne were roughly equimolar meaning the 3:2

505   stoichiometry of Ca to P respectively could not be achieved, possibly explaining the higher concentrations of

506   bioavailable P present in the sediment. This is further supported by the fact that the Washford Pyne site also

507   fails to exhibit the same correlation between total P and Ca as shown for the other sites in Figure 4. The impact

508   of dairy cattle using the site as a drinking point helps explain higher P concentrations in comparison to the

509   most undisturbed sites. Anthropogenic inputs of P at this site are unmatched by Ca unlike at the North Tawton

510   site where Ca is released in tandem with phosphate in creamery effluent.

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511 Several different analyses applied in this study provide evidence supporting the 'calcium cap' theory. The

512 strong correlation observed between TP and Ca in surficial sediments (Figure 4) provides a case for the

513 formation of a 'calcium cap' (Palmer-Felgate et al. 2009). In a similar study where Diffusive gradient in thin-

514 films DET was used to investigate point source sewage discharges, a correlation was not observed between TP

515 and Ca and the formation of a 'calcium cap' was refuted (Palmer-Felgate et al. 2010). In the present study, the

516 'calcium cap' could be preventing the upwards diffusion of P to the SWI even under anoxic conditions in the

517 sediment below as well as providing an active mechanism for removing P from the water column (Withers &

518 Jarvie 2008). In an attempt to confirm C_{DGT}, soil P retention or buffer capacity could have been utilised,

519 however the total element concentration helps answer why by drawing on former conclusions by Withers &

520 Jarvie (2008) and Palmer-Felgate (2010) where total element concentrations were used to help understand the

521 labile P in the system. The total P in the suspended bottom sediment at the North Tawton is very large, mainly

522 due to the creamery point source, however, total calcium correlates with total P, which could be due to

523 creamery effluent also providing an important source of Ca as it produces milk products.

524 The Chawleigh site sampled was downstream of a small sewage treatment facility and runs through sloping

525 pastures and scattered residential areas which are not all on mains sewerage. Sediments were anoxic and the

526 porewater SRP at Chawleigh was second highest yet the C_{DGT} was second lowest. The water column SRP was

527 the highest and the matching C_{DGT} was second highest and almost equivalent to the SWI C_{DGT}. The complexity

528 of these observations means it is difficult to tell if Chawleigh was acting as a source or a sink of P to the water

529 column at the time of sampling, but it would appear that once again a 'calcium cap' mechanism may be

530 retaining P in sediments due to the correlation with TP. The issue in this case is what caused high streamwater

531 SRP concentrations, because historic accumulation matching the stream water SRP is not present at this site.

532 The source of P may be potentially highly mobile and transient, further investigation and a closer look at the

533 STW effluent is required.

534 In the Skaigh Wood reach, the relatively consistent C_{DGT} profile through depth was characteristic of pristine

535 headwater conditions (Jarvie et al. 2008). Without porewater concentrations interpretation of this site was

536 limited, but the water column SRP concentration and resultant C_{DGT} concentrations were the lowest observed

537 and both fell within 'good' P status for a site of that altitude and alkalinity. There was no significant difference

538 between SWI C_{DGT} and the water C_{DGT} and it would be reasonable to assume that sediments were likely to be

539 in equilibrium at this site, with similar amounts of P diffusing in and out of the SWI (Palmer-Felgate at al.

540 2010). The sediment bulk geochemical analysis for Skaigh Wood was unexpected as it revealed the second

541 highest concentration of TP as well as Ca and highest concentration of Fe and Al of sites in the study. This

542 offers further support to the assumption and importance of a 'calcium cap' in the study catchment as both the

543 potential co-precipitation with P as well as the sorption to Fe and Al was rending over 99% of the TP

544 unavailable (based on C_{DGT} 0-2 cm), but this conclusion is limited as porewater SRP needs to be analysed to

545 provide sufficient evidence of this.

546 The Creacombe site was similar to that at Skaigh Wood in that C_{DGT} concentrations were very low compared

547 with the more impacted sites, but the profile was less uniform possibly indicating that whatever made P

548 unavailable at Skaigh Wood was less prevalent at Creacombe, which again may be explained by Ca

549 concentrations, as they were lowest at the Creacombe site. Sediments are likely acting as either a limited sink

550 or source depending on particular temporal environmental conditions. Internal P loading is not expected to

551 have negative effects on water quality at this site as both SWI C_{DGT} and water SRP are within WFD 'good'

552 status.

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554 The selectivity of DGT is a more accurate measure of actual P bioavailability supported by several studies (Liu

555 et al. 2012; Mason et al. 2010; Mundus et al. 2012; Tandy et al. 2011; Zhang et al. 2001, 2004) in comparison

556 to traditional porewater SRP measurements using molybdate based colorimetric determinations which may

557 include colloidal-bound P, whereas DGT excludes them with an approximate pore size of only 1 nm. This may

558 go some way towards explaining why in many cases exceedance of the current P EQS as measured by

559 traditional methods does not correlate with diatom ecology (Österlund et al. 2010). A disconnection between

560 C_{DGT} and porewater SRP occurred at both Chawleigh and Creacombe, moderately to low impacted sites. This

561 was determined by a laboratory comparison between stream water SRP and DGT. The C_{DGT} was less than half

562 of the SRP concentration at each site. Therefore using the molybdenum blue method as a measure of labile P in

563 samples where P is present in colloidal or hydrolysable organic fractions could lead to an over estimate of the

564 P bioavailability, which may have been the case at the Creacombe site, particularly in light of the measured

565 total Fe and Al concentrations.

5. Conclusions

567 There has been no previous widespread study of phosphorus dynamics and availability in riverine sediments

568 using DGT *in situ* to the authors' knowledge. Four major conclusions are drawn from this work ranging from

569 DGT practicality to the potential of DGT deployments in riverine sediments.

570 Phosphate associations with the colloidal/sorbed fraction was shown to render 99% of P in porewaters non

571 labile through the difference in C_{DGT} and porewater SRP concentrations. This has important implications when

572 relying on the SRP method alone to determine potential P bioavailability and shows that it might dramatically

573 over estimate the labile fraction of P in both sediments and overlying waters. It is proposed that DET devices

574 be deployed in tandem with DGT devices to obtain comparable and less biased SRP values with the benefit of

575 obtaining measurements at the same spatial scale as DGT.

576 Sediment chemical composition is critical in in terms of phosphate 'self-cleaning' mechanisms in river

577 channels contaminated by diffuse and point source P. In this study, calcium correlated well with TP in all but

578 one site and it is suggested that this is leads to the formation of a 'calcium cap' which controls a large portion

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579 of phosphate bioavailability as well as capping P diffusion at the sediment-water interface, even under anoxic

580 conditions. At the site that did not fit in the Ca correlation, it was found that not only were P-C_{DGT}

581 concentrations high, but sediments are also acting as a source of SRP to the water column. This site was

582 located next to a cattle drinking point and highlights the importance of farm management when controlling P

583 sources to surficial water courses.

584 The DGT method has been successfully implemented in this study, although its success was heavily reliant on

585 the results of supporting analyses. One of the principal criticisms yet also a key benefit of DGT is its

586 unparalleled potential when aided by a range of other parameters. DGT does well to provide the missing link

587 when assessing flux, reactivity and bioavailability of P in sediments. A study such as this provides valuable

588 data regarding understanding and quantifying river channel storage mechanisms and fluxes at a sub-catchment,

589 even full catchment scale. To supplement that data generated in this work, a temporal DGT study is also

590 recommended to determine if sediments react the same way in the winter under different environmental

591 conditions and further data collection is required to validate the conclusions relating to the nature of sediment

592 P flux. The deployment of both DGT and DET together would provide the most accurate and matching

593 description of C_{DGT} and SRP *in situ*.

594 Overall, this study has successfully employed the use of DGTs in a catchment contaminated by diffuse and

595 point sources of P and provided valuable insight into sediment P kinetics and fluxes under current conditions.

Acknowledgements

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Ref.: Ms. No. ESPR-D-14-02854R1
Determining riverine sediment storage mechanisms of biologically reactive phosphorus in situ using DGT
Environmental Science and Pollution Research

Dear Sean Comber,

Reviewers have now commented on your paper. You will see that they are advising that you revise your manuscript. If you are prepared to undertake the work required, I would be pleased to reconsider my decision. Please make sure to submit your editable source files (i. e. Word, TeX)

The reviewers' comments can be found at the end of this email or can be accessed by following the provided link.

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When revising your work, please submit a list of changes or a rebuttal against each point which is being raised when you submit the revised manuscript.

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To submit a revision, go to http://espr.edmgr.com/ and log in as an Author. You will see a menu item called 'Submissions Needing Revision'. You will find your submission record there.

Yours sincerely,

Dr. Philippe Garrigues
Editor
Environmental Science and Pollution Research

Reviewers' comments:

Reviewer #3: I find in general the paper is much improved giving a cleaner more understandable paper. There are still a couple of points that need addressing though.

Figure 2. You seem to have not understood my point I made about the error bars, unless you carried out more than one repeat chemical analysis on the same eluent from each part of the DGT. You cannot use standard deviation as error bars on points in a figure that are not mean values. This is not scientifically or statistically sound. You can only do this on mean values. Therefore please remove your error bars on all figures except for that of Skaigh Wood.

Done.

L415: You refer to Figure 4 but you should be referring to Figure 3.

Done

L448-451 (clean document): You still do not explain how North Tawton can have R values greater than 1.
North Tawton and Washford Pyne represented point source industrial and agricultural influences respectively. The largest C_{DGT} values were found at these sites indicating a large pool of SRP and the solid

phase has a good ability to resupply the depleted porewater SRP concentrations, almost maintaining equilibrium, as described by a high value of R. However this interpretation is limited to C_{DGT} values less than 800 ug/l as values above this concentration exceed the capacity of the device and will no longer accurately reflect DGT theorized uptake. This is evidenced by R values greater than 1 (figure 3) that correspond with the C_{DGT} values above 800 ug/l (figure 2). R values above 1 occur when the device is no longer responding to DGT theory, in this case reliable capacity of the device has been exceeded. (Zhang et al., 1998). Ding (2010) calculated a capacity per centimeter of the DGT device to be 400 ug/l, our spatial resolution was 2 cm therefore above values of 800 ug/L the integrity of that portion of the device has been compromised. Text changed to explain better.

L501-502: "The impact of dairy cattle using the site for drinking may explain higher levels of Ca present" Actually the opposite is present, at Washford Pyne there is lower Ca with P than the general correlation. Please change.
The impact of dairy cattle using the site as a drinking point helps explain higher P concentrations in comparison to the most undisturbed sites. Anthropogenic inputs of P at this site are unmatched by Ca unlike at the North Tawton site where Ca is released in tandem with phosphate in creamery effluent.

You say you have added the SRP pore water values to the paper but you have only added the mean values for the whole profile in Table 2. I still think it is needed to add these values for the whole depth profile in supplementary information.

There may be some confusion here – as described in the method section:

"Sediment porewaters were obtained by extracting 3 cores of consolidated bed material at each site using an 8 cm diameter plastic tube and plunger and placed into polythene bags prior to centrifugation at 3000 rpm for 15 minutes in a MSR Centaur 2 centrifuge. Due to the nature of the sediment each core was bulked into a single sample. The porewater was filtered using acid washed 25mm diameter Millipore cellulose acetate filters (0.45 μm) into acid washed polythene bottles. P was determined using the molybdenum blue method described above."

Therefore we have 3 core values, but nothing through depth because each core needed to be bulked to get enough porewater to analyse. The porewater data, however, do provide us with valid information in which we drew our conclusions upon.

We have noted thelimitations via the statement regarding use of DET:

"The deployment of both DGT and DET together would provide the most accurate and matching description of CDGT and SRP in situ. "