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River sediments provide a link between catchment pressures and ecological status in a mixed land use Scottish River system

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ABSTRACT

This study evaluates water quality, suspended and bed sediment, ecological and catchment land use data for 13 catchments of the mixed land use River Dee, NE Scotland, where pollution point sources are limited. Samples were collected at key times of biological activity (early and late summers). Mean river water concentrations were smaller in main stem and upland sites and greater in tributaries where agricultural pressures were greater and were 2–41 $\mu g PO_4$-P l^{-1}, 8–58 μg total dissolved P l^{-1} and 1–6 mg l^{-1} of suspended particulate matter (SPM). SPM was 7–372 times enriched in biologically available P (BAP; determined using an FeO paper strip method) and 2–122 times in organic C relative to bed sediments. Ratios in river water concentrations of BAP attributed to the SPM (0.1–1.0 $\mu g P l^{-1}$) to PO_4-P had the greatest range at baseflow (0.01–0.80) with larger values for low land use intensity catchments. During May chlorophyll a concentrations were related to SPM BAP ($p<0.001$), but later in summer to PO_4-P, and there was a corresponding change in the organic composition of SPM observed by IR spectroscopy. SPM concentrations and SPM BAP were better related to intensive grassland land use ($p<0.001$) than was PO_4-P concentration ($p<0.01$) and also predicted abundances of filter feeding macroinvertebrates ($p<0.001$). Within this river system SPM quantity and composition proved to be an indicator of river biogeochemical functioning and requires further investigation as a potentially sensitive monitoring tool and to increase our understanding of chemical ecological links.

1. Introduction

The quality of river waters are often classified according to absolute mean and percentile chemical thresholds, often determined for single locations at larger catchment scales (Scottish Environmental Protection Agency, 1999; Environment Agency, 2002). Such strategies were designed to determine risks from point source pollution. The Water Framework Directive (WFD; 2000/60/EC), newly implemented across Europe, has the requirement for rivers to meet 'Good Ecological Status' and involves classification against reference water bodies according to a combination of physico-chemical, biological and hydromorphological criteria.

Nutrient (N, P) enrichment in streams can alter stream metabolic activity (Peterson et al., 1985) and ultimately have knock on effects on the whole food-web and community structure (Peterson et al., 1993). Statistical models have related nutrient enrichment with either primary producers biomass (Dodds et al., 1998; Carr et al., 2003) or species composition and diversity (Kohler et al., 1973; Thiébaut et al., 2002). While the causality of these relationships can be compounded by other factors such as alkalinity or spate flow

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frequency and magnitude (e.g. Biggs, 1995, 2000), nutrient concentrations are more readily managed, their effects quantified and hence remain central to the regulatory methods for attainment of 'Good Ecological Status.'

Phosphorus is generally perceived to be the limiting nutrient in freshwaters governing eutrophication potential and provides a key focus for water quality targets. Thresholds have generally been developed for soluble reactive *P* (SRP; principally phosphate) thresholds for rivers in the UK (e.g. Duncan et al., 2006; a working range of SRP standards between <20 and $>120\,\mu g\,l^{-1}$), or in terms of total P (also including reactive dissolved organic and particulate forms) in the US (Dodds and Welch, 2000, who compile a range of total P thresholds of 20–415 $\mu g\,l^{-1}$). Different national and regional water quality P standards have been set to reflect eco-regional differences.

Suspended particulate material (SPM) is ubiquitous in virtually all aquatic systems. Inputs of SPM are enhanced by land use factors, such as soil erosion associated with agriculture, or by internal processes such as biological organic matter cycling. The effects of SPM on river ecology is complex and can include inter-relationships between grazers, siltation of habitats and effects of reduced light penetration on photosynthesizers (Osmundson et al., 2002). It is being increasingly recognized that river sediments provide an important vector of nutrients in aquatic ecosystems (Haygarth, 2005). Sediment physicochemical composition affects the mobilization, transport and bioavailability of P (House, 2003; Ernstberger et al., 2004). There may be practical difficulties in monitoring to evaluate 'Good Ecological Status' such as the use of turbidity as a surrogate for SPM concentrations, or of total nutrients which reveal little about bioavailable pools (Cooper et al., 2003).

Few guidelines exist for evaluating suspended and bed sediment data. Sediment criteria are often qualitative in nature (US Environmental Protection Agency, 2003), an exception is the Canadian ecotoxicologically derived quality guidelines (Canadian Council of Ministers, 1999) and these are concerned principally with organic pesticides and metals. More commonly, thresholds for species are developed 'intuitively' from understanding based on habitat surveys. While it is known that suspended particles quantity and quality (plankton, fine particulate organic matter) can impact on macroinvertebrate community structure (Allan, 1995), it remains to test whether existing and new indices may be sensitive.

In this paper, we describe observations of bed and suspended river sediments across a mixed land use major river catchment (NE Scotland) and consider the possible implications for ecology. The River Dee and its tributaries are designated as Special Areas of Conservation for Atlantic Salmon (*Salmo salar*), Otter (*Lutra lutra*) and Freshwater Pearl Mussel (*Margaritifera margaritifera*) under Natura 2000 (http://www.jncc.gov.uk/ProtectedSites/SACselection/sac.asp?EUCode = UK0030251). The River Dee is considered to be of low nutrient status and generally unpolluted but its water quality is under pressure from agricultural practices in many of its tributaries (Langan et al., 1997). Previous work in the catchment has focused on the origins and consequences of dissolved river chemistry (Smart et al., 1998; Edwards et al., 2000; Stutter et al., 2001). However, data from Stutter et al. (in press) shows that a suggested $10\,mg\,l^{-1}$ SPM quantitative threshold for Freshwater Pearl Mussel habitats (Cooper et al., 2003) was exceeded in the River Dee over 35% and 10% of the year 2004–2005 in a tributary and main stem site, respectively. The aim of the present study is to understand the role of river sediment physicochemical composition in the interrelationships between catchment characteristics, ecological status and water quality. The study evaluates whether SPM: (i) varies spatially according to catchment land use, (ii) provides a link between the catchment pressures and aquatic habitat status, and (iii) should be incorporated in monitoring and classification protocols for the Water Framework Directive. To achieve these aims the study examined spatial variation in sediment quantity and quality parameters related to nutrient bioavailability and also the temporal variability of the inorganic and organic nutrient pools.

2. Materials and methods

2.1. Study site

The River Dee catchment (2100 km^2) extends from the Cairngorm Mountains (max. elevation 1220 m) to the North Sea at Aberdeen (57°9′N, 2°9′W). Annual precipitation varies E to W (700–2000 mm). River flows are at their smallest during the summer and greatest during autumn and spring. Mean discharge on the lower main stem is $46\,m^3\,s^{-1}$ and peak flows in excess of $900\,m^3\,s^{-1}$ have occurred. Land use in the catchment consists of heather moorland, bog, unimproved grassland and plantation forestry to the W and SW, with intensified agriculture in the eastern lowlands. Catchment characteristics for the present study were extracted from ARC-INFO GIS, using land cover data derived from the land cover of Scotland 1988 census (MLURI, 1993). The soils have developed over generally acidic drift material (Dalradian metasediments) and granites and are dominated by spodosols, with histosols to regosols on the higher ground (MISR, 1982). Detailed descriptions of the Dee catchment setting and hydrochemistry are given by Maizels (1985), Smart et al. (1998) and Stutter et al. (in press) (Fig. 1).

2.2. Sample collection

River water, suspended particulate matter (SPM) and bed sediments were collected at 13 locations in the River Dee (Table 1). The sites encompass a range of land use types within tributaries and a downstream transect along the main stem. On three occasions SPM was sampled, prior to any disturbance of the stream bed by collecting water samples from mid-depth and mid-channel using a bucket to fill a 30 L polyethylene bottle. Bed sediments (0–3 cm sediment depth) were collected from the same locations at each sampling point, on each date (an area approximately 1 m^2) using a plastic scoop, which was covered as it was brought up through the water column. Bed sediment, together with any water recovered in the scoop, was bagged and transported in a darkened cool box. Samples were taken over a range of flow and antecedent conditions on: (i) 6/5/2004, shortly after the

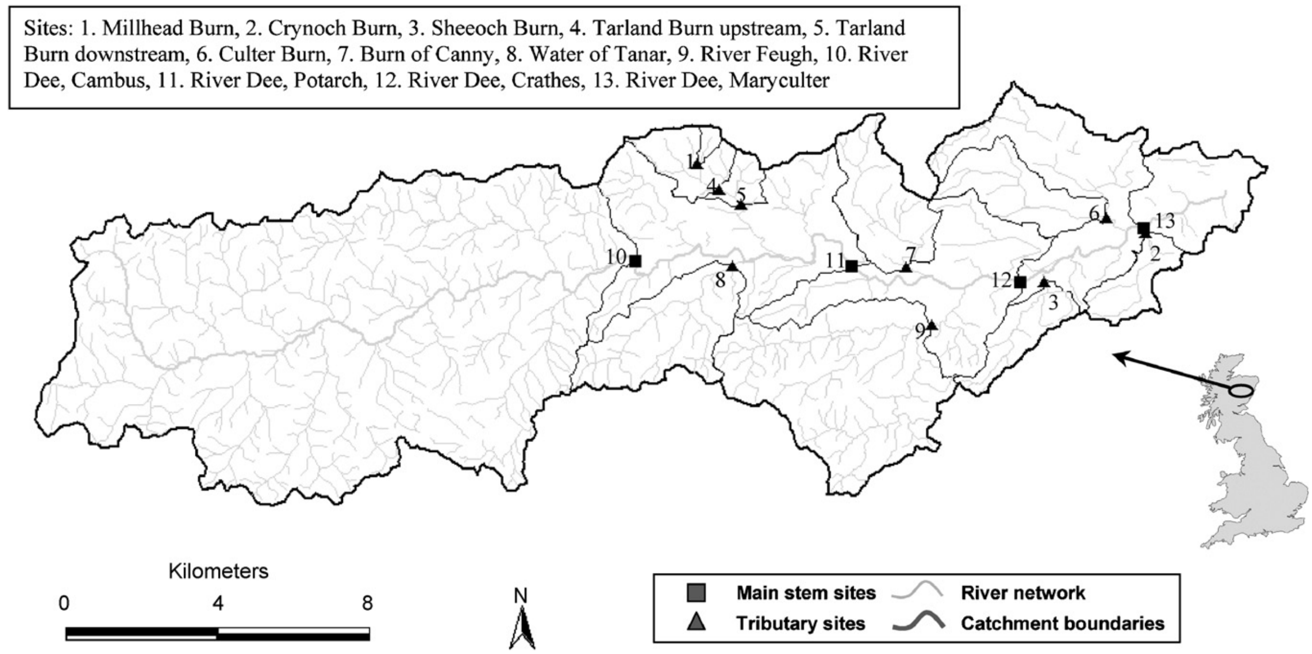

Fig. 1 – The River Dee catchment showing the main river network, sampling sites and their catchments (numbered in ascending size order according to Table 1).

peak discharge of a moderate storm, (ii) 3/8/2004, after a month of stable summer baseflow, and (iii) 11/5/2005, during the recession following a major spring storm period. These flow conditions represented the 6, 99 and 37 percentile discharges (May 2004–2005) at the lowest gauged site on the main stem (Park Bridge NGR 797983; data provided by Scottish Environmental Protection Agency).

2.3. *Physical and chemical analyses*

The bed sediments were air-dried (30 °C) and a portion passed through a 2 mm aperture sieve was retained for particle size analysis. Particle size distributions of bed sediments (<2 mm air-dried fractions) were determined by laser diffractometry (Mastersizer 2000 with HydroG dispersion unit, Malvern, UK) following dispersion (16 h end over end shaking in ~3% ammonia solution). For chemical characterization bed sediments were passed through a 250 μm aperture sieve to minimize size effects in the comparison between bed sediments and SPM. This was based on observations that >90% of the SPM was of an equivalent spherical diameter <250 μm. SPM was recovered from the bulk water samples using a continuous centrifuge (Alfa Laval, Doerr, Wisconsin, USA), hence the smaller colloidal size particles are excluded from this investigation although they may have a considerable role in bioavailable P transport. Concentrated SPM suspensions (~300 ml) were analysed for particle size by laser diffractometry using stirred dispersion only so as not to disaggregate the SPM prior to chemical characterization. Chemical analyses were carried out on air-dried bed sediments and SPM, with values reported on an oven-dried mass basis (105 °C for 2 h). Drying of soils and sediments may induce increased phosphate affinity due to changes in organic, Fe and Al surface complexes and nutrient flushes following cell lysis. However, investigations into drying effects on sample integrity often give contradictory results (Baldwin, 1996) and the procedure remains a common preparation for P analyses (Pierzynski, 2000). Organic C and N were determined by total elemental analysis (Thermo-Finnigan, Flash EA 1112 CN analyser, Naples, Italy). Triplicate samples were analysed, without milling, for oxalate extractable Fe, Al and P (termed Fe_{ox}, Al_{ox}, P_{ox}; extractions according to Farmer et al., 1983) and for P extracted using the Fe oxide paper strip test (termed bioavailable P, BAP; Chardon et al., 1996). Oxalate extractable Fe and Al represent poorly crystalline aluminosilicates, ferrihydrite, and Al– and Fe–humus complexes which are thought important in controlling surface adsorption of PO_4-P (Schroeder et al., 2004). Oxalate extractable P (P_{ox}) represents the P associated with these poorly ordered surface complexes and the P sorption ratio (PSR) the degree of P saturation. Results for BAP are given in two forms (e.g. Table 2); as a concentration per unit mass of sediment (mg kg^{-1}) and in μg P l^{-1} (multiplied by the water SPM concentration) to allow comparison with the pools of dissolved P. The P sorption ratio, PSR, was calculated as $PSR = (P_{ox}/(Fe_{ox}+Al_{ox}))$. Hand ground, oven-dried (105 °C) samples were also analysed by Fourier Transform Infra-red spectroscopy using a Diamond Attenuated Total Reflectance method (Nicolet, Magna IR550, Madison, USA). The spectral region 1900–1300 cm^{-1} gave qualitative information on the nature of the organic matter and clay contents as has previously been used in interpretation of aquatic biofilm development by Galle et al. (2004).

Suspended sediment concentrations were determined gravimetrically on filters (Whatman, 0.45 μm cellulose acetate). The filtrates were analysed by spectrometry (San++

Table 1 – Attributes of the River Dee study catchments (ordered by increasing catchment size)

Site no.		NGR	Area (km^2)	% areas of catchment land use[a]						Physical attributes[b]		
				Arable	IG	BlW	CW	Moor	Urban	Channel width (m); modifications[c]; features[d]	Substrate[e]	Flow[f]
(i) *Tributaries*												
1	Millhead Burn	NJ 473060	4	21	25	1	21	33	0	0.8; RS; NO	GP to CO	RP
2	Crynoch Burn	NJ 859001	31	36	31	2	14	15	0	3; NO; NO	SI, GP	RP
3	Sheeoch Burn	NO 772959	35	24	8	0	58	9	0	4; NO; RO	SA to BO	RP
4	Tarland Burn 1	NJ 492038	37	23	40	2	19	15	1.0	3; RS; NO	SA to GP	RP, SM
5	Tarland Burn 2	NJ 511025	51	25	35	2	19	18	0.7	3; RS; PB	SA	SM
6	Culter Burn	NJ 825014	58	43	26	4	14	9	1.6	4; NO; RO	SI to CO	RP
7	Burn of Canny	NO 653972	71	22	34	4	21	17	0.7	5; RS; RO	SA to CO	RP
8	Water of Tanar	NO 504973	94	0	2.1	2	10	77	0	4; NO; RO	SA, BO, BE	RP, CH
9	River Feugh	NO 675922	212	3	7	1	13	75	0	10; NO; PB	SA to CO	RP
(ii) *Main stem sites*												
10	Cambus	NO 421976	1005	0	3	3	6	84	0.1	12; NO; NO	SA, BE	SM
11	Potarch	NO 607963	1348	3	6	3	9	73	0.2	15; NO; RO	SA, BE	CH, SM
12	Crathes	NO 752958	1775	5	8	3	12	67	0.3	20; RS; RO, PB	SI to BO	RP, SM
13	Maryculter	NJ 858004	2005	9	10	3	13	60	0.5	25; RS; PB, MI	SI to CO	RP, SM

[a] Land use classes: IG, Intensive grassland; BlW, Broadleaved woodland; CW, Coniferous woodland; Moor, Moorland+Montane.
[b] Physical attributes according to definitions and notation of the River Habitats Survey (Environment Agency, 2003).
[c] Channel modifications: NO, None; RS, Resectioned.
[d] Channel features: NO, None; RO, Exposed rock/boulders; PB, Unvegetated point bar; MI, Mature island.
[e] Predominant substrate: SI, Silt/mud; SA, Sand; GP, Gravel/pebble; CO, Cobble; BO, Boulder; BE, Bedrock.
[f] Predominant flow: CH, Chute; RP, Rippled; SM, Smooth.

analyser, Skalar, Breda, the Netherlands) for NO_3-N and soluble molybdate reactive P (hereby termed PO_4-P), then for total dissolved P (TDP) and dissolved organic carbon (DOC) using an automated persulphate/UV digestion procedure, all according to the manufacturer's standard methods. The detection limit for P was $1\,\mu g\,l^{-1}$ using a quartz cell with an optical path of 4 cm. Concentrations of P from iron oxide paper extracts were determined as soluble molybdate reactive P and other metal concentrations determined by ICP-OES (Agilent 7500ce, Tokyo, Japan). River water chlorophyll a concentrations were determined by UV absorbance of acetone extracts of filter papers (Whatman GF/F, 0.7 μm) according to the method of Greenberg et al. (1981). The wet filters were stored frozen from the day of sample collection until extraction.

2.4. *Invertebrate community data*

Abundance scores of benthic macroinvertebrates, attained using three minute kick samples, were taken from two data sources: (a) from the Scottish Environmental Protection Agency (SEPA) for three tributary and three main stem sites, and (b) from the Macaulay Institute (unpublished data) for three additional tributaries. Protocols and identification training were common to these two data sources. Three ecological indices were derived from the data (means of four sampling dates between spring 2004 and autumn 2005):

(i) the British Monitoring Working Party (BMWP) score, which comprises a count of invertebrate species multiplied by a factor proportional to their degree of pollution intolerance (Hawkes, 1997). This index is often used to indicate point sources of organic matter pollution,
(ii) the Average Score Per Taxa (ASPT) calculated as the BMWP score divided by the number of taxa present, and
(iii) a score of filter feeder abundance. This was derived as the sum of abundance of filter feeding invertebrates at the family level multiplied by a correction factor for the proportion of species within each family that are potentially filter feeders (Tachet et al., 2002).

Table 2 – Mean chemical and biological properties of the River Dee sample sites over the three sampling dates

Sampling site	Classifications		Dissolved chemistry			SPM chemistry						Macroinvertebrates		
	WQ[a]	WFD[b]	PO_4-P ($\mu g\,l^{-1}$)	TDP ($\mu g\,l^{-1}$)	NO_3-N ($mg\,l^{-1}$)	Chl *a* ($\mu g\,l^{-1}$)	SPM mass ($mg\,l^{-1}$)	BAP ($\mu g\,l^{-1}$)	POC ($\mu g\,l^{-1}$)	PON ($\mu g\,l^{-1}$)	BAP (mg kg^{-1})	BMWP	ASPT	Filter feeder abundance
(i) *Tributaries*														
Millhead Burn	A2	1a, D, M	10.4	16.2	2.1	1.3	3.4	0.3	560	46.2	9.4	114	6.6	205
Crynoch Burn	A2	1a, D, M	31.8	49.7	1.7	2.8	4.7	0.6	918	84.4	22.2	nd[c]	nd	nd
Sheeoch Burn	A2	1b, D, M	5.4	15.7	1.9	1.3	2.2	0.3	480	41.2	3.8	nd	nd	nd
Tarland Burn 1	A2	1a, D, M	14.2	22.7	3.6	2.7	5.6	1.0	735	71.9	5.9	115	6.4	82
Tarland Burn 2	A2	1a, D, M	10.5	19.5	3.3	2.7	5.6	0.7	743	66.9	5.5	101	6.2	103
Culter Burn	B	1a, D, P, M	14.6	28.2	3.2	5.1	4.5	1.0	1016	109	9.5	nd	nd	nd
Burn of Canny	U	1a, D, P, M	41.0	57.6	2.6	3.8	5.1	0.9	881	80.0	1.9	110	6.1	91
Water of Tanar	A1	1b, D, M	1.5	8.16	0.0	0.6	0.4	0.1	119	6.2	1.8	153	6.8	216
River Feugh	A1–A2	2b	3.7	10.2	0.4	1.5	2.6	0.2	621	44.1	2.2	146	6.8	220
(ii) *Main stem sites*														
Cambus	A1	1b, M, A	1.4	8.23	0.1	0.9	1.8	0.2	408	28.4	6.0	148	6.6	197
Potarch	A1–A2	1b, M, A	1.6	10.5	0.3	2.0	3.6	0.5	832	59.9	7.4	130	6.1	161
Crathes	A2	1b, M, A	2.3	10.3	0.4	1.5	2.6	0.5	529	40.9	10.6	168	6.6	160
Maryculter	A2	1b, M, A	2.7	12.7	0.7	1.8	3.1	0.5	659	52.3	11.9	nd	nd	nd

[a] Water quality classification (2002) based on combined chemical and ecological status (http://www.sepa.org.uk/pdf/guidance/water/annexes/annex_f.pdf). A1, sustainable fish population, natural ecosystem; A2, sustainable fish population, modified ecosystem; B, fish may be present, impacted ecosystem; U, unclassified.
[b] Water Framework Directive screening tool assessment (2005) based on chemical, ecological and hydromorphological criteria (http://www.sepa.org.uk/pdf/consultation/closed/2004/wfd_char/characterisation_consultation.pdf). 1a, at risk; 1b, probably at risk; 2a, probably not at risk; 2b, not at risk. On the basis of pressures due to: D, diffuse pollution; P, point source pollution; M, morphological alteration; A, abstraction.
[c] nd denotes not determined at these sites.

2.5. Statistical analyses

Data for regression and correlation analyses were tested for normality by interpretation of normal probability plots. Where required to achieve data normality, concentration data were $\log_{10}$ transformed and catchment land use areas transformed using the logit ($\log_{10}$ ($p/(1-p)$)) of the proportion (p) of land use. The independence of data from the river sample points was tested by plotting the residuals from the regression relationships for 12 adjacent connected pairs of upstream (x) and downstream (y) sample points. Consistent random scatter confirmed that data along connected river transects were independent.

3. Results and discussion

The data are presented and discussed below in sections describing spatial and temporal changes in water quality parameters and subsequently linked to factors of land use and ecosystems.

3.1. Spatial variation in sediment and water quality

Mean values for dissolved and particulate chemical determinants over the three sampling dates showed considerable variability in water quality across the catchment (Table 2). Concentrations of NO_3-N were generally $<3\,mg\,l^{-1}$ in tributaries, but increased with increased intensity of land use, notably in the Culter and Tarland tributaries. Nitrate concentrations in the main stem remained small (0.1–0.7 $mg\,N\,l^{-1}$) probably as a result of dilution by upland waters deficient in inorganic N (e.g. the Water of Tanar). Water quality parameters can be assessed in relation to the criteria of the SEPA classifications (http://www.sepa.org.uk/pdf/guidance/water/annexes/annex_f.pdf). Concentrations of PO_4-P were generally $<15\,\mu g\,l^{-1}$ in tributaries and $<3\,\mu g\,l^{-1}$ in the main stem; within the PO_4-P criteria for the SEPA A1 (very good) classification ($<20\,\mu g\,l^{-1}$). Concentrations of PO_4-P in the Crynoch Burn and Burn of Canny of $>30\,\mu g\,l^{-1}$ were within the A2 (Good) criteria (range 20–100 $\mu g\,l^{-1}$). River Dee sites where data were available passed the SEPA invertebrate score criteria for the A1 category (>6 for ASPT and >85 for BMWP). Ratios (in $\mu g\,l^{-1}$) of river concentrations of BAP to PO_4-P varied considerably; both temporally and spatially (0.02–0.47 May-2004, 0.01–0.80 Aug-2004, 0.01–0.11 May-2005), but were greater for low intensity land use and main stem catchments.

More recent work undertaken by SEPA as part of the implementation of the WFD identified the pressures and impacts from diffuse and point source pollution, abstraction and hydromorphological alteration (Table 2). Tributary sites where risks from diffuse and point source pollution were highlighted had the greatest concentrations of bioavailable P (BAP), particulate organic C and N (POC and PON). The point source input from a wastewater treatment plant (WWTP) to the Culter Burn may account for the observed large concentrations of SPM, POC, PON and chlorophyll *a* and the lowest water quality classification of the study catchments (B, an impacted ecosystem). Larger SPM concentrations and nutrient compositions for the impacted tributaries (Culter Burn, Burn of Canny, Tarland Burn) can be compared with sites of low-intensity land use (Water of Tanar and River Dee, Cambus), which provide regional reference values. The Water of Tanar catchment stands out as having particularly small concentrations of SPM associated C, N and P in the water column (Table 2). However, considering the other catchments, the range in concentrations of SPM, POC and PON commonly varied by a factor of two, whereas, greater variation in the range of concentrations of BAP ($\mu g\,l^{-1}$; a factor of five) and in chlorophyll *a* (a factor of four) demonstrate greater changes in the composition rather than quantity of SPM between 'non-pristine' catchments.

3.2. Characteristics of suspended particulates and bed sediments

Physicochemical data in Table 3 highlight the greater reactivity of SPM than bed sediments with the aquatic ecosystem. Greater concentrations of chemical components of SPM than bed sediments may be related to greater surface areas of the smaller SPM particles relative to bed sediments. However, greater mean enrichment of SPM relative to bed sediments in BAP (26) than for P_{ox}, Al_{ox}, Fe_{ox}, or PSR (4–10) may show different biological associations or interactions with dissolved P forms of suspended and bed sediments. The greater enrichment values between SPM BAP and bed sediment BAP occurred for the upland site 8 and main stem sites. Wide ratios resulted from limited bed sediment BAP and large SPM BAP on a $mg\,kg^{-1}$ basis although at these sites river SPM concentrations, and hence water BAP in $\mu g\,l^{-1}$ were small. The small range in SPM BAP:bed sediment BAP values in Aug-2004 resulted from larger concentrations of bed sediment BAP at this time. Increased bioavailable nutrients in bed sediments relative to SPM during baseflow may be related to the smaller range in ratio of SPM:bed sediment organic C in August (2–48), than at either May-2004 (9–95), or May-2005 (8–122).

No correlations were apparent for either suspended or bed sediments between P_{ox} and BAP. The magnitude of P_{ox} relative to BAP suggests the weak nature of the FeO strip extraction, which defines BAP. For bed sediments there was a relationship between the temporal mean PSR and catchment area of intensive grassland (PSR $= 0.054 \pm 0.006 + 0.025 \pm 0.006 \times$ logit IG; $R^2 = 0.57$, $p<0.01$). This relationship suggested that P inputs from diffuse pollution resulted in increased P saturation of the Fe and Al oxalate extractable surface complexes. This P could have been adsorbed either in the terrestrial environment via fertilizer uptake on soil particles, or in-stream via dissolved P adsorption onto sediments. A relationship between PSR and BAP for the bed sediments ($\log_{10}$ BAP $= 0.20 \pm 0.11 + 17.9 \pm 4.8 \times$ PSR; $R^2 = 0.52$, $p<0.01$) indicated that the P associated with Fe and Al surface complexes contributed to the pool of bioavailable, or was enriched by the same factors. At low saturation of surface complexes with P the reduced bioavailability of P indicates it is strongly held, whereas it becomes more readily desorbable and hence bioavailable at greater saturations. Such relationships were not apparent for SPM and hence it is less likely for SPM relative to bed sediments that the BAP test result is controlled by simple sorption processes. The greater organic content of SPM indicates biotic and chemical interactions between the

Table 3 – Physico-chemical properties of (i) suspended particulate matter, (ii) river bed sediments at sites in the River Dee[a], and (iii) the site ranges and spatio–temporal mean in enrichment ratios between SPM/bed sediment concentrations

	Date	Q %ile	BAP ($mg\,kg^{-1}$)	Oxalate extractable metals ($g\,kg^{-1}$)			PSR[b]	Particle d_{50} (μm)
				P_{ox}	Al_{ox}	Fe_{ox}		
(i) Suspended particulate matter	May-2004	6	144±65%	5.0±45%	4.6±37%	15±52%	0.33±102%	56±200%
	Aug-2004	99	258±67%	nd	2.3±58%	21±66%	nd[c]	26±26%
	May-2005	37	177±75%	3.2±130%	22±88%	50±72%	0.05±60%	32±28%
(ii) Bed sediments	May-2004	6	4.3±98%	0.8±39%	4.4±45%	6.8±46%	0.08±36%	345±53%
	Aug-2004	99	9.6±79%	0.4±67%	1.6±82%	5.9±60%	0.05±36%	419±38%
	May-2005	37	8.8±71%	0.2±62%	0.9±61%	4.0±43%	0.03±48%	339±60%
(iii) Enrichment ratio (SPM/Bed sed)	May-2004		7–342	2–19	0.1–2.4	0.9–12	1–36	0.03–0.95
	Aug-2004		8–132	nd	0.2–4.1	1.1–14	nd	0.04–0.69
	May-2005		9–372	0–461	3–131	3–62	0–15	0.03–0.23
Mean			26	10	4	5	4	0.1

Note the use of different units between BAP ($mg\,P\,kg^{-1}$) and P_{ox} ($g\,P\,kg^{-1}$).
[a] Errors are ± coefficients of variation ($n = 13$).
[b] P sorption ratio, PSR = $P_{ox}/(Al_{ox}+Fe_{ox})$.
[c] nd = not determined.

SPM P and organic matter, with especially tight cycling of P between the SPM and biota during summer.

3.3. *Organic matter controls on SPM composition and function*

SPM and bed sediment organic matter differed in inorganic and organic constituents (Tables 3 and 4). SPM had consistently greater organic C contents than bed sediments. During baseflow in August mean C:N and C:P ratios were lower for SPM than bed sediments. This could be attributed to particle size differences, but may also suggest more recent, labile SPM organic matter, compared to more refractory N- and P-depleted material deposited on the stream bed. As well as adsorption of P to inorganic surface complexes P may be incorporated into organic phases of SPM by mechanisms of P scavenging by algae and microbes and incorporation into autochthonous organic matter (Mainstone and Parr, 2002), or inputs of terrestrial or anthropogenic (e.g. WWTP-derived) allochthonous organic matter enriched in P. The variation in the composition of the SPM between the early and late summer sampling times (Tables 3 and 4) indicated the importance of in-stream biological cycling on SPM chemistry. During baseflow conditions in August the mean BAP content ($mg\,P\,kg^{-1}$; Table 3) of SPM at all sites was greater than during the two May sample times. Jarvie et al. (2002) also observed seasonality in the P contents of biofilms from the River Kennet, UK with greatest inorganic P concentrations occurred in August simultaneous with increased river PO_4-P concentrations and low flow conditions. However, these authors attributed the increased biofilm P to point sources, whereas P sources in the current study catchments are dominantly diffuse in nature.

Smaller C:N and C:P ratios of SPM in late summer suggested accumulation of N and P in recent biomass. However, the percentage of organic C attributed to chlorophyll-bearing phytoplankton (%phyto POC; calculated assuming a C: Chlorophyll pigment ratio of 35:1 (Sobczak et al., 2002)) was smaller in August (13%) than at either of the May sampling times (27–35%). Therefore, it is suggested that changes in the biological components associated with SPM through the period of biological activity alter the nature of the SPM organic matter. Investigation of the composition of SPM in the present study by Infra-red spectroscopy revealed that organic components were consistent at all the main stem and tributary sites between the two May samplings, despite the different flow conditions (examples of each are given in Fig. 2). The particular three-peaked shape of the region 1460–1360 cm^{-1}, corresponding to CH and CO deformations resembled terrestrial, humified organic matter. In comparison, the August organic matter at all sites showed strong contributions from lignin (peak at 1516 cm^{-1}) and amide groups (peak and shoulder at 1543 and 1657 cm^{-1}, respectively). These spectroscopic indications of proteinaceous and

Table 4 – Temporal variability in mean nutrient compositions of (a) suspended particulate matter (SPM), (b) bed sediments and (c) dissolved constituents of river waters[a]

Date	Q %ile	% org C	POC ($mg\,l^{-1}$)	Org C:org N	Org C:bioavailable P	Phyto C[b] (% of POC)	Phyto P[c] ($\mu g\,l^{-1}$)	BAP ($\mu g\,l^{-1}$)
(a) *SPM*								
May-2004	6	19±19%	0.9±56%	13±16%	1954±52%	27±65%	1.78±55%	0.61±79%
Aug-2004	99	21±26%	0.5±56%	11±37%	1225±66%	13±97%	0.64±93%	0.63±65%
May-2005	37	22±30%	0.5±70%	15±50%	1765±59%	35±90%	1.08±85%	0.32±77%

Date	Q %ile	% org C	orgC:orgN	orgC:bioavailable P
(b) *Bed sediments*				
May-2004	6	0.8±68%	12±19%	2958±75%
Aug-2004	99	2.4±101%	19±70%	2737±60%
May-2005	37	0.8±101%	18±36%	1286±75%

Date	Q %ile	DOC ($mg\,l^{-1}$)	DOC:DON	DOC:DOP
(c) *Dissolved forms*				
May-2004	6	6.2±38%	36±36%	534±82%
Aug-2004	99	2.9±44%	28±47%	303±45%
May-2005	37	3.7±46%	38±58%	2080±108%

[a] Errors are ± coefficients of variation ($n = 13$).
[b] Phytoplankton C assumes a C: chlorophyll pigment ratio of 35:1 (Sobczak et al., 2002).
[c] Phytoplankton P calculated from phyto C assuming the Redfield C:P ratio of 106:1.

polysaccharide groups have been previously related to biofilm development in sediments (Galle et al., 2004). Hence, a changing composition of organic matter from photosynthetic algae earlier in the biologically active period to biofilm-type material later in the summer affects the chemical composition of SPM and its interaction with the aquatic ecosystem.

Evidence of the dependence of photosynthetic algal biomass on P uptake was observed in the significant relationships between riverine concentrations of chlorophyll *a* and the dissolved and SPM bioavailable pools of P (Fig. 3). Concentrations of chlorophyll *a* were more strongly related to the SPM bioavailable P than to either total dissolved P (or to PO_4-P; data not shown) during the two early summer periods. A possible mechanism is that algal cells mobilized in the water column become seeded around particulates, relying on a close association with the surface to access nutrients. During these early summer times the greater algal biomass P (calculated from the chlorophyll contents; Table 3) than BAP contents may reflect the ability of algae to actively extract P more efficiently than the FeO paper strip test. However, in late summer this relationship between chlorophyll *a* and SPM bioavailable P showed considerable scatter and, for the majority of sites, the calculated biomass P became smaller than the BAP content, suggesting that ageing algal communities loose the ability to actively compete for P with surfaces. Better relationships during late summer between chlorophyll *a* contents and dissolved P forms suggest a decoupling of the active biological community from the SPM P content and also an increasing ability to access dissolved P where baseflow conditions increase water residence times. Neal et al. (2006) observed that chlorophyll *a* concentrations (1.7–$94\,\mu g\,l^{-1}$) were positively related to soluble reactive P (3–$2077\,\mu g\,l^{-1}$), SPM, POC and PON concentrations in eutrophied rivers in England. However, these authors found that the strongest positive factors in chlorophyll *a* development were catchment area and flow, which they related to water residence time. However, they noticed a lack of chlorophyll *a* response to reductions in soluble reactive P due to WWTP P-stripping. Hence, in nutrient enriched rivers residence time for algal growth was more important than changes in nutrient concentrations. In contrast, in the oligotrophic waters of the River Dee the present study shows that phytoplankton production is dependant on variation in a small weakly held pool of bioavailable P associated with the SPM. Future investigations should include the influence of the BAP of both bed and suspended sediments on benthic algal communities, which likely dominate algal biomass in most river systems, to compare the response with phytoplankton. Catchment area was not a factor in chlorophyll *a* concentrations in either simple or multiple linear regressions.

3.4. *The influence of land use and catchment size on sediment and water quality*

The influence of catchment factors was assessed by correlating land use and catchment area with water quality parameters (Table 5). No significant correlations were apparent between log-transformed catchment area and water quality parameters, nor between bed sediment BAP and land use parameters. Land use proportions of arable, intensive

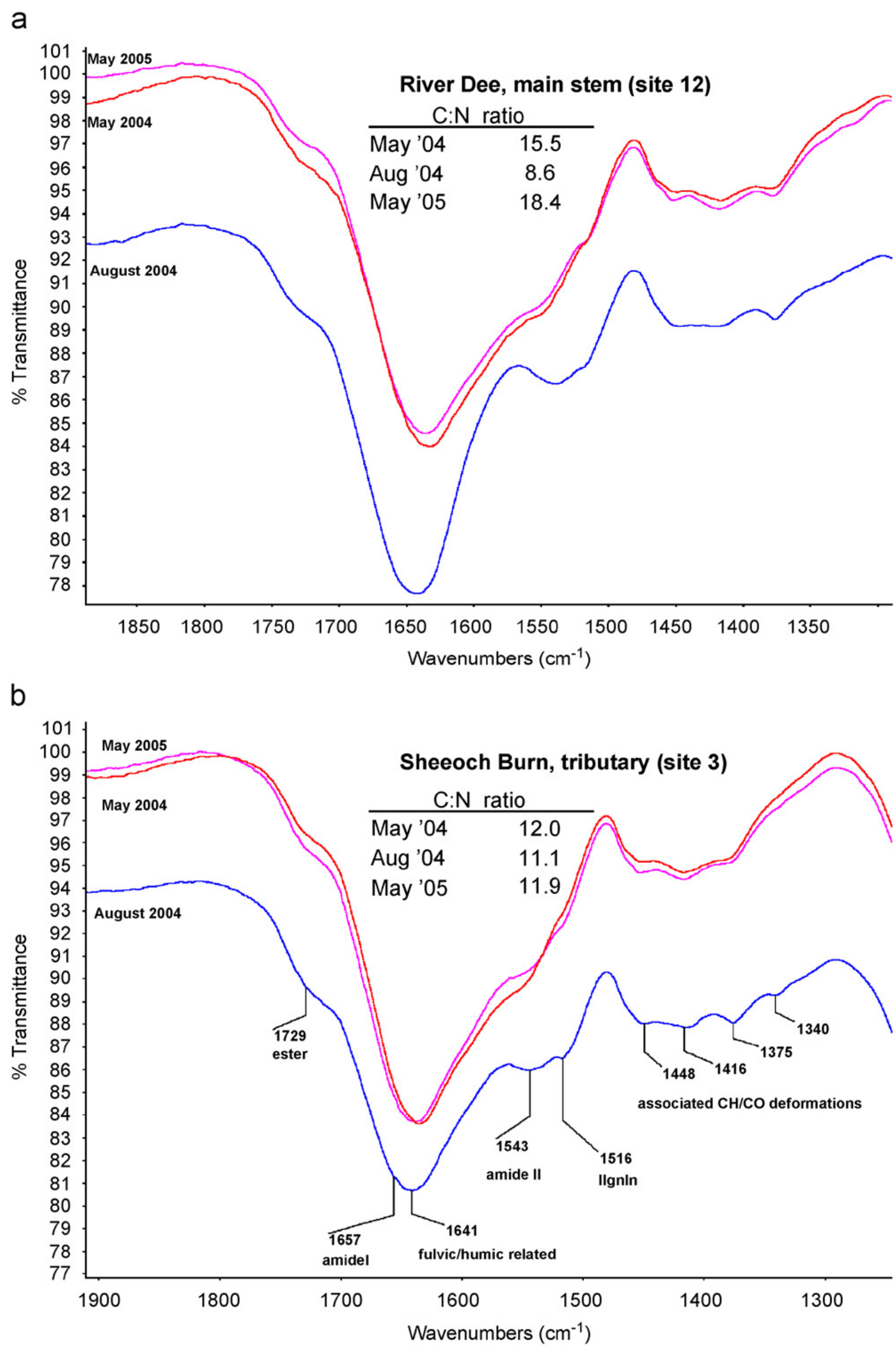

Fig. 2 – Infra-red spectra of the principal organic matter region showing seasonal differences in organic matter composition between spring and late summer, for (a) the main stem and (b) a tributary site.

grassland gave positive and negative correlations with chemical and ecological parameters, respectively. Agriculture is associated with non-point source inputs of nutrients and enhanced soil erosion; hence the strong correlations for intensive grassland and arable land use with PO_4-P, NO_3-N and SPM concentrations. Streams in agricultural areas also tend to have impaired habitats due to loss of riparian woodland, stream straightening, increased bank erosion and accumulated fine sediments in pools (Allan, 2004).

The logit transformed proportion of catchment intensive grassland was the best predictor for most ecological and chemical properties, especially for temporal mean river SPM concentration ($[SPM] = 5.8 \pm 0.3 + 2.9 \pm 0.3 \times \text{logit IG}$; $R^2 = 0.85$, $p < 0.001$) and BAP $\mu g\,l^{-1}$ concentrations ($[BAP] = 0.94 \pm 0.10 + 0.51 \pm 0.10 \times \text{logit IG}$; $R^2 = 0.66$, $p < 0.001$). These relationships were also significant ($p < 0.01$) during the individual sampling dates. The fit of the raw data (Fig. 4) indicated that small increases in intensive grassland (2–10%) brought large in-

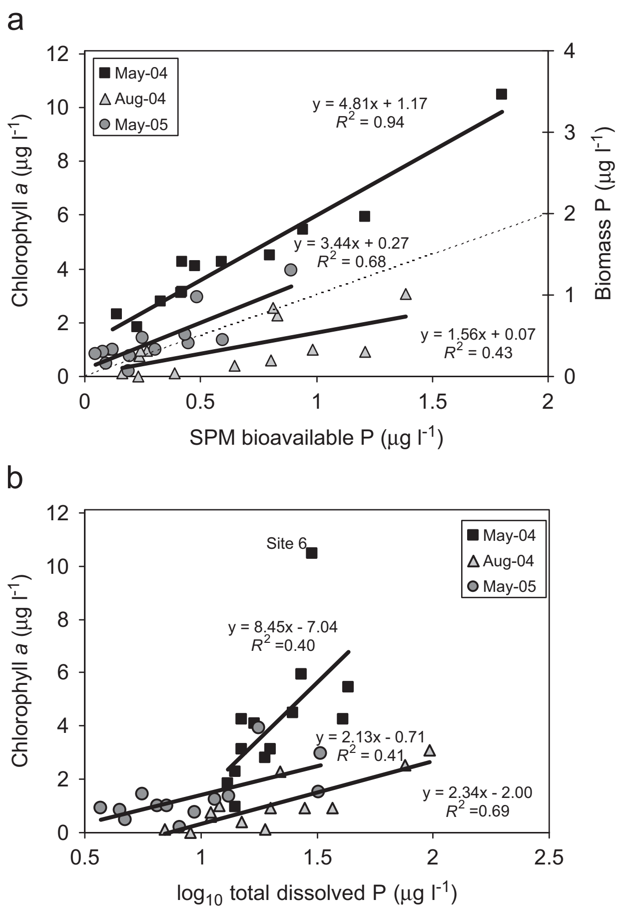

Fig. 3 – Relationships for the different sampling dates between river chlorophyll *a* concentrations and: (a) suspended particulate matter bioavailable P and (b) total dissolved P (note the log scale used). In (a) the phytoplankton biomass P (calculated from Chlorophyll *a* concentrations—see Table 4) is given for comparison with the SPM bioavailable P and the dashed line indicates the 1:1 relationship.

creases in soil erosion leading to SPM (0.5–3 $mg\,l^{-1}$). Extrapolating such relationships between nutrient enrichment factors and anthropogenic land use classifications back to the intercept may provide useful indications of expected regional reference conditions in the absence of human activities (Dodds and Oakes, 2004).

The catchment's area of improved grassland may be particularly influential on stream quality due to the location of grassland in riparian areas. River corridor soils prone to occasional flooding are often used for grassland rather than arable purposes; hence a strong spatial connexion with watercourses. Grasslands constitute up to 70% of UK agricultural land and are associated with high P enrichment and artificial drainage (Hooda et al., 1999; Preedy et al., 2001). Grassland is often associated with losses of P in dissolved forms. However, Turner and Haygarth (2000) observed that particulate P constituted 21–46% of the P export from four grassland lysimeters in England, with greater losses

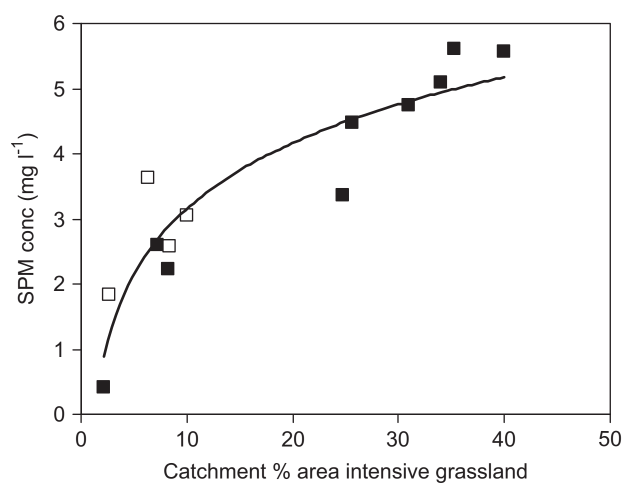

Fig. 4 – Untransformed data for the relationship between SPM concentration and intensive grassland land use. Solid and open symbols show data for the tributary and main stem catchments respectively.

Table 5 – Significant ($p < 0.05$) correlations (r) between chemical, ecological properties and catchment land use.

	Land use (proportions of cathment area)				
	Logit Arable	Logit intensive grassland	Broadleaved woodland	Logit coniferous woodland	Logit Moorland+Montane
log_{10} PO_4-P ($\mu g\,l^{-1}$)	0.86	0.71			−0.84
log_{10} TDP ($\mu g\,l^{-1}$)	0.82	0.83			−0.80
log_{10} NO_3-N ($\mu g\,l^{-1}$)	0.96	0.93		0.62	−0.90
SPM ($mg\,l^{-1}$)	0.77	0.93			−0.68
Chl *a* ($\mu g\,l^{-1}$)	0.72	0.72	0.56		−0.69
SPM BAP ($\mu g\,l^{-1}$)	0.72	0.83			−0.68
POC ($mg\,l^{-1}$)	0.71	0.75			−0.58
PON ($mg\,l^{-1}$)	0.81	0.81			−0.72
BMWP	−0.81	−0.82		−0.70	0.84
Filter feeder abundance	−0.73	−0.78			0.82

associated with sandy soils (soils in the NE of Scotland are predominantly sandy textured). These authors concluded that preferential flow pathways, which are maximized in permanent grassland that is not physically disturbed by ploughing, were conduits for transport of P enriched particles (<0.45 μm) through such soils. In addition, cattle access to streams for watering is a common practise in the region of the present study and this causes bank erosion, poaching of near-channel soils and contributes to sediment mobilization.

The degree of scatter in the relationships was slightly decreased and the correlations increased with the exclusion of the main stem sites (data not shown). Hence, as the catchment size increased the overall catchment land use became less influential than that in the vicinity of the sampling point. The inclusion of catchment size in multiple regressions did not improve the majority of relationships in Table 5. The exception was in the prediction of filter feeder abundance (Filter feeders $= 260 \pm 15.8 + 120 \pm 10.2 \times$ logit Moor $-46.8 \pm 7.06 \times \log_{10}$ catchment area; $R^2 = 0.95$, $p < 0.001$) where moorland and catchment area were both significant terms ($p < 0.001$). This may be partly due to large proportions of moorland being found for the larger catchments as well as to complex hydromorphological differences between smaller managed and larger natural watercourses.

3.5. *Relationships between SPM and macro-invertebrates*

In the River Dee, although stream water POC concentrations were smaller than dissolved organic C (DOC) concentrations (Table 4), the POC would have greater metabolic availability related to smaller C:N and C:P ratios than dissolved organic matter. As the SPM comprised 19%–22% POC (and hence approximately 40% organic matter content) any changes in composition would greatly affect the quality of SPM as a food source for higher trophic levels. Storms occurring during winter to spring bring terrestrial particles into the rivers from erosion and early in the year SPM organic matter comprises humified soil organic matter of limited metabolic accessibility. Increasing temperature and light in spring initiates accelerated biological activity and an active growth period of phytoplankton mass. These algae can accumulate P where it is available in the water column (Jarvie et al., 2002) and increasing autotrophic organic matter and decomposition detritus makes the SPM a more favourable energy source for consumer species. Later in summer, further microbial cycling of algal and detrital organic matter as biofilms develop enriches the SPM in protein, providing an important food source to higher trophic levels such as macro-invertebrates (Carlough, 1994). However, any excess enrichment in pollutants adsorbed onto, or incorporated into SPM may be readily transferred through the food chain.

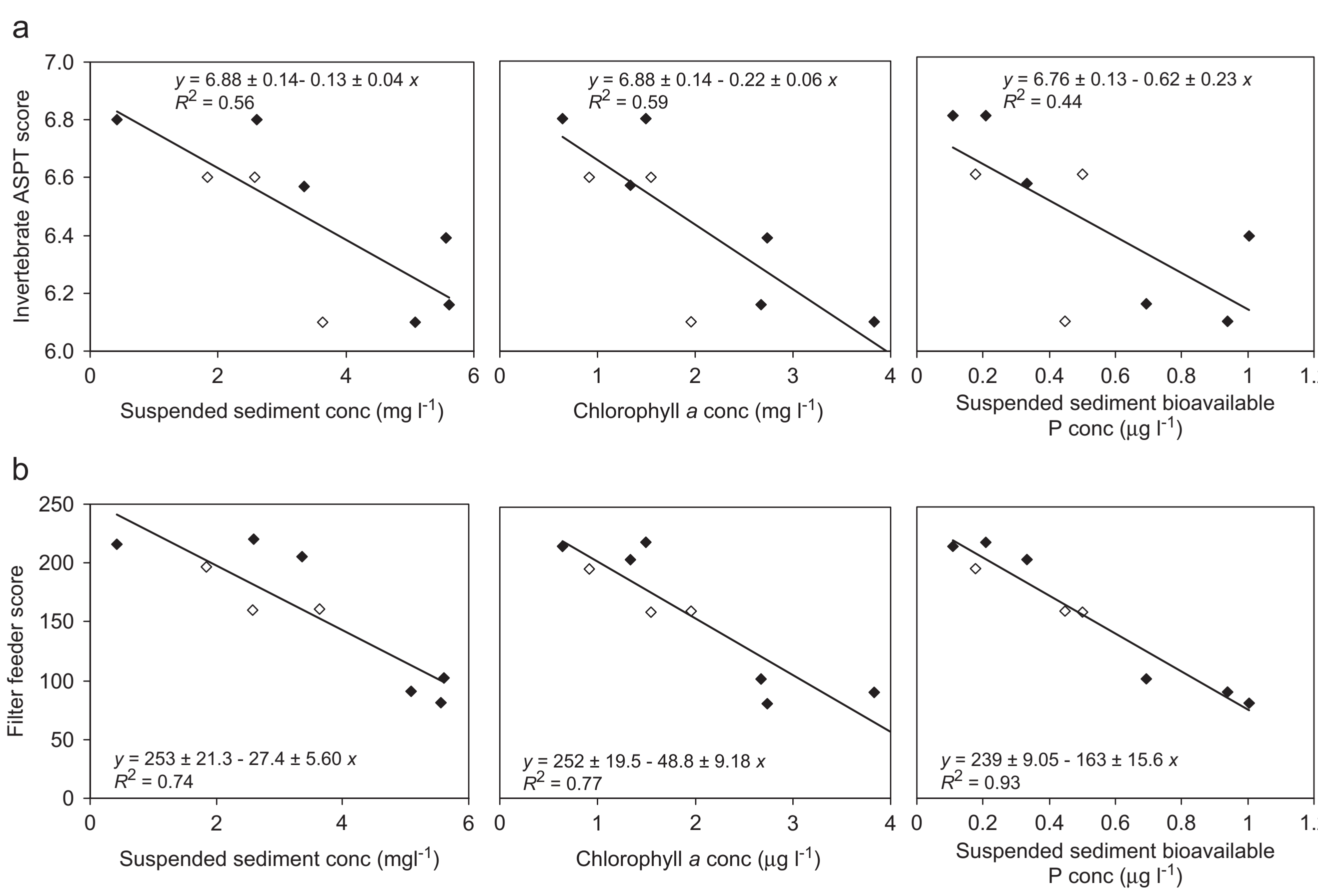

Fig. 5 – Relationships between macro-invertebrate indices and physicochemical properties. Solid and open symbols show data for the tributary and main stem catchments respectively. Linear regression lines are depicted for all sites data with values ±1 standard error.

Properties of SPM could be closely linked to stream invertebrates through two macro-invertebrate indices, namely; ASPT scores and the abundance of filter feeding macro-invertebrates (Fig. 5). Only NO_3-N and SPM concentrations were significant correlated with the BMWP scores (R^2 values of 0.61 and 0.64, respectively, both $p<0.01$). Relationships with ASPT scores were much stronger and followed the order: water column SPM bioavailable P concentration < SPM concentration < chlorophyll *a* concentration (Fig. 5a). The slightly greater scatter to the main stem sites indicated that catchment scale and hydromorphological differences influenced these relationships, although catchment size was not a significant covariate in multiple regressions. These SPM quality parameters gave even better predictions of filter feeder total abundance (Fig. 5b) and the relationships unified the main stem and tributary site observations. The SPM bioavailable P concentration became the strongest indicator of filter feeding macro-invertebrates ($R^2=0.93$, $p<0.001$). Concentrations of PO_4-P, TDP and NO_3-N were not significant predictors of ASPT score and were poorer predictors of filter feeder abundance (R^2 values of 0.41, 0.55 and 0.47, respectively) than SPM parameters. The strong relationship between filter feeders and bioavailable P confirms that it is sediment quality, in terms of reactive nutrient load, not quantity that of importance to biota. A direct relationship between bioavailable P and filter feeding invertebrates suggests these species are particularly vulnerable due to their feeding habit of actively ingesting the SPM material, the physicochemistry of which seems dependant on catchment pollution pressures. However, the increased nutrient status of the SPM and the observed relationships between SPM bioavailable P and algal biomass may also be expected to provide a greater quality food source. Hence, the mechanisms explaining such a significant relationship may be complex. An increased autotrophic biomass production may affect invertebrate species compositions through dissolved oxygen stress and the presence of sediment fines may impact on interstitial habitats for crevice-dwelling invertebrates.

4. Conclusions

Within the environmental gradient of upland to moderately intensive agricultural catchments SPM appears to provide a crucial link between catchment pressures related to phosphorus enrichment, internal riverine processes of organic matter cycling and the ecology of at least the primary and secondary trophic levels. The nutrient and organic matter compositions of the SPM are a sensitive indicator of aquatic habitat quality. A sequence of mechanisms for this seems to involve the close association of phytoplankton with bioavailable P and SPM during the active growth period, further uptake of dissolved nutrient pools into algae through the summer, microbial biofilm development and the incorporation of recent, labile organic matter, but with accumulated reactive P, into higher trophic levels. Bed sediment interactions with water column P appear to involve dominantly physico-chemical controls such as sorption, although the interactions of sediments and benthic algal communities should be investigated. The properties of SPM require further study as to how they may be exploited to aid a better mechanistic understanding of the classification of impacted river reaches against regional reference conditions in the Water Framework Directive methodology. Empirical relationships with catchment land use pressures may provide a means of assessing regional baseline conditions. Where other factors are comparable extrapolation towards the axis of zero intensive land use may: (i) provide an insight into the natural conditions for a system in the absence of agricultural catchment pressures, or (ii) give target conditions for improvements backcasting along the relationship towards conditions of decreased disturbance.

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