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## Multi-element signatures of stream sediments and sources under moderate to low flow conditions

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### ABSTRACT

This study assesses a simple sediment source tracing method using major- (Al, Ca, Fe, K, Mg, Mn, Na, P, Si, Ti) and trace-element (Ba, Be, Ce, Co, Cr, Mo, Nd, Pb, Sr, Th, V, Y, Zn) signatures of stream suspended particulate matter (SPM), bed sediments and soils in a small agricultural catchment in NE Scotland. Whilst most erosion studies characterise the large amounts of material mobilised at the highest flows, this study aimed to assess properties of sediments during moderate to low flow periods. These occur more frequent than intense storms and are important in linking stream sediments, near-channel sources and aquatic ecosystem impacts. Data were transformed by multivariate statistical methods to compare elemental signatures of SPM (ranging from 3 to 53 mg L<sup>-1</sup> in the stream) and stream bed sediments with a limited number of near-channel source soils. Increased concentrations of Ce, Nd, Th and Y in subsoils contributed to the ability to discriminate between surface fieldslope and stream bank erosion sources. Stream bed sediments showed close matches with compositions of stream bank and arable surface soils, but signatures of SPM differed greatly from any of the sources. Large concentrations of Cr, Pb and Zn in SPM, particularly during summer (677, 177 and 661 mg kg<sup>-1</sup>, respectively) exceeded water quality standards and were linked to an accumulation of trace elements associated with biological material. The potential for within-stream alteration of SPM in relation to erosion sources was confirmed by changes in the nature of the SPM organic matter observed by IR spectroscopy. Thus the potential is shown for multi-element signatures to give information on catchment sediment sources to aid land management decisions, given careful consideration of the effects of in-stream alteration of eroded material. However, this combined information may be beneficial to process understanding linking land use and stream ecosystems at critical ecological periods.

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### 1. Introduction

Soil erosion is a substantive environmental problem for soil loss, contaminant transport and for its ecological impacts on receiving waters (UNESCO, 1983; Quinton and Catt, 2007; Stutter et al., 2007). In intensively managed catchments this erosion process provides a pathway for the transport of metals, organic contaminants and faecal-associated microorganisms which partition with solid phases rather than into solution (Allan, 1986; House et al., 1998; Warren et al., 2003). Maximum concentrations and large proportions of annual sediment loads are associated with infrequent, large runoff events in catchments. However, there is an increasing understanding that more frequent, lower intensity events can transport material that may contribute disproportionately to some reactive, or contaminant components of the sediment budget (Quinton et al., 2001; Quinton and Catt, 2007). The progressive transport of material towards stream channels over successive smaller erosion events can result in particle fraction-

ation as fines are preferentially transported and transient storage of material in riparian areas, or the channel itself (Russell et al., 2001).

The source is a fundamental parameter controlling chemical and physical properties of the sediment, contaminant transport potential, and the extent and timescales of material transport to water courses. Therefore, the management of soil erosion and particulate-bound contaminants in agricultural ecosystems requires an understanding of the nature and location of potential source materials. Sediment fingerprinting is a method currently under development to determine the sources of eroded material to watercourses (Walling, 2005) and has supplemented conventional ground surveying assessment of soil loss (e.g. Haigh, 1977). Walling et al. (1993) showed that no single parameter could reliably discriminate sources due to complex physico-chemical sorting of material during erosion. Since then, modern applications of sediment fingerprinting have used composite signatures involving a wide range of determinants. Often large and complex combinations of parameters are employed, for example physical (particle size, surface area), mineral–magnetic, chemical (acid, oxalate and dithionite extractable metals) and radiometric (Pb and Cs isotopes)

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properties, which may be extremely costly and time constraining analytically (Collins et al., 1997; Collins and Walling, 2002; Walling, 2005). These then often require correction factors for the effects of differing organic matter and surface area on determinant concentrations between sources and sediments (Collins et al., 1997; Russell et al., 2001). Multivariate statistical methods and mixing models are applied to these properties to determine their potential to discriminate different source materials and their proportional contributions to stream sediment loads (Yu and Oldfield, 1989; Walling et al., 1999).

The fingerprinting process can also yield important spatial information on the nature of the source material and alterations in the stream (Yu and Oldfield, 1989; Russell et al., 2001). This includes comparisons between source and watercourse bed sediments and suspended particulate material, the selectivity of chemical properties in the erosion process, erosion under different land uses (Walling et al., 1999) and temporal changes in sedimentation (Owens et al., 1999). One particular focus for sediment research is the delivery of P from agricultural land to watercourses where this, often limiting, nutrient is an important control on ecosystem trophic status (Edwards and Withers, 2007). Particulate bound P is often much more prevalent in surface waters than dissolved P forms (Stutter et al., 2008a), but this has complex relations with: (i) erosion controls such as precipitation and stream flow giving spatio-temporal variability in particulate P transport, (ii) the P status of different source materials under different soil management, and (iii) biogeochemical cycling during erosion and in the stream itself (Stutter et al., 2007, 2008a,b). Variation in the timing and form of the sediment and associated P delivery, or in residence time in the watercourse will affect the potential for eutrophication of surface waters. Data from the fingerprinting process can thus provide valuable assessment of the links between the chemical status of the source materials, the potential impacts on the aquatic ecosystem and the means of ameliorating them.

This study aims to assess the application of a wide suite of major and trace elements, rare earth metals, nutrients and particle size data in the characterisation of stream suspended particulate matter (SPM) and bed sediments and their potential source soils in a small agricultural catchment in NE Scotland. A simple sediment tracing method is presented using total element concentrations after dissolution of sample solids. Hence, the total elemental signatures encompass the fractionation of minerals during the erosion process and any subsequent cycles of deposition and redistribution on land and in the stream. It is thought that metal compositions following total sample digestion will provide a more conservative tracing approach than using reagents which bring about selective dissolution of surface-bound elements (e.g. acid leaching). A secondary aim was to explore the linkage between the catchment near-channel soils and stream network during spring to autumn periods of moderate to low flows, a period critical to stream ecology. Most erosion studies focus on characterising the large amounts of material mobilised at the highest flows (Walling et al., 1999; Russell et al., 2001; Stutter et al., 2008b). However, this work aimed at assessing properties of sediments during more frequent, less intensive hydrologic events that are important in linking stream sediments, near-channel sources and aquatic ecosystem impacts (Quinton et al., 2001).

## 2. Methods

### 2.1. Study site and sample collection

Eleven soil, three stream bed sediment and eight stream SPM samples were collected during May 2004–May 2005 from the Tarland Burn, an agricultural tributary of the River Dee, NE Scotland.

The River Dee is considered to be relatively unpolluted (Langan et al., 1997), although agricultural diffuse pollution is of concern in tributaries and in the main river stem. Agriculture in the Tarland catchment comprises a mosaic of arable and grassland land use, including beef cattle, sheep, barley and potato (Table 1; data MLURI, 1993).

Stream suspended particulate matter (SPM) was sampled, prior to any disturbance of the stream bed, by collecting water samples from mid-depth and mid-channel to ensure that the recovered sediment best represented suspended material. Samples were collected in 30 L polyethylene bottles previously rinsed with dilute  $\text{HNO}_3$ , then rinsed on-site with stream water. Samples were taken during moderate to low flow conditions on 6/5/2004, 3/8/2004, 4/10/2004 and 11/5/2005 (shown on the hydrograph; Fig. 1) at two locations; in the Millhead Burn headwater and 5 km downstream in the Tarland Burn (Table 1). Single bulked samples of stream bed sediments were collected from Millhead Burn at each sampling date across a 1 m<sup>2</sup> area of stream bed (over the entire channel width of ~1 m) using a lidded plastic scoop (a method used previously by Stutter and Lumsdon, 2008). Bed sediments were sampled to a depth of 0–3 cm since observations showed this depth of material was readily entrained and deposited by varying flow. The material, together with any water recovered in the scoop, was bagged and transported in a darkened cool box. It was assumed that integrating the sample over this area of stream bed would encompass local variation in sediment and provide a representative sample.

Collection of 11 soil source materials in the headwater catchment took place on 20/9/2004. Stream bank subsoils were collected at depths of 40–50 cm from the soil surface as dictated by the stream channel morphology. This depth was just above the water level at baseflow (B horizon of a poorly developed cultivated podzol). Subsoils were collected from both banks in five locations along a 400 m transect above the sediment collection site at Millhead. Bank soils were scraped back to allow sampling of freshly exposed material. All soils were sampled with an acid washed plastic trowel. Surface soil samples were collected (0–3 cm depth; Ap horizons) from fields on opposite stream sides with similar slopes (3–5°) and parent materials. Soil sample points were three locations on each side of the stream over a transect of 100 m parallel to the stream (starting 400 m upstream of the sediment sample point) and 10 m away from the stream since it is known that near-channel soils are spatially important sources of material entering streams over subsequent erosion events (Russell et al., 2001). These soils characterised the two main land covers adjacent to the stream, namely permanent pasture (west aspect) and arable barley rotation (east aspect). The barley crop had been harvested several weeks prior to soil collection. Hence, soils were not sampled under other types of land cover in the catchment (rough grassland, woodland; Table 1) since they were located at greater distances from the stream and not typically of concern as dominant erosion sources where agricultural land dominates.

Further details of the catchment hydrochemistry during the period of sampling (May 2004–May 2005) are given in Stutter et al. (2008a,b). In summary: (i) discharges at Millhead Burn and Tarland Burn during the period were 0.03–0.66 and 0.19–4.57 m<sup>3</sup> s<sup>-1</sup>, respectively, (ii) annual SPM fluxes from Millhead and Tarland catchments were 71 and 116 kg ha<sup>-1</sup> a<sup>-1</sup>, respectively, (iii) annual particulate P fluxes were 0.12 and 0.21 kg P ha<sup>-1</sup> a<sup>-1</sup>, (iv) with contributions of particulate P to total P fluxes of 56% and 57% (using daily plus 4-hourly storm flow-triggered sampling). Field drains were discounted as sediment sources in this study as they were previously shown to contribute 3% to stream loads of SPM (Stutter et al., 2008a). The soils on the slopes around the headwaters are derived from mixed acid and basic tills (Tarves

**Table 1**

Land use and catchment characteristics for the Millhead Burn headwater and downstream Tarland Burn catchment.

	Millhead Burn	Tarland Burn
Catchment area (km <sup>2</sup> )	4.33	51.4
Gauging/sampling point	NJ 474 060	NJ 511 025
Altitude range (m a.s.l.)	190–619	133–619
Channel form	Ditched, 0.8 m width	Canalized, straight, 2 m width
<i>Land use (%)</i>		
Arable	21	25
Improved grassland	25	35
Rough grass/moor/montane	33	18
Woodland	21	21
Urban	0	0.7

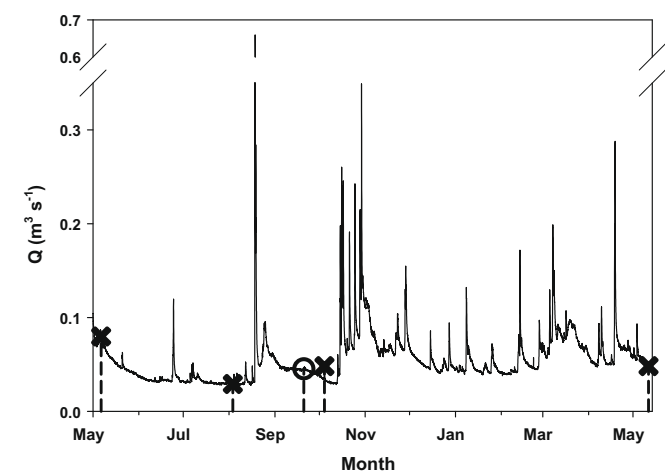
Association; MISR, 1957) with a medium loam to medium clay loam texture. Downstream the Tarland Burn crosses an extensively drained former floodplain with soils comprising coarser, sand dominated fluvio-glacial materials (Boyndie and Corby Associations and alluvium; MISR, 1957).

### 2.2. Soil and sediment preparation and size fractionation

Soils and bed sediments were air-dried (30 °C) then dry-sieved by hand to <250 µm to provide a more direct comparison between source materials and the SPM. Previous tracing studies have utilized <63 µm fractions of source materials by dry-sieving of air-dried materials (Walling et al., 1999, 2008; Russell et al., 2001). However, in this region of generally coarse glacial parent materials it was observed that the 63–250 µm fraction was an important component (up to 20% of total particle numbers; Fig. 2) of the SPM.

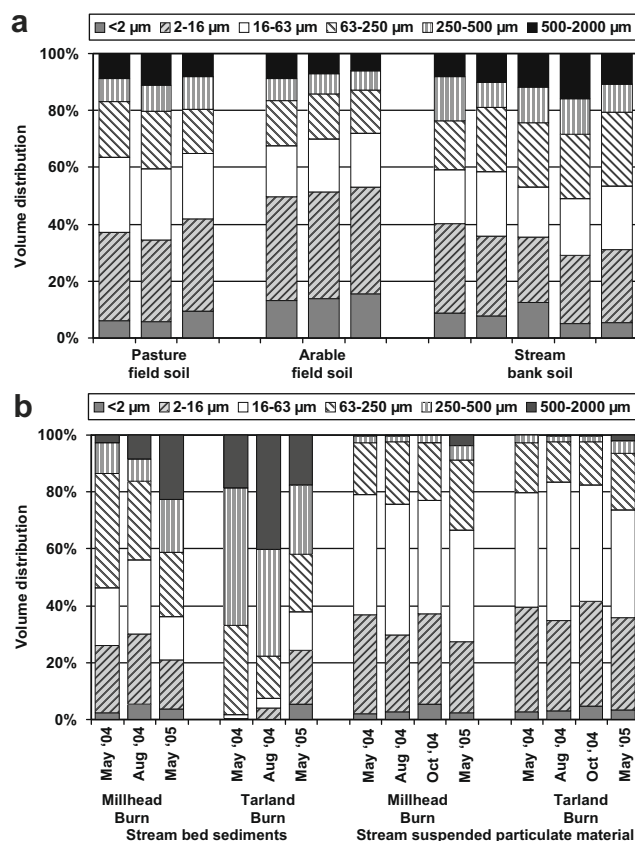
### 2.3. Physical and chemical analyses

Within 48 h of collection SPM was recovered from the bulk water samples using a continuous centrifuge (Alfa Laval, Doerr, Wisconsin, USA). Prior to this and up until SPM was air-dried it remained at 4 °C in the dark to limit biological growth during storage. Suspensions (~300 mL) of concentrated particulates were analysed for particle size by laser diffractometry without chemical dispersant and using stirred dispersion only (Mastersizer 2000 with HydroG dispersion unit, Malvern, UK). Particle sizes of soils and bed sediments (<2 mm air-dried fractions) were determined following dispersion (16 h end over end shaking in 1.6 mol L<sup>-1</sup> NH<sub>3</sub> solution).



**Fig. 1.** Flow conditions in the Millhead Burn headwater in relation to times of sampling of sediments (X) and catchment soils (O).

Chemical analyses were carried out on air-dried materials with values reported as oven-dried mass (105 °C for 2 h). Samples were hand milled with an agate pestle and mortar, ignited (1000 °C for 1 h) and analysed for total metals using a Li metaborate fusion flux digest method (original method Verbeek et al., 1960; validated for modern instrumental analysis by Liberatore, 1994). The bead was completely redissolved in 4 M HNO<sub>3</sub> at 60 °C prior to metal analyses. The digest was performed in two different ways: (i) by necessity of small sample recoveries a micro-scale digest used 2–15 mg ignited SPM mass in micro Pt crucibles, (ii) more conventionally for soil and bed sediments a macro-scale digest used 2 g of ignited sample in larger Pt crucibles. A geological certified reference material with a wide availability of certified element values (a basalt; BCR1; Institute for Reference Materials and Measurements, Geel, Belgium) underwent both micro- and macro-scale procedures with each batch of samples. A wide suite of metals for which certified values of the reference material were available were screened for



**Fig. 2.** Particle size analyses of soils, bed sediments and suspended particulate matter.

analytical quality control (Table 2). An additional laboratory standard comprising an air-dried, ball-milled agricultural soil from NE Scotland was used to test analytical precision on a sample of comparable matrix to that of the soils in this study. Both the BCR1 and the in-house topsoil were included with each batch of samples (giving five replicates of each of each standard for each of the micro- and macro-scale digests). Elements were then chosen for use in the fingerprinting method on the basis of the analytical precision of these standard reference material results by a %CV <15% for the BCR1 standard ( $n = 5$ ). Quality control results are shown for the BCR1 reference material in Table 2 and these were used to select the elements for which sample data are given in Table 3. For elements selected for inclusion as tracers the analytical precision of the topsoil standard is included in Table 2. Total elemental concentrations were determined by inductively coupled plasma spectroscopy using matrix-matched standards and blanks; either by mass spectroscopy (ICP-MS; Agilent 7500i, Tokyo, Japan), or by the optical emission method (ICP-OES; Agilent 7500ce, Tokyo, Japan) where concentration ranges of ICP-MS were exceeded (Al, Ca, Fe, K, Mg, Mn, Na, P, Si, Ti). To determine total elemental concentrations in these complex matrices the strongest emission band (for ICP-OES) and most abundant mass fragment (for ICP-MS) which were clear of major interference were used for each element on the basis of expert judgement.

Additional properties determined to characterise materials were: organic C and N by total elemental analysis using 2 mg

milled samples following pre-treatment with concentrated HCl to dissolve carbonates (Thermo-Finnigan, Flash EA 1112 CN analyser, Naples, Italy), oxalate extractable Fe, Al and P (termed  $Fe_{ox}$ ,  $Al_{ox}$ ,  $P_{ox}$ ; extractions according to Farmer et al., 1983) and P extracted using the Fe oxide paper strip test (Chardon et al., 1996), termed bioavailable P. The P sorption ratio, PSR, was calculated as  $PSR = (P_{ox}/(Fe_{ox} + Al_{ox}))$ . The in-house topsoil reference material was used in triplicate with these analyses. The results indicated analytical precisions of 5% and 10% for organic C and N, respectively, 8%, 8% and 13% for  $Fe_{ox}$ ,  $Al_{ox}$ ,  $P_{ox}$ , respectively, and 7% for bioavailable P.

Changes in the nature of the SPM organic matter were investigated as indicators of the degree of within-stream processing of SPM (Stutter et al., 2007). River water chlorophyll *a* concentrations were determined by UV absorbance of acetone extracts of filter paper SPM (Whatman GF/F, 0.7 mm) according to the method of Greenberg et al. (1981). The wet filters were stored frozen from the day of sample collection until extraction. The contribution of organic C in SPM attributed to chlorophyll-bearing phytoplankton (%phyto POC) was calculated assuming a C:Chlorophyll pigment ratio of 35:1 (Stutter et al., 2007). Hand ground, oven-dried (105 °C) samples were also analysed by Fourier Transform Infrared 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.

**Table 2**

Analytical quality control data for major and trace elements. BCR1 geological certified reference material values (together with standard deviations where given) with recoveries and analytical precision (as % coefficients of variation; %CV) from five replicates of the BCR1 reference material in each of micro-digest and macro-digest sample runs. Additional %CV values (in brackets) show the precision of five replicates of an agricultural topsoil for elements selected for use as tracers. All concentrations in  $mg\ kg^{-1}$  ignited sample mass.

Element	BCR1 certified value ( $\pm 1s$ )	Micro digest			Macro digest		
		Mean	%CV <sup>a</sup>	Recovery (%)	Mean	%CV	Recovery (%)
Al	71,415	65,941	8 (5)	92	71,990	3 (5)	101
Ca	47,671	47,657	7 (7)	100	49,241	2 (6)	103
Fe	91,974	93,196	8 (7)	101	94,856	3 (5)	103
K	14,113	13,358	7 (10)	95	14,564	4 (5)	103
Mg	20,807	21,222	7 (7)	102	21,310	3 (5)	102
Mn	1084	1449	3 (6)	134	1412	1 (2)	130
Na	24,778	23,928	9 (9)	97	25,008	3 (5)	101
P	1532	2108	3 (2)	138	1007	33 (18)	66
Si	253,492	244,694	10 (6)	97	199,246	15 (10)	79
Ti	13,189	11,908	14 (18)	90	14,280	13 (11)	108
As	<5	bdl <sup>b</sup>			5.3	66	
Ba	670 $\pm$ 13	690.2	10 (10)	103	679.4	2 (5)	101
Be	1 $\pm$ 0.04	1.5	6 (7)	150	1.5	11 (24)	150
Bi	<25	bdl			0	186	
Cd	<2	3.7	67		0.2	67	
Ce	51 $\pm$ 2.5	53.5	3 (19)	105	53.4	1 (6)	105
Co	36.5 $\pm$ 1.8	35.6	6 (18)	98	39	9 (5)	107
Cr	15 $\pm$ 0.4	9.0	15 (8)	60	12.3	12 (14)	82
Cu	12 $\pm$ 0.6	19.8	61	165	11.8	73	98
Ga		46.2	22		45.1	7	
La	26.2 $\pm$ 1.3	46.5	20	177	15.8	116	60
Mo	<5	1.7	5 (11)		1.5	5 (18)	
Nd	37 $\pm$ 7.4	28.3	6 (21)	76	29.8	3 (6)	81
Ni	12.4 $\pm$ 1.2	92.1	162	743	10.3	18	83
Pb	12 $\pm$ 7.2	11.5	11 (8)	96	13.8	8 (6)	115
S		1079	53		bdl		
Sb	<18	bdl			1.2	66	
Sc		150.5	73		31	82	
Sn	5.1 $\pm$ 2.5	bdl			2.5	58	49
Sr		307.7	4 (7)		339.6	6 (5)	
Th	<25	5.7	5 (17)		6.1	3 (8)	
U	<25	1.2	43		1.7	12	
V		396.6	6 (10)		445	4 (6)	
W	<8	bdl			5.3	66	
Y		30.9	7 (15)		33.9	3 (7)	
Zn	131 $\pm$ 3.9	125.4	7 (6)	96	138.6	4 (5)	106

<sup>a</sup> Coefficient of variation of analysis of BCR1 (and in brackets for topsoil standards).

<sup>b</sup> bdl = below instrumental detection limit (determined as three times the standard deviation of blanks).

**Table 3**

Temporal (four sampling dates) and spatial variability (headwater and downstream sites) in SPM and source material characteristics (citing element parameters that satisfied quality control evaluation). Units of concentrations are expressed on the basis of ignited sample mass for digest elements and oven-dried mass for other determinants. Different letters denote significant differences between source materials (Tukey simultaneous tests,  $p > 0.05$ ).

Date	Millhead Burn SPM				Tarland Burn SPM				Pasture soil		Arable soil		Bank subsoil		Bed sediment	
	May-2004	August-2004	October-2004	May-05	May-04	August-2004	October-2004	May-05	n = 3	n = 3	n = 5	n = 3	n = 5	n = 3	n = 3	
Q (m <sup>3</sup> s <sup>-1</sup> )	0.08	0.03	0.05	0.06	1.31	0.23	0.55	0.71								
Q <sub>50ile</sub> <sup>A</sup>	12	98	59	50	9	99	60	46								
SPM (mg L <sup>-1</sup> )	4.1	2.9	53	3.1	7.4	2.7	33	6.7								
SPM <sub>50ile</sub> <sup>B</sup>	65	90	3	87	46	90	7	49								
Hydrograph at sampling <sup>C</sup>	F	S	R	F	F	S	R	F								
Chl a (µg L <sup>-1</sup> )	3.13	0.12	nd <sup>E</sup>	1.77	4.51	2.27	nd	1.25								
% Phyto OC <sup>D</sup>	17	1		5	16	23		5								
Particle d <sub>50</sub> (µm)	23	30		35	22	24		26	30	abc	15	bc	47	abc	93	a
% C	16.1	17.7	13.0	16.5	13.3	12.8	13.1	13.3	4.1	a	3.4	a	1.9	a	1.5	a
% N	1.2	1.6	1.1	1.4	1.1	1.5	1.3	1.2	0.3	a	0.3	a	0.2	a	0.1	a
C:N	13.3	11.0	12.0	12.0	12.0	8.3	10.2	11.6	12.7	a	12.2	a	12.8	a	16.1	a
Bioavail. P (mg kg <sup>-1</sup> )	102	133	125	63	107	313	45	67	9	a	17	a	3	a	9	a
PSR	0.03	0.08	0.05	0.03	0.16	nd	0.07	0.08	0.06	ab	0.09	b	0.04	a	0.06	ab
Al <sub>ox</sub> (g kg <sup>-1</sup> )	4.8	1.9	0.5	3.4	4.7	2.0	0.8	5.6	4.8	ab	6.2	b	2.4	a	2.9	ab
Fe <sub>ox</sub> (g kg <sup>-1</sup> )	10.8	12.1	1.8	12.8	14.5	27.6	4.6	27.1	7.7	a	9.2	a	13.7	a	8.6	a
P <sub>ox</sub> (g kg <sup>-1</sup> )	0.5	1.1	0.1	0.4	3.1	nd	0.3	2.6	0.7	ab	1.4	b	0.6	a	0.8	ab
LOI (%) <sup>F</sup>	38	37	33	39	33	28	35	31	12	a	10	a	5	b	4	b
Al (g kg <sup>-1</sup> )	116	101	148	89	112	79	100	97	103	a	93	a	79	a	74	a
Ca (g kg <sup>-1</sup> )	22	16	20	27	20	16	23	23	29	a	29	a	29	a	28	a
Fe (g kg <sup>-1</sup> )	102	101	128	91	99	110	111	106	101	a	90	a	119	a	107	a
K (g kg <sup>-1</sup> )	15	15	12	14	15	13	17	16	8	a	10	a	8	a	9	a
Mg (g kg <sup>-1</sup> )	20	16	18	19	20	14	18	21	20	a	17	ab	16	b	16	ab
Mn (g kg <sup>-1</sup> )	2	2	2	2	2	6	3	4	1	a	2	a	2	a	2	a
Na (g kg <sup>-1</sup> )	10	11	10	16	12	11	12	16	21	a	18	a	17	a	16	a
P (g kg <sup>-1</sup> )	4	5	- <sup>G</sup>	-	6	6	-	-	1	a	3	a	3	a	1	a
Si (g kg <sup>-1</sup> )	285	276	259	272	279	286	259	226	192	a	194	a	195	a	184	a
Ti (g kg <sup>-1</sup> )	8	6	7	6	8	5	7	5	29	a	26	a	52	a	47	a
Ba (mg kg <sup>-1</sup> )	931	1186	1162	1435	973	1033	936	1286	491	a	567	a	523	a	494	a
Be (mg kg <sup>-1</sup> )	3	2	4	3	3	2	3	4	1	a	2	a	2	a	1	a
Ce (mg kg <sup>-1</sup> )	66	59	69	63	84	69	97	86	38	a	49	ac	89	b	71	bc
Co (mg kg <sup>-1</sup> )	53	59	44	50	55	83	49	67	33	a	30	a	31	a	26	a
Cr (mg kg <sup>-1</sup> )	174	677	-	390	155	359	170	261	62	a	64	a	76	a	217	a
Mo (mg kg <sup>-1</sup> )	5	36	-	17	7	18	3	20	2	a	4	a	3	a	2	a
Nd (mg kg <sup>-1</sup> )	36	32	31	33	48	35	49	45	17	a	24	ac	44	b	35	bc
Pb (mg kg <sup>-1</sup> )	74	177	119	132	70	134	64	101	15	a	21	a	14	a	16	a
Sr (mg kg <sup>-1</sup> )	244	185	233	276	248	175	245	255	332	a	317	a	285	a	281	a
Th (mg kg <sup>-1</sup> )	3	3	-	3	5	4	6	6	3	a	6	ac	10	b	8	bc
V (mg kg <sup>-1</sup> )	339	303	333	286	305	295	263	295	379	a	306	a	365	a	323	a
Y (mg kg <sup>-1</sup> )	30	26	25	30	32	26	29	31	14	a	22	ac	30	b	24	bc
Zn (mg kg <sup>-1</sup> )	546	655	348	381	438	661	380	441	111	a	127	a	126	a	125	a

<sup>A</sup> Percentile discharge at time of sampling (Q<sub>50ile</sub>) calculated for each site from the May 2004–May 2005 hourly flow data.

<sup>B</sup> Percentile SPM concentrations taken from daily to 4-hourly (storm-triggered) sampling over the same period (Stutter et al., 2008a).

<sup>C</sup> Hydrograph position at sample (R = rising limb, F = falling limb, S = prolonged stable flow).

<sup>D</sup> Phyto OC indicates the % of organic C associated with algal pigmentation of the total OC.

<sup>E</sup> nd, denotes not determined.

<sup>F</sup> LOI, Loss on ignition values from the digestion procedure.

<sup>G</sup> - denotes poor analytical results which are not reported.



#### 2.4. Statistical analyses and fingerprinting procedure

Analyses of variance and simultaneous tests (Tukey;  $p \leq 0.05$ ) to determine differences between sediment and soil sources were performed after testing the data for normality and transforming (Box Cox transformation to optimal lambda) where necessary (Minitab v.14.12). Comparisons of metal signatures of sediments with those of the soils (using concentrations on the basis of ignited sample mass) were performed by multivariate techniques using Genstat (v.8.1). For the fingerprinting procedure the data were initially transformed into the first three principal components by Principal Components Analyses to reduce the dimensionality of the data prior to the Discriminant Analyses. The three principal components were then carried forwards into Discriminants Analysis and further reduced into the two Canonical Variates (CV) components grouped by source type and unknowns (these components CV1 and CV2 are the data which are plotted). Previous studies (for example Burns et al., 2001; Frey et al., 2007) have used principal components transformed (as opposed to raw concentration data) for the ultimate goal of quantifying relative source contributions by analysis using numerical mixing models.

### 3. Results

#### 3.1. Quality control results of digests

From data (Table 2) on the accuracy and precision of the BCR1 reference material digest metal recoveries (one included in each sample batch) 10 major elements and 13 trace metals (as in Table 3) were selected for the subsequent description of sample properties and sediment sources. Quality control criteria of <15% CV of BCR1 reference sample replicates was judged as giving a combination of acceptable quality and number of metals. It was less important that absolute recoveries were close to 100% but more that micro- and macro-scale digests gave similar results. The analytical precision of these selected elements is also shown for the agricultural topsoil standard in Table 2. Precision was comparable with that of BCR1 for major elements, but slightly poorer for trace elements Ce, Co, Nd and Y determined by the micro-digest. BCR1 reference data for P and Si showed poor precision and recovery for macro-digests and although sample values for these elements are reported in Table 3 they were not used in the source tracing statistics. Summation of trace plus major element oxide masses from all analyses gave an additional quality check, being 95–108% for micro-digests and 79–97% for macro-digests (smaller values for the latter explained by poor recoveries for Si). Good recoveries for Pb (Table 2) showed that there was minimal loss by volatilisation at the high flux temperatures.

#### 3.2. Physico-chemical characteristics of sediments and soils

The particle size characteristics of the SPM from the headwater were similar over most flow conditions (Fig. 2), although SPM was coarser in May 2005 during a period of hydrograph recession (Fig. 1). SPM collected downstream in the Tarland Burn had slightly smaller contents of particles >63  $\mu\text{m}$  diameter than in the headwater, but conversely bed sediments downstream were coarser than upstream. Field surface soils and stream bank subsoils were dominated by particles <250  $\mu\text{m}$  diameter (Fig. 2). Soil <250  $\mu\text{m}$  particle contents decreased in the order arable > pasture surface soil > bank subsoil. There was limited spatial variability for soils in relation to particle size. In contrast, the stream bed sediments showed large spatial and temporal variation in particle size. At Millhead greater contributions of <250  $\mu\text{m}$  particles to bed sediments occurred at baseflow (Aug-04), with least after the May-05

storm. Conversely, at Tarland Burn, bed sediments had the greatest contributions of fines following the May-05 storm.

Sampled SPM concentrations were greatest during the rising limb of the Oct-04 storm (53 and 33  $\text{mg L}^{-1}$  at the headwater and downstream sites, respectively, representing the 3% and 7% ile SPM concentrations of daily to 4-hourly sampling data taken from Stutter et al., 2008a). Between sample times SPM organic C contents varied little, but were generally greater in the headwater. C/N values were decreased during baseflow in Aug-04 relative to other sampling times. This enrichment in particulate organic N during Aug-04 corresponded with enhanced concentrations of Cr, Pb and Zn and, especially at the downstream site, in bioavailable P. SPM element concentrations in general were dominated by Si, Fe and Al, with Ba, V, Sr, Cr and Zn the most concentrated trace metals. Temporal variability in SPM for the majority of determinants exceeded inter-site differences. It should be noted that elemental concentrations are expressed on the basis of ignited sample mass (40–50% greater than on an oven-dried mass basis) since these values are used later in discriminant analyses. There were few clear relationships that were consistent between the two sites for determinants against SPM concentrations, C content, or discharge (as might be expected due to the complex hysteresis behaviour of SPM). The exception was that  $\text{Fe}_{\text{ox}}$  concentrations inversely correlated ( $p \leq 0.01$ ) with SPM concentrations at both sites. Also, at both sites, Ti and Ba concentrations, respectively, showed negative ( $p \leq 0.01$ ) and positive ( $p \leq 0.001$ ) correlations with median particle size.

An initial test of the suitability of the data for discriminating between sample types was made using Tukey simultaneous analyses ( $p \leq 0.05$ ) to determine concentration differences between surface soils, bank subsoils and bed sediments (different letters in Table 3). Many properties showed limited differences between sample types and there were no significant differences between pasture and arable surface soils due to large, within-class spatial variation. Arable surface soils generally had greater concentrations of total P, Ba, Ce, Mo, Nd, Pb, Th and Y than pasture soils. Conversely, pasture soils were only appreciably more concentrated in V than arable soils. However, none of these differences were significant due to the greater spatial variability within, than between land use classes. However, it is important for sediment tracing potential that some properties can distinguish between surface soils which are generally enriched in nutrients and subsoils from erosion of stream banks. Therefore the following groups of properties were identified where mean values for bank subsoils significantly differed from those for: (a) both pasture and arable surface soils (LOI, Ce, Nd, Th, Y), (b) pasture soils only (Mg), or (c) arable surface soils only ( $\text{PSR}$ ,  $\text{Al}_{\text{ox}}$ ,  $\text{P}_{\text{ox}}$ ).

#### 3.3. Sediment source discrimination

Eigenvalues for elemental fingerprinting properties showed that the first 3 principal components (explaining 77% of the variance) represented a mixture of positive (Ba, Pb, Zn; 0.27–0.28) and negative loadings (Ca, Ti, V; –0.27), the second principal component a positive loading of Al (0.32) and a mixture of negative loadings (Ce, Mg, Nd, Y; –0.33 to –0.36) and the third principal component was dominated by negative Be (–0.50) and positive Cr (0.46).

Although bed sediment resuspension is a potential source of SPM it was decided to treat bed sediments and SPM as statistical unknowns in order to compare their properties against those of the catchment's soils. The results of Discriminant analyses are given in Table 4 and Fig. 3. The power of separation between centroids of the source materials using the multivariate elemental signatures decreased in the order pasture surface soil against stream bank subsoil > pasture surface soil against arable surface

**Table 4**  
Results of canonical variates and discriminant analysis of <250  $\mu\text{m}$  size fractions of source materials and suspended particulate matter using transformed multi-element data.

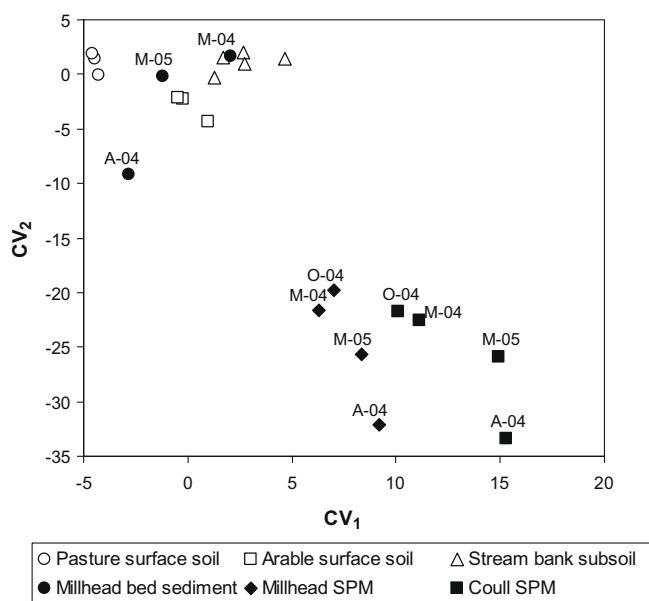
	Groups		
	Pasture field soil	Arable field soil	Stream bank soil
<i>n</i>	3	3	5
<i>Intergroup squared distances</i>			
Pasture field soil	–		
Arable field soil	36	–	
Stream bank soil	50	23	–
Group classification probability (%)	100	100	100
<i>Unknown to group mean squared distances</i>			
Pasture field soil			Stream bank soil
<i>Millhead Burn bed sediments</i>			
May-2004	43	25	1
August-2004	108	48	137
May-2005	12	9	16
<i>Millhead Burn SPM</i>			
May-2004	628	387	529
August-2004	1284	933	1146
October-2004	563	330	454
May-2005	876	585	750
<i>Tarland Burn SPM</i>			
May-2004	799	507	633
August-2004	1575	1159	1352
October-2004	730	454	579
May-2005	1099	746	879

soil > arable surface soil against stream bank subsoil. The method suggested clear similarities between stream bed sediments in the headwater (Millhead) and source materials. At the time of highest discharge (May-04) the elemental compositions of bed sediment closely matched those of stream bank subsoil. During the flow recession after the May-05 storm bed sediment compositions became more similar to arable surface soils. Separation distances were greatest between source materials and bed sediments during prolonged baseflow (Aug-04). Fig. 3 shows that SPM elemental signatures plotted well away from the area bounded by these charac-

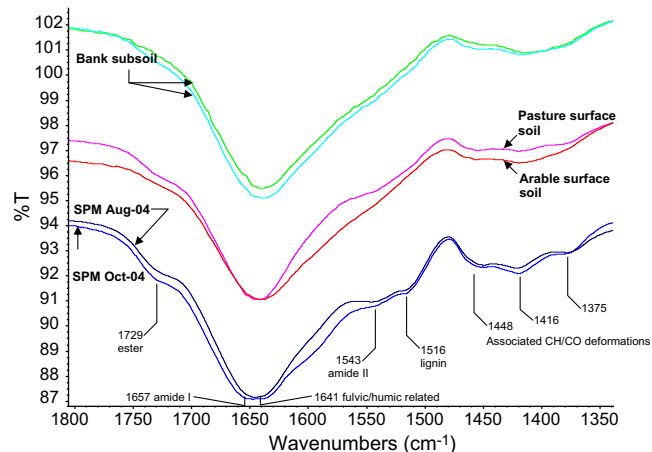
terised source materials. Hence, separation distances in Table 4 between SPM and soils were particularly large. Neither was SPM elemental signatures found to be similar to those of bed sediments. Separation distances between Tarland Burn SPM (5 km downstream of the collected source materials) and the soils and bed sediments of the headwater were only slightly greater than between Millhead SPM and the adjacent source materials. SPM elemental compositions plotted away from the sources with decreasing stream concentrations of SPM at both sites (Table 3).

#### 3.4. Changes in SPM organic matter composition

The FT-IR spectra presented (Fig. 4) provide evidence of the typical changes in the compositions of organic matter between SPM and soils. Spectra of bed sediment organic matter regions (not shown) had similar patterns to soils. SPM organic matter spectra showed well developed organic matter functional groups associ-



**Fig. 3.** Plot of the Canonical Variates components CV1 and CV2 for the stream sediments (closed symbols) and potential catchment sources (open symbols). SPM compositions are shown for the headwater site Millhead (closed diamond symbols) and downstream site Coull (closed squares). Dates of sampling for stream sediments are given by the notation M-04, A-04, O-04 and M-05 for May, Aug and Oct 2004 and May 2005, respectively.



**Fig. 4.** Infra-red spectra of the principal organic matter region showing examples of the difference in organic matter composition between SPM collected at baseflow (Aug-04) and during a storm (Oct-04) compared to the potential catchment soil sources.

ated with proteinaceous material of recent biological origin; ester structures ( $1729\text{ cm}^{-1}$ ), amide structures ( $1657\text{ cm}^{-1}$  and  $1543\text{ cm}^{-1}$ ) and lignin (a second shoulder at  $1516\text{ cm}^{-1}$  and associated CH/CO deformations between  $1448$  and  $1375\text{ cm}^{-1}$ ). The organic region peak for the bank subsoils, pasture and arable surface soils showed the broader, smoother peak attributed to fulvic/humic-type material with little of the well-defined structure of the SPM organic matter. It was surprising that the markedly different organic matter structure of SPM than that of soils occurred not only during the Aug-04 baseflow period, but also in Oct-04 when large SPM concentrations were sampled on the rising limb of a storm. Patterns were also similar for SPM during intermediate flow conditions in May-04 and 05 and at the downstream site (not shown). Algal-associated organic C contributed 1–23% of overall SPM total organic C (as calculated from the chlorophyll *a* concentrations; Table 3).

#### 4. Discussion

##### 4.1. Assessment of the source tracing method using element compositions

It was sought to determine whether differences in total elemental concentrations for a limited number of near-channel soils from an agricultural headwater could be utilised to discriminate between potential sources of sediment to the stream. The study was undertaken in a region dominated by mixed acid-basic, igneous to metamorphic geology, with granite to gabbro parent materials and trioctahedral vermiculite and kaolinite clays (Wilson et al., 1984). Trace metals were dominated by concentrations of Ba, Sr and V ( $>300\text{ mg kg}^{-1}$  ignited sample mass) but the association of these metals with primary and secondary mineral soil components is difficult to confirm. Elemental compositions were assessed to discriminate between soil sources in two ways: (i) spatially between land uses and (ii) with depth between surface soil erosion and bank erosion of subsoils. Sampling soil surface layers (0–5 cm) from pasture and arable fields on opposite sides of the stream aimed to assess which land use type contributed more eroded material to the stream. Despite the contrasting management the element concentrations did not significantly differ between pasture and arable soils since differences were small relative to within-type spatial variability. Between-type differences may have become more apparent and significant if a more comprehensive range of source characterisation was undertaken, such as farm yard sediments, or soils under different land use. However, given the limited number of sources examined here it was observed that arable soil was generally enriched in bioavailable P, oxalate extractable Al, Fe and P relative to pasture soil. This enhanced ability for arable soils to complex and exchange P has importance to eutrophication issues related to particulate P delivery to the stream if arable land use was associated with greater erosion of material. The greater P status also shows the effects of chemical fertilizers applied to the arable field (approximately  $220$  and  $80\text{ kg ha}^{-1}\text{ a}^{-1}$  for N and P, respectively; Stutter et al., 2008a). However, it would be reasonable to assume that pasture land also receives chemical fertilisers and both would have manure applications. These results show a limited ability for individual element concentrations to discriminate between these two land uses and no characteristic signal of different fertiliser amendments was observed in the trace metals. Hence, determining spatial variation in source areas would have to rely on artificially applied tracers (e.g. Polyakov and Nearing, 2004) or distinct geological boundaries that are reflected in the overlying soils.

Another common requirement is to discriminate between surface and sub soils to indicate the relative importance of surface

runoff erosion and stream bank erosion to sediment sources. Stream banks can become the dominant source of material eroding to streams (Olley et al., 1996; Lefrançois et al., 2007). The importance of distinguishing between surface soil and bank subsoil contributions to stream particles is evidenced by results from the present study showing greater bioavailable P in surface soils than bank subsoils (Table 3). The strong particle affinity of P applied to the land surface in fertilisers causes P accumulation at soil surfaces (although this may be mixed to the plough depth in arable systems). Radionuclides with atmospheric deposition sources are commonly employed to discriminate between surface and subsoil erosion in sediment sourcing studies (Olley et al., 1996). However, the current study found significant increases with depth for Ce, Nd, Th and Y concentrations between surface- and subsoils. Further investigation into these depth changes and their occurrence for other soil parent materials outside of this region would seem warranted. There was no evidence that metals with surface-applied sources such as Zn and Pb (atmospheric deposition and animal manure sources) and Cr (inorganic fertilisers and atmospheric deposition sources; Nicholson et al., 2003) showed any differences with depth.

In contrast to strong differences between SPM compositions and the characterised sources, there were substantially closer matches between soils and bed sediments. Lefrançois et al. (2007) observed that bank degradation through low to intermediate flow periods of spring to late summer recharged the stream channels with sediments and these stores subsequently became mobilised by major hydrological events in autumn and winter. Although it was observed in the present study that bed sediments matched bank subsoils during this period (Fig. 3) a large enough storm with sufficient energy to remobilise this stored material as SPM was not captured. Bed sediments showed closest matches to bank subsoils in May-04, arable surface and subsoils in May-05 and least similarities in Aug-04. Given that May-04 was the highest flow sampled, this may have been a time of active bank erosion with local deposition of material in the channel at the time of sampling on the flow recession. Sampling in May-05 (when the bed sediments resembled arable field soils) occurred after 64 mm of rainfall had fallen following fertiliser application, tillage and sowing of arable fields (5–6/4/05; data from Stutter et al., 2008a). These inputs of eroded soil into the channel are of consequence to physical degradation of stream bed habitats even though there was no apparent increase in the P nutrient status of the bed sediments as a result of inputs during these events.

It is possible that the limited sampling of the bed sediments and soils close to the point of SPM collection failed to characterise some major sources of SPM. Alternate sources could be from road runoff, soil drainage pipes or more distant soil erosion within the catchment, indicating that SPM is mobilised over long distances. However, it has previously been determined that subsurface drainage made a limited contribution to overall SPM budgets in this catchment (Stutter et al., 2008a). In addition, SPM concentrations during storms have previously been shown to respond very rapidly to runoff initiation (strong clockwise concentration-discharge hysteresis) suggesting sources of SPM that were near to, or within the channel itself (Stutter et al., 2008b). This latter result prompted this current study to look only at the limited range of source soils adjacent to the stream channel in this headwater to try to match them to SPM. It was however observed that Oct-04 SPM was the nearest to the compositions of sources and this was the only time when sampling caught the rising limb of a storm event. Surface soils from near the stream networks are recognised as spatially important sources of sediments (Russell et al., 2001). However, the links between riparian soils under agricultural management and stream SPM is not clear in this study.



#### 4.2. To what extent is within-stream alteration of SPM responsible for differences between SPM and source materials?

SPM was relatively concentrated in Ba, Cr and Zn compared to soil sources and stream bed sediments. This may be due to associations of these metals with either an expected enhanced clay mineral content of SPM (for which there is no data), or the observed different organic matter components of SPM compared with soils or bed sediments. Conversely, relative accumulation of Ti and Na in soils and bed sediments indicated enrichment in residual mineral components as more weatherable mineral fractions became selectively eroded. Elemental compositions may vary with particle size differences between samples because of certain element associations with mineral or organic components concentrated differently between the particle sizes. Stone and Droppo (1996) observed that river sediment Zn and Pb were concentrated in the finest size fractions (<8 µm diameter). Whilst particle size differences may be important for bed sediments, which were consistently coarser than SPM, fine particle contents were more similar between soils and SPM (Fig. 2). SPM also had much greater bioavailable P concentrations than any of the source materials. This indicated both the importance of SPM as a vector of bioavailable particulate P across the range of flow conditions, but also that biological, or erosion selection processes acted to increase readily-available forms of P in SPM relative to sources. The fact that Al<sub>ox</sub>, Fe<sub>ox</sub> and P<sub>ox</sub> were not significantly enhanced in SPM relative to soils or bed sediments suggests that variations in trace elements arise from differing organic matter quantities or compositions rather than with different reactive surface coatings such as Fe(oxy)hydroxides (Quinton and Catt, 2007). This is further supported by temporal changes in SPM organic matter related to the progression of the summer biological period and increased residence of SPM with decreased flow.

Tracing the composition of the SPM to source materials requires that the properties are conservative through the system. Hence the discriminatory power of comparisons in elemental contents is weakened through alteration by in-stream processes. There may be some accumulation of sediment organic matter through selective erosion of size fractions enriched in organic matter (Quinton and Catt, 2007). However, the greater organic matter contents of SPM than for soil or bed sediment materials is consistent with observations that a large component of SPM can be autochthonous organic matter (da Cunha et al., 2000; Lartiges et al., 2001; Stutter et al., 2007). This was verified by the FT-IR observations of pronounced functional groups of SPM organic matter relating to proteinaceous materials that were not apparent for source soils and bed sediments (Fig. 4). Since contributions of algal-associated C were generally low this SPM organic matter appeared to be microbial-dominated biofilm communities. Biofilm development may cause aggregation of SPM particles (Rother and Kohler, 2005), can affect the surface binding potential of metals and the development of biogenic metal precipitates (Dong et al., 2005). This could alter trace metal contents compared to source materials (dominated by more lithological metal compositions).

SPM collected during baseflow in Aug-04 would be expected to have a composition likely to show the greatest extent for alteration by within-stream biological processes, giving a comparison with other sampling times during moderate-sized storms when there would be expected to be greater connectivity between catchment source regions and stream SPM. An accumulation of recent, autochthonous organic matter would explain how differences between the compositions of SPM and soil sources were most apparent during August baseflow. Aug-04 SPM in the present study was coarser, had greater concentrations of bioavailable P, P<sub>ox</sub> and a lower C:N ratio. Although the amide and lignin functional groups were

most pronounced during Aug-04, the FT-IR spectra indicated that biofilm-type organic matter was present during all the times SPM was sampled, even during storm events. This suggests that biological alteration has the potential to disrupt comparisons between SPM and sources used in tracer studies. This effect may be likely throughout the summer period of biological activity and into autumn since during scouring autumn events SPM may be remobilised from fine bed sediments including biological material settled out during summer.

Sediment tracing studies should examine contributions from catchment sources at periods other than hydrograph peak events in order to better evaluate catchment – water quality – ecology linkages. However, studies should also include properties not affected by biological processes, such as mineralogy. Given the limited sampling of sources in the present study, differences between SPM elemental compositions and the described soils cannot be ascribed as purely caused by this within-stream alteration. However, this process should be given attention in future studies.

#### 4.3. Sediment compositions assessed against published quality guidelines

Fingerprinting using elemental compositions has the added benefit that the data gathered are relevant to linking land management, erosion and ecosystem quality (Quinton and Catt, 2007). Concentrations of some trace elements associated with SPM in the Tarland Burn exceeded freshwater sediment probable adverse effects concentrations of 90, 91 and 315 mg kg<sup>-1</sup> for Cr, Pb and Zn, respectively (US National Oceanic and Atmospheric Administration screening quick reference tables; Buchmann, 1999) and median toxicity values for Cr and Zn of 370 and 410 mg kg<sup>-1</sup> dry mass, respectively, (ANZECC/ARMCANZ, 2001) (all expressed as dry mass of sediment). In the present study baseflow SPM during Aug-04 exceeded these standards for Cr (259 and 430 mg kg<sup>-1</sup>), Pb (97 and 112 mg kg<sup>-1</sup>) and Zn (477 and 416 mg kg<sup>-1</sup>) at the headwater and downstream sites when expressed similarly on the basis of dry mass of sediment. Concentrations of Cr in bed sediments also exceeded the median toxicity values during Aug-04 (498 mg kg<sup>-1</sup> dry mass) being considerably enhanced relative to May sampling times (57–95 mg kg<sup>-1</sup> dry mass).

### 5. Conclusions

The results suggest that fingerprinting using natural concentrations of major elements and trace metals has potential as a tool to investigate sources of sediments to streams. The application using a limited number of samples from within a small agricultural catchment with soils derived from glacial tills of mixed acid-basic igneous mineralogy showed that differences in Ce, Nd, Th and Y concentrations with depth facilitated discrimination between surface soils and stream bank subsoils. However, the lack of differences between surface soil under arable and pasture management suggested limitations in the determination of spatial 'hot-spots' of sediment sources across this study catchment. By collecting stream sediment samples during moderate to low flow events the authors sought to characterise stream sediments at a sensitive period for stream ecology. Combined elemental signatures during such periods showed that bed sediments could generally be accounted for by mixing of the sampled source soils, whereas sediments in suspension in the water column were different from these sources. Hence, agricultural soil management (for example P status) has the potential to influence water quality at times when bed sediments are interacting with longer residence time, lower flow waters and biota. However, this preliminary investigation suggested that within-stream biological processes transformed SPM organic contents and compositions leading to

accumulations of certain elements during both baseflow and moderate flow conditions. This has implications for the use of element signatures in sediment tracing studies and indicates substantial stores of labile, biologically-altered material which may be remobilised from within-stream stores during storm events following summer.

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