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The distribution of phosphorus between soluble and particulate phases for seven Scottish East Coast rivers

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Abstract. Phosphorus (P) fractions were quantified in water samples collected on four occasions from sites at the lower tidal limit of seven Scottish East Coast rivers. Individual catchment characteristics ranged from those dominated by semi-natural land use to those where agriculture predominated. Together the rivers displayed attributes ranging from nearly pristine to those impacted by point and diffuse sources of pollutants. Sampling times were chosen to coincide with periods of low river flows where conditions should result in low concentrations of suspended particulate matter (SPM) but favourable for phytoplankton growth. Total phosphorus (TP) concentrations were < 0.004 mg l^{-1}, 0.005–0.048 mg l^{-1} and 0.28–2.2 mg l^{-1} for pristine, agricultural and point source impacted rivers respectively. Soluble reactive phosphorus (SRP) represented from < 5% to > 90% of TP and dissolved P dominated all samples. The total phosphorus content (TPC) of SMP ranged from 0.1 to 1.1% and was significantly related to SRP. Organic matter was a significant component of SPM and organically bound phosphorus was the dominant form of particulate P. The C/P ratio of organic matter was wide, between 500–1200 for the more pristine systems which narrowed to < 400 for heavily impacted rivers. Exchangeable P increased during the summer but was generally a minor component of TP and therefore likely to be a significant source of SRP only in pristine rivers. Phytoplankton constituted between 5 and 46% of organic matter and concentrations of chlorophyll-a were significantly correlated with both TP and SRP.

Introduction

Globally rivers transport 22 Tg y^{-1} of P to the ocean and carry 91% of this amount in particulate form (Howarth et al. 1995). Sediment transport represents a major factor in determining total P fluxes down rivers and inputs to coastal waters. Much of the emphasis of recent research has therefore been focused upon quantifying the spatial and temporal aspects of particulate P loss (Dorioz et al. 1998; Sharpley et al. 1995) while also understanding catchment scale source apportionment. Howarth et al. (1995) estimate that between 23% and 69% of particulate P (PP) is biogeochemically active, implying that this amount could potentially become labile and enter biogeochemical cycles. With the increased recognition of the role that SPM plays in nutrient transport and dispersion has come the need to fractionate PP which has been achieved using operationally defined extraction procedures (Bonetto et al. 1994; Chase and Sayles 1980; Lebo 1991; Lucotte and d'Anglejan 1983).

The need to quantify total P loss has also meant that sampling and analysis programmes have tended to ensure an adequate characterisation of the short-term and highly episodic nature of erosion events. The result is an improved estimate of the P fluxes from terrestrial to aquatic ecosystems. However, when considering likely ecological impacts, the timing of P loss in relation to periods of active biological growth and uptake becomes important (Edwards et al. 2000). Generally the extended periods of reduced river discharge when suspended loads are comparatively small have been neglected despite being the period when the effects of eutrophication are most likely to be manifested in rivers and estuaries.

As a prerequisite to assessing the extent of solid/solution interactions and in an attempt to emphasize conditions pertaining to biological impacts this paper quantifies the distribution and composition of particulate and dissolved phosphorus in contrasting rivers sampled under low flow conditions.

Material and methods

Study areas

Together the seven catchments situated along the Scottish East Coast possessed a diverse range of attributes and river types and were subjected to varying degrees of human impact. Individual land areas ranged between 369 km^2 and 4590 km^2 (Figure 1) and the dominant land cover varied widely (Figure 2). Agriculture typically included extensive sheep/beef grazing in the uplands progressively giving way to more intensive mixed arable and livestock farms in the lower coastal areas. The proportions of agricultural land increased from $\sim 10\%$ for the Ness up to 95% for the Ythan. Non-agricultural land consisted of rough grassland, heather moorland or blanket bog. The Ness is typical of a relatively pristine highland system while the Conon, Dee and Tay also contain significant areas of extensively managed semi-natural uplands they include intensive agricultural activity in their lower reaches. The remaining rivers (Ythan, Almond and North Esk) possess substantial areas of low gently undulating land where intensive agriculture dominates. Inclusion of the Almond also allows comparison with a point source impacted system. Under low flow conditions in summer up to 60% of its river flow may be derived from sewage effluent (Scottish Environmental Protection Agency, pers. comm.). Further information can be obtained from Marsh and Lees (1993) and Benzie et al. (1991). Organic rich soils predominate upland areas which give way to increasingly cultivated and more mineral soils of the agricultural lowlands. Soil parent materials are variable and include acid/basic igneous, metamorphic gneiss and fine or coarse-grained sedimentary rocks.

Existing river flow and water quality data for each site have been compiled and these provide the longer-term context for the current sampling. River flows tend to be semi-continuous while the quality data consisted of approximately monthly samplings since 1974 and for SPM and SRP represented a minimum of 230 individual

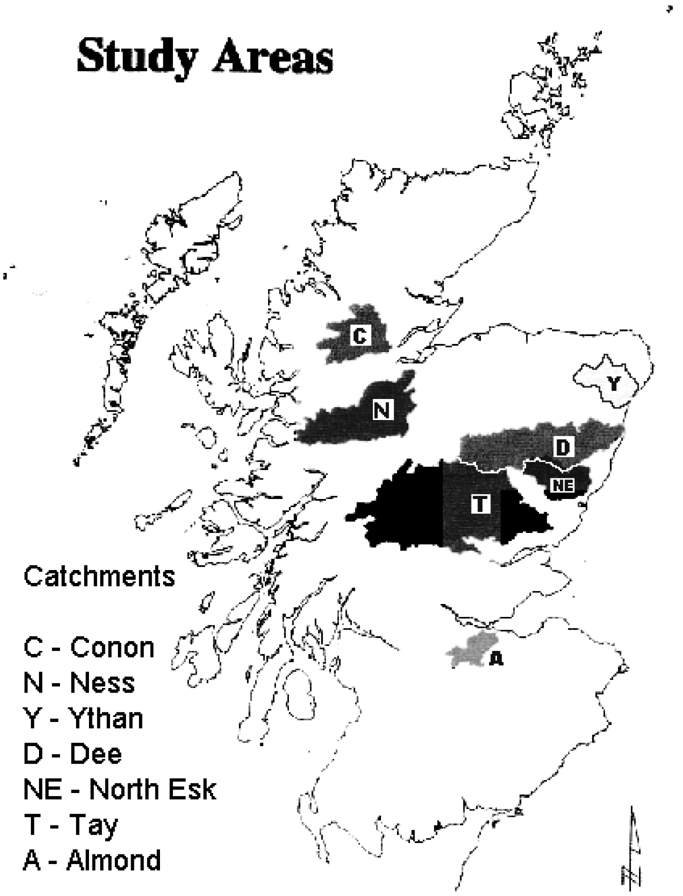

Figure 1. Location of selected river catchments draining the East coast of Scotland.

samples for each river. A fewer (17 – > 100) number of samples had TP. The analytical quality of data is variable and has been discussed by Ferrier et al. (2001).

Water sampling

River water samples were taken midstream from bridges using a plastic bucket and from an approximate depth of 0–30 cm. Sampling sites were all close to the lowest flow gauging station (maintained by SEPA) on each river (Table 1) and upstream of the tidal limit in order to obtain river water representative of the freshwater inputs to individual estuaries. River flow measurements were obtained for each of four sampling occasions during the months of February, March, July and August 1995. In the following sections samples are sometimes grouped into 'winter' (February and March) and 'summer' (July and August) periods.

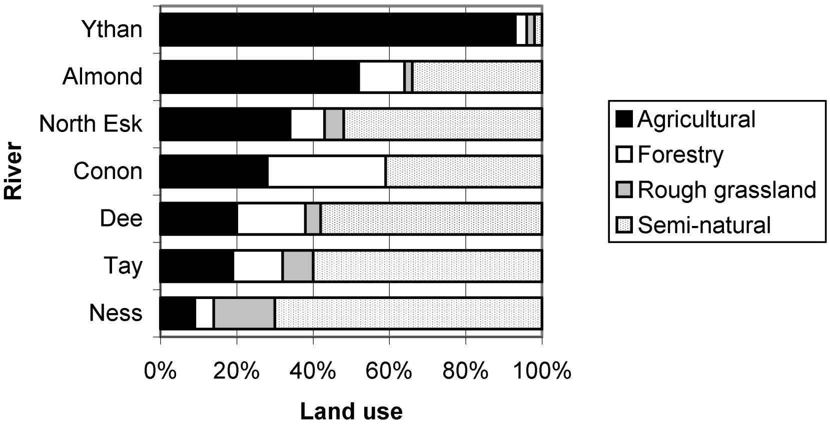

Figure 2. Proportions (%) of major land covers in the seven catchment areas arranged in order of decreasing agricultural area.

Hydrological context

Averaged annual river flow for individual catchments varied between 1600 and 420 mm (Table 1) with a distinctly uneven seasonal distribution (Figure 3). All rivers display a similar monthly trend, typically reaching a minimum during July but with amounts declining in the more southerly and lowland catchments. The sampling year (1995) was characterised by slightly above average annual precipitation (Table 1) at all sites. The majority of February and March samples were collected under conditions similar to the long-term average daily flow, those collected during July and August were taken at flows below the average for those months.

Analytical procedures

River water was analyzed in triplicate for Soluble Reactive P (SRP), Total Dissolved P (TDP) and Particulate P (PP) by sequential extraction. Dissolved Organic P (DOP) was determined as the difference between TDP and SRP. The sum of TDP and PP concentrations gives a quantitative analysis of total P (TP) in river water. The distinction between dissolved and PP was made on the basis of filtration through Whatman GF/F filters (0.7 μm nominal pore size). GF/F filters were chosen since they allowed higher particle loadings to be achieved (up to 10 mg) for the analysis of PP by sequential extraction. Filtration of samples was completed on the day of collection and the filtrate stored refrigerated in glass bottles with dissolved P analysis completed within two days. Samples of SPM collected on GF/F filters were stored frozen in labelled petri dishes until analysis by sequential extraction. Filters were not allowed to dry before freezing.

SRP was measured colorimetrically (detection limit 0.0008 mg P l^{-1}) by the molybdenum blue method (Strickland and Parsons 1972). TDP was determined by the method of Solorzano and Sharp (1980) which involved evaporation of the

Table 1. Catchment characteristics including area (km^2), long-term average annual rainfall (mm), percentage of average during the sampling year shown in brackets and BFI.

River	Lowest gauging station	Water sampling sites	Area (km^2)	Flow (mm)*	Rainfall (mm)**	BFI
Conon	Moy Bridge (HN 482 547)	Moy Bridge (HN 482 547)	962	1599	1770 (105)	0.55
Ness	Ness Side (NH 645 427)	Island Bridge (NH 662 436)	1792	1298	1779 (104)	0.60
Ythan	Ellon (NJ 947 303)	Ythanbank Bridge (NJ 905 340)	523	460	826 (113)	0.74
Dee	East Park (NO 798 983)	Park Bridge (NO 798 983)	1844	793	1081 (111)	0.54
North Esk	Logie Mill (NO 699 640)	Marykirk (NO 685 650)	732	816	1074 (105)	0.53
Tay	Ballathie (NO 147 367)	Railway Bridge (NO 149 372)	4587	1145	1425 (103)	0.65
Almond	Craigiehall (NT 165 752)	Cramond Bridge (NT 179 755)	369	507	896 (115)	0.39

* Average annual river flow for variable time periods (minimum 20 years)

**Average annual rainfall 1961–90

BFI – Base flow index (positively related to permeability and groundwater content)

sample to dryness and mineralisation of organic P at 500 °C in a muffle furnace. Following acid hydrolysis the solution is analyzed as for SRP. Standards prepared from KH_2PO_4 underwent the same procedure as samples.

The sequential extraction scheme of Lebo (1991) was used to distinguish between exchangeable P (P_{exch}), aluminium oxyhydroxide sorbed P (P_{Al}), organic P (P_{org}), amorphous iron oxyhydroxide sorbed P (P_{am}), reducible iron oxyhydroxide sorbed P (P_{red}) and ″apatite″ (P_{Ca}). Individual fractions are expressed on the basis of uncombusted material. The sum of individual fractions gives the total phosphorus content (TPC) which when multiplied with SPM concentration yields the PP.

Sequential extraction was carried out in triplicate by transferring filters into 10-ml centrifugation tubes and adding extractants, equilibration for stated times on a shaking table, followed by centrifugation and withdrawal of the extracts (Ernstberger 1999; Lebo 1991). The extraction procedure was carried out also with blank filters that were underlying the filters used for residue collection. The following

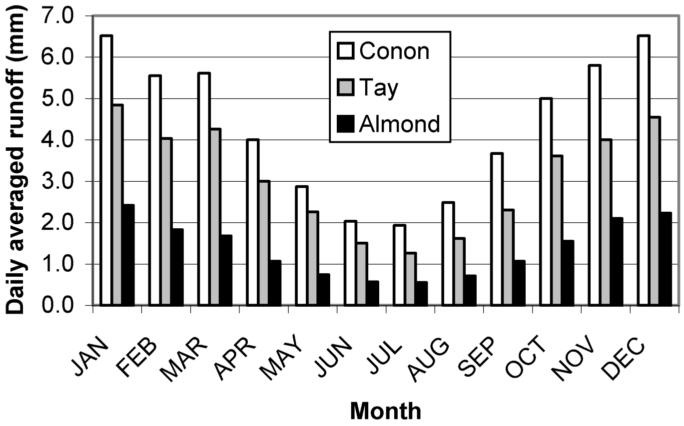

Figure 3. Averaged (minimum 30 year) daily river flows (mm) for individual months and three catchments.

changes to the original scheme were made: Extraction of the phosphomolybdenum complex into isobutanol (Lebo 1991) was abandoned due to a lack of precision. A total digestion of the citrate-dithionite extract with perchloric acid eliminated the interference of citrate (Ernstberger 1999) and removed the need for dilution prior to colour development (Yuan and Lavkulich 1995). An imidazol buffer (Dawson et al. 1986) at pH 7 was added during the extraction of P_{exch} in order to eliminate the influence that solids exerted on pH. Residual Phosphorus was not determined due to poor precision (Ciavatta et al. 1990) and since it is generally a small and recalcitrant fraction of PP in SPM it was considered of little environmental significance (Sonzogni et al. 1982). The sum of P_{am} and P_{exch} fractions has previously been equated with bioavailable particulate P (PP_{avail}) (Dorich et al. 1985).

A quality control step was incorporated in the extraction scheme by including a reference material (fine fraction (< 53 μm) of stream sediment) into each analysis batch. The largest variations were obtained for P_{red} (SD = 0.26 mg g^{-1}) and P_{org} (0.2 mg g^{-1}). However, relative to the size of the fraction the variations were largest for the small fractions P_{am} (RSD = 52%) and P_{exch} (RSD = 44%). The poorer precision for the smaller fractions is attributable to the small amounts (ca. 5 mg) of sediment analyzed.

Collection and analysis of suspended particulate material

The concentration of SPM in river water was determined in triplicate by filtration through Whatman Cyclopore polycarbonate filter membranes (47 mm diameter; 0.4 μm pore size). Filters were left in petri dishes to dry overnight at room temperature before the weight increase due to SPM was recorded. Any bias introduced by using filter sizes of 0.4 vs 0.7 was regarded as small, as the maximum loading of GF/F filters would tend to lower its nominal size during filtration, and minimize the difference in particle sizes collected on both filters.

Table 2. Averaged concentrations (mg l^{-1}) of SPM and SRP together with the SRP expressed as a proportion (%) of TP and P composition (%) of SPM (with SE in bracket) (for more information about samples see Ferrier et al. (2001)).

River	SPM	SRP	SRP% of TP	P content of SPM
Ness	1.56 (0.12)	0.010 (0.003)	75 (3.0)	0.537 (0.150)
Tay	5.03 (0.54)	0.023 (0.002)	90 (4.8)	0.221 (0.135)
Dee	2.55 (0.29)	0.017 (0.002)	54 (5.2)	0.820 (0.190)*
Conon	1.84 (0.15)	0.007 (0.001)	66 (2.6)	0.270 (0.046)
North Esk	10.2 (2.25)	0.040 (0.003)	55 (7.6)	0.725 (0.138)
Almond	18.6 (2.50)	0.742 (0.042)	77 (1.8)	2.070 (0.294)
Ythan	7.34 (0.62)	0.050 (0.004)	75 (2.5)	0.600 (0.169)

* three extreme values removed

Particulate organic carbon (POC) was determined using a Perkin Elmer CHN analyzer. SPM was collected on GF/F filters (25-mm diameter; prebaked at 450 °C for 2 h) mounted on glass holders. Filters were stored frozen and before analysis were subjected to acid fumes to remove inorganic carbonates (Nieuwenhuize et al. 1994). Chlorophyll *a* (Chl-a) was determined fluorometrically (Yentsch and Menzel 1963). Chl-a values were converted to organic carbon using a factor of 50 (Leach 1971). C/Chl-a ratios for individual diatom species may range from 22 to 69 (Darley 1977), indicating that the margins for these estimates are large. Scanning electron microscopy (SEM) was used to optically characterize the nature of SPM collected on 0.4 μm Nuclepore filters.

Results

The long-term averaged concentrations of SPM ranged from < 2 mg l^{-1} for the rivers Ness and Conon up to 18 mg l^{-1} for the Almond (Table 2). Average concentrations of SRP varied over an order of magnitude between rivers, lowest being associated with the Conon, Ness and Dee (all < 0.020 mg P l^{-1}) and highest in the Almond (0.74 mg P l^{-1}). On average SRP represented between 54–90% of the TP measured for each river. Concentrations of P in SPM varied widely between rivers being the lowest in the Tay and Conon (< 0.3%) and highest in the Almond (2.0%).

Concentrations of suspended particulate material and total P in water samples

Concentrations of SPM were variable but generally small with individual rivers displaying different seasonal trends (Table 3). The majority of rivers had similar SPM concentrations on all sampling occasions (< 2.3 mg l^{-1}) although the ’winter’ samples for the River Ythan were greater. The River Almond had larger SPM concentrations that decreased by more than half in July and August samples. Total phosphorus concentrations (Table 3) differed over more than three orders of magnitude between sites. The near pristine rivers Ness and Conon supported concen-

Table 3. Flow on day of sampling (mm d^{-1}) and averaged concentrations (mg l^{-1}) of SPM, TP, SRP DOP and PP (95% confidence intervals shown in brackets) and proportion of TDP expressed as a % of TP and SRP are derived from 3 replicate measurements. Underlined values are below the detection limit.

	Survey	Flow	SPM	TP	SRP	DOP	PP	TDP
Ness	February	8.2	0.36	0.002	0.000 (0.003)	0.001 (0.003)	0.001	57.1
	March	5.4	0.32	0.002	$\overline{0.001}$ (0.001)	$\overline{0.000}$ (0.007)	0.001	50.0
	July	1.4	0.74	0.002	$\overline{0.000}$ (0.001)	$\overline{0.000}$ (0.005)	0.002	16.7
	August	0.7	0.43	0.004	$\overline{0.000}$ (0.001)	$\overline{0.003}$ (0.003)	0.001	69.2
Tay	February	4.5	0.98	0.005	$\overline{0.000}$ (0.001)	$\overline{0.002}$ (0.004)	0.002	53.3
	March	4.9	1.79	0.008	$\overline{0.000}$ (0.002)	$\overline{0.002}$ (0.007)	0.006	28.0
	July	0.9	0.86	0.010	$\overline{0.001}$ (0.001)	$\overline{0.005}$ (0.009)	0.004	62.5
	August	0.6	0.88	0.015	0.001 (0.003)	$\overline{0.010}$ (0.007)	0.004	72.3
Dee	February	2.3	1.10	0.006	0.002 (0.001)	0.002 (0.003)	0.002	63.2
	March	1.5	0.83	0.005	0.003 (0.001)	$\overline{0.000}$ (0.003)	0.002	52.9
	July	0.4	1.05	0.020	0.005 (0.002)	$\overline{0.009}$ (0.008)	0.006	71.2
	August	0.2	2.27	0.035	0.003 (0.002)	0.016 (0.020)	0.016	54.5
Conon	February	8.6	1.19	0.004	0.000 (0.001)	0.002 (0.001)	0.002	46.2
	March	4.8	1.07	0.003	$\overline{0.001}$ (0.001)	0.001 (0.007)	0.002	36.4
	July	1.1	1.01	0.002	$\overline{0.000}$ (0.001)	0.001 (0.005)	0.001	57.1
	August	1.1	0.62	0.004	$\overline{0.000}$ (0.001)	0.002 (0.003)	0.001	66.7
N. Esk	February	1.8	1.31	0.022	$\overline{0.009}$ (0.001)	0.011 (0.006)	0.002	88.9
	March	1.2	1.10	0.010	0.008 (0.005)	0.000 (0.008)	0.002	75.8
	July	0.3	2.14	0.037	0.012 (0.001)	0.016 (0.008)	0.008	78.0
	August	0.3	1.40	0.026	0.007 (0.002)	0.010 (0.004)	0.009	67.1
Almond	February	1.7	10.3	0.281	0.185 (0.005)	0.029 (0.063)	0.067	76.2
	March	2.4	18.3	0.299	0.169 (0.010)	0.000 (0.055)	0.130	56.5
	July	0.2	6.28	2.153	1.538 (0.028)	0.546 (0.670)	0.069	96.8
	August	0.2	4.52	1.605	1.510 (0.044)	0.052 (0.243)	0.043	97.3
Ythan	February	1.1	4.14	0.034	0.016 (0.002)	0.002 (0.002)	0.016	53.2
	March	1.0	3.29	0.033	0.012 (0.001)	0.006 (0.002)	0.016	53.3
	July	0.3	2.10	0.048	0.018 (0.002)	0.021 (0.007)	0.009	81.8
	August	0.2	2.11	0.038	0.007 (0.002)	0.023 (0.018)	0.008	79.7

trations < 0.004 mg l^{-1} compared to those of the Almond where they approached 2.2 mg l^{-1}. Generally TP concentrations were greatest in the 'summer' samples. The rivers could be ranked in the following order of their increasing averaged TP contents although some overlap between individual samples did occur: Ness, Conon, Tay, Dee, North Esk, Ythan, Almond.

Dissolved phosphorus

Concentrations of SRP varied widely between rivers (Table 3) and could be ranked by increasing SRP concentrations in a similar order as for TP. All rivers, except the Almond had SRP concentrations < 0.02 mg l^{-1} and for the Conon, Ness and Tay were at or below the detection limit in all surveys. The North Esk and Ythan show little variation between sampling occasions while the Dee and the Almond show a trend of higher summer SRP concentrations. The contribution of SRP to TP for individual samples ranged from < 4% to 94% and was significantly correlated ($P = 0.01$), both with the inclusion of the Almond data ($R^2 = 0.978$) and without ($R^2 = 0.762$). Concentrations of DOP varied between being undetectable and 0.55 mg l^{-1} (Table 3). The Conon and Ness rivers show the smallest DOP concentrations that were at or below the detection limit. For all rivers except the Almond DOP concentrations were below 0.025 mg l^{-1}. While the trend between the seven rivers is similar to that of TP and SRP it is less clear-cut. DOP concentrations tended to be higher in 'summer' and this was especially clear for the Tay, Dee, Ythan and Almond. Summer DOP concentrations exceeded SRP for all rivers except the Almond. In the majority of cases TDP dominated the TP present in water samples which was more apparent for the July and August samples where for the Almond it approached 100%.

Particulate phosphorus

Concentrations of PP varied between 0.001 mg l^{-1} and 0.13 mg l^{-1} (Table 3). Lowest PP concentrations were found in the Conon and Ness, followed by the Tay, North Esk, Dee and Ythan, with highest PP concentrations in the Almond. For the Ythan and Conon PP concentrations increase with river flow. An opposite behaviour was observed for the North Esk and Dee. The Ness, Tay and Almond showed no clear trends. Concentrations of PP for all rivers were positively correlated with SPM concentration.

Fractionation of SPM

The total phosphorus content (TPC) of SPM varied over one order of magnitude (Figure 4) between 0.1% (Conon, July) and 1.1% (Almond, July). A positive relationship ($TPC = 0.0759 \ln(SRP) + 0.8369$) existed between SRP concentrations and TPC ($R^2 = 0.681$). There was clear evidence for a seasonal change in TPC with the highest increases occurring for the Dee and Almond. The P content of SPM collected form the River Almond was always greater than that of any other river.

The individual significance of P fractions in SPM varied between rivers and sampling date (Figure 5). The PP fraction was usually dominated by P_{org} that regularly accounted for more than 50% of the TPC. Three other fractions P_{exch}, P_{Al} and P_{red} together made up most of the remaining TPC although their relative significance's varied. All rivers except the Conon and Ness experienced higher P_{exch} during the two 'summer' samplings.

Composition of SPM

The POC varied between 12.6%–42.2% although there was little evidence for any seasonal trend (Table 4). An inverse relationship ($R^2 = 0.506$) between POC and

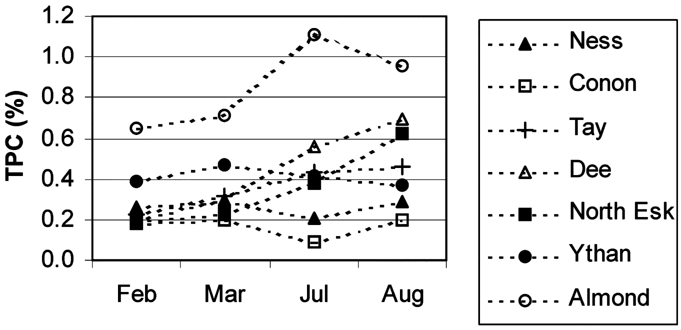

Figure 4. Comparison of P contents (%) of SPM between rivers and at different sampling times.

SPM existed (POC = $26.775*SPM^{-0.2501}$) and at SPM concentrations < 10 mg l^{-1} POC values between 15 and 40% of SPM were typical (Figure 6). Chl-a was generally small, below 1 μg l^{-1} for the Ness, Conon and Tay, with intermediate values for the Dee, North Esk, and Ythan and up to 5 μg l^{-1} for the Almond (Table 4). Concentrations of Chl-a were positively correlated with either TP (TP = $0.0019e^{1.5463Chl\text{-}a}$; $R^2 = 0.785$) or SRP (SRP = $0.0002e^{2.1019Chl\text{-}a}$; $R^2 = 0.738$) (Figure 7). Phytoplankton was estimated to account for between 10 to 25% of POC in half the samples (Table 4) and more than 25% in 4 samples.

Ratios of POC to P_{org} (C/P_{org}) show a wide variability between rivers (Table 4) being between 700 and 1200 for the River Conon compared to 100–200 typical of the Almond. Seasonal variations within rivers were less pronounced. The C/P_{org} ratio is a function of POC content of SPM (Figure 8) and there is a positive correlation between the C/P_{org} ratio and POC ($R^2 = 0.46$).

Discussion

Partitioning of P between the solid and solution phases present in river systems is highly sensitive to the attributes of upstream sources of P and the prevailing local environmental conditions. Over the longer-term most streams retain only a small fraction of the P load that they actually receive (Melack 1995) however factors can operate over shorter time periods that can influence P retention (House et al. 1998). The transport of P within rivers represents a highly dynamic process responding rapidly to changes in the flow regime. Periods of greatest sediment and P transport tend to occur under high flow conditions in response to episodic erosion events. Typically these storm driven events may represent perhaps only 5–10% of the total year (Foster 1995) be characterised by short retention times and contribute disproportionally to the total annual P budget. These 'hydrologically active' periods of maximum P loss tend to occur outwith the 'biologically active' growing season and therefore are likely to have the major impact for receiving waterbodies downstream.

Within individual stream reaches the most intensive period of biological activity is likely to be associated with summer low flow conditions. For this reason the

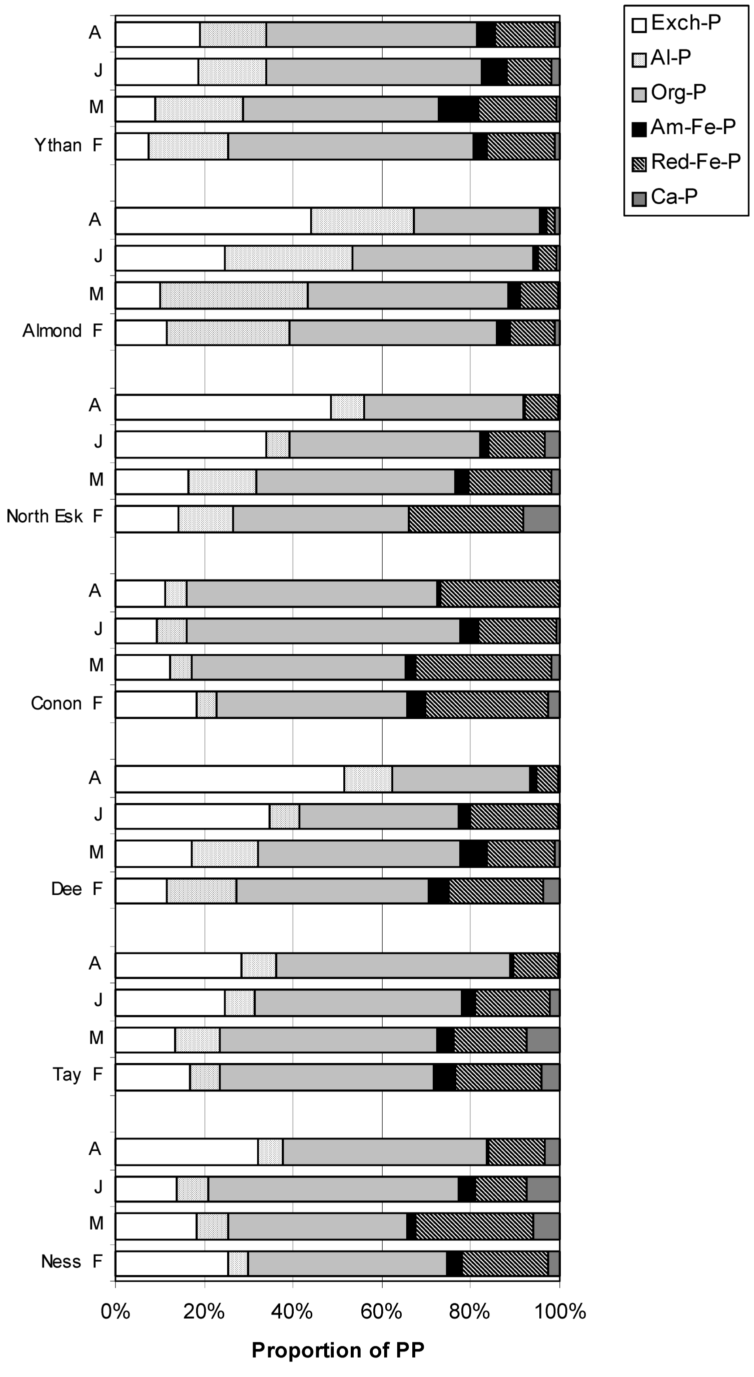

Figure 5. Fractionation of P in SPM of seven Scottish rivers where exchangeable (P_{exch}), aluminium oxyhydroxide sorbed (P_{Al}), organic (P_{org}), amorphous iron oxyhydroxide sorbed (P_{am}), reducible iron oxyhydroxide sorbed (P_{red}) and apatite (P_{Ca}) are expressed as a % of PP.

Table 4. Summary of Chlorophyll *a* (Chl-a) concentrations (μg L^{-1}), Particulate Organic Carbon (POC) content (Wt%) of suspended particulates, and the atomic ratio of organic C/P for all sampling occasions. An estimate of the amount of carbon bound in phytoplankton is expressed as a percentage of POC.

	Survey	Chl-a	POC	POC/Org-P	Algal-C/POC
Ness	February	1.06	31.8	739	46
	March	0.82	42.2	763	30
	July	0.29	23.7	570	8
	August	0.30	35.7	721	10
Tay	February	0.98	25.0	547	20
	March	0.83	16.2	279	14
	July	0.66	23.4	282	16
	August	0.70	26.4	286	15
Dee	February	0.89	18.8	575	21
	March	1.00	40.6	745	15
	July	1.66	39.8	510	20
	August	2.25	29.2	347	17
Conon	February	0.64	30.8	1069	9
	March	0.70	27.2	711	12
	July	0.45	32.0	1187	7
	August	0.59	40.9	888	12
North Esk	February	0.95	15.9	573	23
	March	1.13	19.8	537	26
	July	1.94	20.6	332	22
	August	1.25	25.7	299	17
Almond	February	1.64	16.1	139	5
	March	2.75	12.6	99	6
	July	5.01	22.8	126	17
	August	3.71	22.5	212	18
Ythan	February	1.05	15.2	182	8
	March	2.32	21.1	261	17
	July	2.72	15.9	204	41
	August	1.39	20.9	313	16

present study has focused upon quantifying P forms and concentrations under low flow conditions where daily P fluxes may well be of limited quantitative significance to the annual P budget. During high flow conditions particulate forms of P should dominate while under low river flows the emphasis would be expected to shift towards dissolved P (Hilger et al. 1999). Dissolved P was the dominant fraction in all the water samples collected during the current study. Averaged figures for the contribution of TDP to TP were 56% and 70% for 'winter' and 'summer' samples respectively. Concentrations of TP were always above the limit of detection although only 3 samples collected from the group of four near pristine catchments (Ness, Tay, Dee and Conon having < 30% agricultural land use) were > 0.01 mg P l^{-1}. Concentrations of SRP were often below the limit of detection and sel-

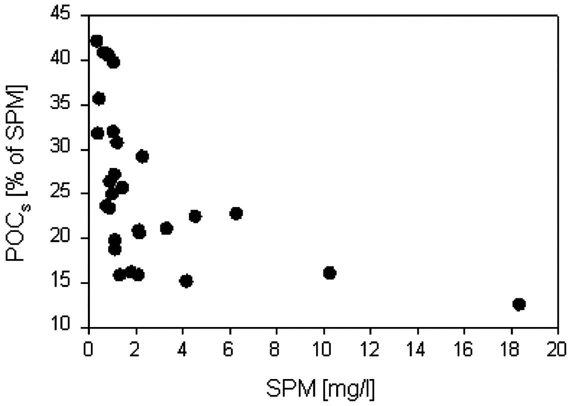

Figure 6. Relationship between particulate organic carbon (POC) and the concentration of suspended particulate matter (SPM) in river water.

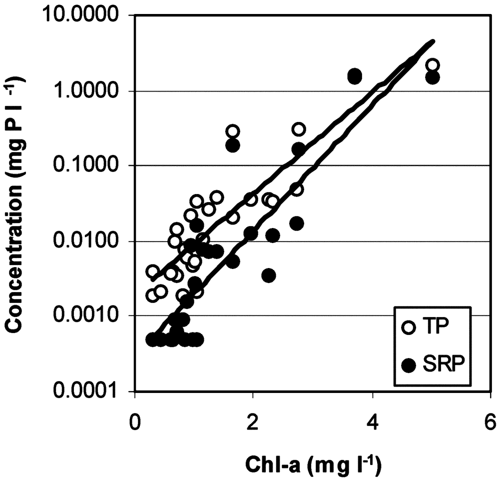

Figure 7. Relationship between concentrations of TP or SRP and chlorophyll *a* plotted for all samples.

dom rose above 0.01 mg P l^{-1} except for river systems draining the more agriculturally dominated catchments (North Esk and Ythan) and the River Almond where 'summer' concentrations reached 1.5 mg P l^{-1}. The increasing SRP concentration during summer low flow periods observed for the Almond are typical of point source impacted rivers (Muscutt and Withers 1996). When concentrations of SRP were small the relative significance of DOP was increased making on some occasions it the dominant form of dissolved P. The ratio of inorganic to organic P has been shown to widen from < 2 in upland streams to > 4 in the lower reaches of rivers (Owens and Walling 2002) in the present study it was < 1 in all samples except for those from the Almond and the two winter samples from the Ythan. The potential biological significance of the dissolved P fraction which dominated TP

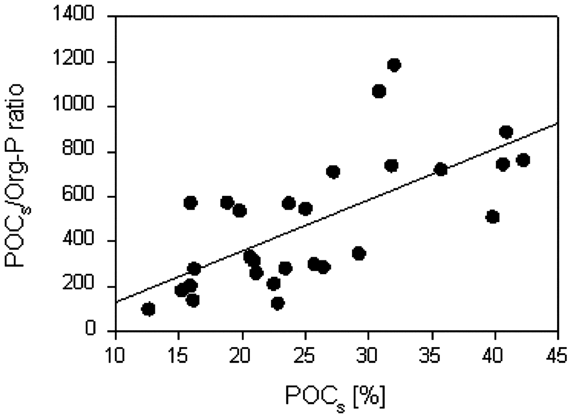

Figure 8. Molar ratio, (C/P)org, of particulate organic carbon, POC, and particulate organic phosphorus, P_{org} as a function of POC. The regression line is included.

under low flow conditions is born out by the positive relationship between either TP or SRP and chlorophyll *a*.

The SPM present in rivers originates externally from a combination of terrestrial (e.g., soil) and industrial/domestic effluent or will be the result of ’instream’ biological production/transformation. The relative significance of any given source will vary both spatially and temporally. In the present study concentrations of SPM were generally small particularly for the near pristine systems (often < 1 mg l^{-1}) but comparable to surveys of the adjacent River Don where concentrations were typically 1–10 mg l^{-1} during base flow compared to 150 mg l^{-1} under high flow conditions (Hillier 2001). Organic matter frequently made up 60 to 80% of SPM in the Conon, Ness and Dee although was slightly lower for the remaining rivers (30 and 50%). An inverse relationship existed between POC and SPM which has also been reported in other studies (Cauwet et al. 1990; Meybeck 1982) and indicated a shift in emphasis from organic to inorganic components at higher SPM concentrations.

Up to half of the POC was associated with phytoplankton, but values of 20% were more typical and SEM observations indicated the presence of inorganic and organic particulate material together with abundant phytoplankton (diatom). An amorphous organic component also acted as a cementing agent. Organic matter contents of SPM from the River Don ranged from approximately 24% during low flow to 13% during the storm events (Hillier 2001) with wax/proteins dominating under low flow conditions whilst humate/fulvate material being more clearly identifiable during high flows. These differences probably reflect a change from in-stream primary production at low flows compared with greater contributions from more terrestrial origins under high flows.

A ’world’ averaged P content of 0.1% for SPM (Froelich 1988) is similar to those found in the near pristine systems studied here and is exceeded by an order of magnitude in samples from the more impacted rivers which are more typical of those quoted for the Rhine (van der Weijden and Middelburg 1989). The significance of different levels of contamination on the amount and composition of PP in three different English rivers has recently been demonstrated by Owens and Walling (2002). The relative richness of SPM in P may be partly attributable to the greater sorption capacity of fine-grained material typical of these soils (He et al. 1995; Maguire et al. 2002) as well as the presence of biological material with higher P contents (House and Casey 1989).

The general significance of organic matter within the SPM was also evident in the fractionation of PP. Generally P_{org} was the dominant form of P present often being > 50% of the total and similar findings have been reported for SPM from other rivers (Mayer et al. 1991) and estuaries (Conley et al. 1995). The proportion of P_{org} and TPC were inversely related to particle size for soils from the North East of Scotland, many typical of those contributing to the SPM of these rivers (He et al. 1995). Absolute values of P_{org} found by He et al. (1995) in the smallest size fraction ranged from 0.03–0.1% and were comparable to some values found in this study although many did exceed this range reaching values up to 0.45%.

The composition of organic material did not remain constant becoming depleted in P with increasing POC suggesting either a source of P-deficient organic matter or the operation of some transformation/mineralisation process that selectively released P (Froelich et al. 1982). Atkinson (1987) conducted a study on coastal sediments and argues that an widening C/P_{org} ratio of organic matter in the early stages of mineralization was attributable to a rapid release of about 50% of the P content of plant material. Preferential mineralisation of labile P_{org} such as algal P would result in a widening of the C/P_{org} ratios in SPM (Atkinson 1987; Hecky et al. 1993; Ramirez and Rose 1992). It is also possible that a potential underestimation of P_{org} may contribute to wide C/P_{org} ratios. Lebo (1991) has shown that phytoplankton release P in the saline rinse (P_{exch}) and Mayer et al. (1991) attributed high C/P_{org} ratios of *ca.* 1000 observed in SPM from the Niagara river to this artefact.

Catchment characteristics exerted a major influence on C/P_{org} ratio. It was apparent that differences between sampling occasions are of minor significance compared to the variation in the C/P_{org} ratio between rivers. Atomic C/P_{org} ratios from this study (100–1200) fall within the range reported by Ramirez and Rose (1992). Those rivers, which derive a large proportion of water from upland areas, exhibited the widest C/P_{org} ratios (Ness, Conon, and Dee) while those ratios observed for the lowland rivers Almond and Ythan are narrower and form a separate group. The SRP concentration appeared to be inversely related to the C/P_{org} ratio in SPM. The degree of pollution may be an integral factor responsible for the narrow C/P_{org} values with Ramirez and Rose (1992) suggesting a threshold of $C/P_{org} = 500$ to distinguish between polluted and unpolluted rivers. The C/P_{org} ratios obtained for the agricultural Ythan were in the range 200–300 and are surprisingly consistent with this idea. The wider C/P_{org} of SPM from the near pristine rivers presumably reflects a combination of the organic, humic acid rich soils which typically have C/P ratios > 500 together with a lower than optimum growth rate of phytoplankton/epiphyton. Phytoplankton composition in rivers may differ from the commonly quoted Redfield stoichiometry (106:1 C:P) (Redfield et al. 1963) due to luxury uptake at high ambient SRP concentrations which may lead to narrowing of the C/P ratio, whilst C/P of 1000 can be observed when grown under nutrient limiting conditions (Goldman et al. 1979). The occurrence of Redfield type ratios for the Almond coincides with this river having the largest Chl-a of the rivers studied.

Large increases in P_{exch} were observed for the two summer samplings of the Dee, North Esk and Almond. Samples collected in the summer from these rivers also had the largest diatom numbers, indicating that phytoplankton may contribute to the observed increase in P_{exch}. Additionally, adsorption of SRP from solution onto particles during low flow may also contribute to the summer increases in P_{exch} (House et al. 1998). When summed P_{exch} and P_{am} have been equated to PP_{avail} (Dorich et al. 1985) and may serve as an additional source of labile P if dissolved P becomes depleted. PP_{avail} exceeded SRP only at very low SRP concentrations and when SRP concentrations > 0.008 mg l^{-1} dissolved P was at least 4 times larger than PP_{avail}. A shift in importance from dissolved to particulate transport will occur at higher SPM concentrations induced by higher than average flows emphasizing the significance of flood events transporting large quantities of SPM. In a study on lakes, Santiago and Thomas (1992) have shown that phytoplankton utilization of particulate derived P appeared to proceed when SRP concentrations dropped below a threshold of about 0.015 mg l^{-1}, a level similar to that for which buffering of dissolved phosphate is observed in turbid rivers.

Conclusion

Comparison with long-term data indicated that the objective of quantifying P dynamics under conditions of low flow had been achieved. The near pristine conditions of the highland rivers Ness, Conon and Dee were characterised by small concentrations of SPM and TP which were < 0.01 mg P l^{-1} and regularly below detection limit. The rivers draining more agriculturally dominated catchments supported greater concentrations of SPM and TP that became particularly enhanced in the point source (industrial and domestic) impacted River Almond. Concentrations of TP tended to be greater on the two 'summer' sampling occasions. In the majority of water samples the soluble P fraction dominated and in the most extreme cases accounted for > 90% of the TP. Amounts of dissolved organic P were generally small but became a more significant component in the near pristine rivers and during the summer.

The composition of SPM varied containing between 10 and 40% organic carbon, a significant fraction of which was algal in origin. The P content of SPM ranged between 0.1 and 1.1% and was directly related to the extent of human impact within each catchment. A significant relationship existed between either TP or SRP and algal biomass. Organic-P tended to be the dominant particulate form of P in all samples. Readily exchangeable particulate P was in many cases the second most abundant fraction becoming more significant during the summer. However, under these low flow conditions the readily exchangeable particulate P fraction only represented a small component of the TP and would be likely to represent a significant source of labile P only where SRP concentrations were particularly small, such as in the near pristine systems.

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