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Role of riverine colloids in macronutrient and metal partitioning and transport, along an upland-lowland land-use continuum, under low conditions.

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Abstract

An integrated assessment is made of the role of riverine colloids in macronutrient (nitrogen, phosphorus and carbon), metal and trace element partitioning and transport, for five rivers in the Ribble and Wyre catchments in north-western England, under baseflow/near-baseflow conditions. Cross-flow ultrafiltration was used to separate colloidal (<0.45 >1kDa) and truly dissolved (<1kDa) fractions from river water. Clear patterns were observed, along the upland-lowland land use continuum, in the partitioning and transport of macronutrients and metals between the colloidal, truly dissolved and acid-available particulate (>0.45µm, suspended) fractions. Of these operationally-defined fractions measured, colloids were generally more important for both macronutrient and metal transport in the upland than in the lowland rivers. The results suggest that organic moieties in truly dissolved form from sewage effluent may have a greater capacity to chelate metals. Organic-rich colloids in the upland moorlands and metal oxide colloidal precipitates in the industrial rivers had a higher capacity for binding metals than

the colloidal fractions in the urban and agricultural lowland rivers. Aggregation of these colloids may provide an important mechanism for formation of larger suspended particulates, accounting for a much higher degree of metal enrichment in the acid-available particulate fractions of the upland moorland and lowland industrial rivers than in the lowland agricultural and urban rivers. This mechanism of transfer of contaminants to larger aggregates via colloidal intermediates, known as 'colloidal pumping' may also provide a mechanism for particulate P formation and the high proportion of P being transported in the particulate fraction in the uplands. The cross-flow ultrafiltration data also allowed refinement of partition coefficients, by accounting for colloids within the solids phase and replacing the filtered (<0.45µm) fraction with the truly dissolved (<1kDa) concentrations. These provided a clearer description of the controls on metal and P partitioning along the upland-lowland continuum.

1. Introduction

Rivers transport large quantities of macronutrients (N, P and C) and metals to the sea (Meybeck, 1982; Seitzinger et al., 2010), with important implications for not only pollutant flux transfers, but also the water quality and ecology of rivers, lakes and coastal areas (Carpenter et al., 1998; Smith et al., 1999; Turner and Rabalais, 1994). The bioavailability, behaviour, fate and transport of macronutrients and metals along the aquatic continuum from land to sea are dependent on their partitioning between dissolved, colloidal and labile (acid-leachable) particulate phases (Koukal et al., 2003; Vignati et al., 2005; Vignati et al., 2009; Wang and Guo, 2000). Routine water quality monitoring studies largely use a single filtration step with a membrane pore size of 0.45µm to provide an operational separation between “dissolved” and “particulate” concentrations of macronutrients and metals, but several studies have shown the role of sub-0.45µm colloids as important metal and macronutrient ‘nano-vectors’ which pass through the membranes pores and are therefore measured as part of the “dissolved” phase (Horowitz et al., 1996; Morrison and Benoit, 2004; Vignati et al., 2009). However, there is relatively little published data which directly measures colloidal metal and macronutrient concentrations and their partitioning in river waters (Guo and Santschi, 2007; Lead and Wilkinson, 2006; Shafer et al., 1997; Vignati et al., 2009) . Using cross-flow ultrafiltration, this study provides a first assessment of the role of colloids in *both* macronutrient, metal and trace element partitioning and transport along a continuum represented by five river types draining typical land use types in northwestern England. The study is based on the Ribble and Wyre basins of northwestern England which encompass a wide range of land uses from upland moorland to lowland agricultural, urban and industrial settings. Given the time-intensive nature of sample processing using cross-flow ultrafiltration, one bulk sample was taken at each of the 5 sampling sites under low-flow conditions. The work is set within a wider context of hydrochemical monitoring for a major Source-to-Sea research platform within the Ribble/Wyre basin in northwest England (Neal et al., 2011a; Neal et al., 2011b).

The aims of the study were to (i) examine the utility of cross-flow ultrafiltration techniques to quantify colloidal and truly dissolved fractions in macronutrient, metal and trace element transport in rivers; (ii) examine the controls on macronutrient, metal and trace element partitioning between colloidal, labile particulate and truly dissolved phases along an upland-lowland land use continuum and (iii) assess the role of colloids as biogeochemical ‘nuclei’ linking macronutrient and metal cycling in rivers. These aims were addressed by the following specific objectives, to: (a) directly quantify the partitioning of macronutrients, metal and trace element concentrations between particulate, filtered, colloidal and truly dissolved concentrations; and (b) evaluate the affinity of macronutrients, metals and trace elements for colloidal and truly dissolved organic carbon fractions and for solid and solution phases, by considering both acid-available particulate and colloidal fractions within the solids phase.

2. Study Area

The study area covers the rivers Ribble and Wyre in northwest England (SI, Fig 1), which have catchment areas of 1084 km^2 and 273 km^2, respectively. Both rivers flow southwards then westward to the Irish Sea, draining upland areas of outstanding natural beauty (Yorkshire Dales and the Trough of Bowland). In its lower reaches, the Ribble drains some of the major urban and industrial areas of Lancashire (Accrington, Blackburn, Burnley and Wigan), whereas the Wyre basin is much more rural in nature. The upper reaches of both rivers drain acid moorland, while the lowland vales are dominated by grassland with sheep and intensive dairy farming. The lower Ribble valley has a legacy of the industrial revolution, with industrial and post-industrial urban conurbations, including the impacts of mine waste and mine water pollution and heavy industry.

Five river sampling sites were chosen to cover a continuum of representative catchment land-use types: upland moorland, lowland agricultural, lowland urban and lowland industrial. Further information on these sampling sites and catchment characteristics can be found elsewhere (Neal et al., 2011b).

- *Upland moorland*: there were two upland sites, the Tarnbrook, in the headwaters of the Wyre, and the Dunsop, a tributary of the Hodder that subsequently joins the lower River Ribble. These upland sites represent acid moorland areas impacted from long-term acidic deposition, with minimum population and agricultural pressures
- *Lowland agricultural*: the Eller, in the south-western Ribble basin, which is dominated by arable farming. The Eller drains into the lower River Douglas.
- *Lowland urban*: the lower Douglas was chosen as a heavily urban and sewage-impacted site: the monitoring point was just downstream of Wigan and Skelmersdale sewage treatment works (STWs).
- *Lowland industrial*: the Hyndburn, which drains through Accrington with a long legacy of contamination from heavy industry, but no direct sewage effluent discharges.

3. Materials and Methods

3.1 Sampling and filtration

Bulk river-water samples were collected and filtered through 0.45µm high-capacity capsule filters prior to cross-flow ultrafiltration (see below for details). A 0.45µm filtration was chosen as this is used as an operational separation between "dissolved" and "particulate" fractions in routine water quality monitoring programmes (Neal et al., 1997). Although formal definition of "colloidal" refers to material within the 1 nm to 1µm size range (Lead and Wilkinson, 2006), in this study the term colloidal refers to colloidal material in the <0.45µm fraction to allow comparison with routine river water quality monitoring datasets.

Water sampling, filtration, cross-flow ultrafiltration and chemical analysis were carried out from 8-13 September 2008. Sampling was targeted at baseflow conditions. However, during the weekend before sampling (6-7 September), a rainfall event meant that sampling was undertaken on the falling limb of a small hydrograph, meaning that flow conditions were slightly elevated above baseflow (see Supporting Information, SI Fig. 2). For example, the mean daily river flow for the River Douglas during the cross-flow ultrafiltration survey was 6.5 $m^3 s^{-1}$, compared with a mean daily flow of 5.0 $m^3 s^{-1}$ over the 2-year water quality monitoring period.

During the cross-flow ultrafiltration survey, a 20 L sample of river water was collected at each of the five sites using acid-cleaned polypropylene bottles, but on different days. Only one sample could be processed each day due to the total time required to collect, transport and process the samples and undertake analysis of unstable analytes. For example, a working day for one sample was over 9 hours. The programme could not be speeded up as diligence was required throughout the exercise to safely transport the samples, reduce contamination and filtration errors and to ensure that analyses were undertaken on the day of analysis where appropriate. The details are as described below.

Samples were returned immediately to the laboratory and, within 2 hours of sampling, each river water sample was filtered through an Opticap XL4 Durapore 0.45 µm capsule filter. To avoid any adsorption to, or release from, the filter, the first 1 L of filtered river water was discarded. The remaining filtered river water was collected for cross-flow ultrafiltration and a sub-sample analysed for macronutrients, major anions and cations and trace elements. A sample of unfiltered river water was used for measurement of pH, alkalinity, suspended solids total phosphorus and total acid-available total concentrations of major and trace elements (see chemical analysis section below).

Additional supporting data from routine water quality monitoring as part of the Ribble/Wyre Source to Sea programme (Neal et al., 2011b) are provided to place the cross-flow ultrafiltration study within wider context. Full details of the routine monitoring and analysis programme can be found in (Neal et al., 2011b). Routine sampling was undertaken fortnightly for twelve months, starting on 18th February 2008, with monthly sampling thereafter for a further year.

3.2 Cross-flow ultrafiltration

Cross-flow ultrafiltration (CFUF) was used to separate the colloidal and truly dissolved fractions within the <0.45µm filtered river water. A standard Millipore Pellicon 2 Cross CFUF system was used, with a 1 kDa (~1 nm) nominal pore size regenerated cellulose membrane (0.5 m^2 surface area), connected to a peristaltic pump; this equipment has been used by other investigators for sampling and concentration of riverine colloids (Cai and Guo, 2009; Guo et al., 2001; Liu et al., 2007; Wilding et al., 2005). Before use, the whole system was cleaned by several recycling and flushing cycles using 0.1N HNO_3, then with DDI water and then flushed with 2L of the <0.45 µm fraction river water to condition the system. The CFUF system was closed to minimise any sample contamination. 15 L of the filtered (<0.45µm) river water was subject to CFUF under continuous recycling concentration mode under the following conditions: feed inlet pressure 15-20psi, retentate outlet pressure 10 psi and permeate flow rate 30-40 ml/min (Liu and Lead, 2006; Wilding et al., 2004). The flow of the retentate (in which the colloidal material is retained and concentrated) was directed back into a retentate flask and the permeate (which passes through the ultrafiltration membrane) was directed into a large permeate container. A constant volume of 5 L in the retentate flask was maintained by re-supply of the remaining 10 L of filtered (<0.45µm) river water from a larger feed container, using a secondary peristaltic pump, at the rate of permeate production, until the remaining 10 L of filtered river water in the feed flask had been exhausted. CFUF was then continued until the volume of retentate reached c. 1L. This final retentate volume was chosen to achieve a retentate concentration factor of c. 15, as recommended for recovery of colloidal material from river waters by Liu and Lead (2006) and Liu et al. (2007). The volume of retentate collected (V_r) was recorded and compared with the volume of permeate (V_p) to calculate the concentration factor (cf):

$$cf = V_p / V_r$$

Sub-samples of filtered river water, permeate and retentate were taken for chemical analysis as described below. These concentrations were then used to calculate a mass balance recovery coefficient (M_r), as follows:

$$M_r = (C_r . V_r) + (C_p . V_p) / (C_f . V_f)$$

C_r is the concentration of the analyte in the retentate, C_p is the concentration in the permeate, C_f is the concentration in the filtered (<0.45µm) river water and V_f is the starting volume of filtered (<0.45µm) river water used for CFUF.

3.3 Chemical Analysis

All the samples were stored in the dark at c. 4°C prior to analysis, to minimise sample degradation. A summary of the chemical analyses performed on the different water fractions (unfiltered river water; <0.45 µm filtered river water, CFUF retentate and <1kDa permeate) is shown in Supporting Information SI Table 1. Full details of the chemical analyses can be found in (Neal et al., 2011a; Neal et al., 2011b).

Suspended sediment concentration was determined gravimetrically by filtering one litre of unfiltered river water through a Whatman GF/C filter and drying to 105°C.Conductivity, pH and Gran alkalinity were also measured on unfiltered samples. Gran alkalinity was measured using a Mettler-Toledo DL53 auto-titrator and a two-point pH 4.50 and 4.20 methodology and pH was measured on the day of sampling using a Radiometer GK2401C glass electrode, taking care to avoid de-gassing of the samples. Electrical conductivity (25°C) was measured using a Jenway 4320 meter.

For the metals and trace elements analysis, sub-samples were acidified to 1% with concentrated nitric acid (Baker Ultrex 70%). The acidification step was introduced to avoid sample deterioration and release particulate bound components in the case of the unfiltered samples. A Perkin Elmer DV4300 Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) was used to determine boron, silicon, iron, aluminium and the major cations. The concentrations of an extensive suite of trace elements were determined using a Perkin Elmer Elan DRC 11 Inductively Coupled Plasma-Mass Spectrometer (ICP-MS).

The labile acid-available particulate fraction (AAP) was calculated as the difference between the acid-leached concentrations measured from an unfiltered water sample and the filtered (<0.45 µm) river water. The AAP concentration represents an operational measurement of the more labile acid-soluble fractions associated with suspended particulate matter, but excludes the more refractory and acid unreactive components.

Molybdate reactive phosphorus (MRP) and ammonium-nitrogen (NH_4-N) were analysed colorimetrically using a Seal AQ2 discrete analyser by molybdenum blue and indo-phenol blue chemistry, respectively. To avoid sample deterioration, MRP was measured on the day of sampling. Total phosphorus (TP) was also determined by molybdenum blue colorimetry as with the MRP, but prior to analysis, the sample was autoclaved under strongly acidic conditions with a persulphate oxidant to break down particulate organic and polymeric colloidal forms of phosphorus. Organic phosphorus (OP) was calculated as the difference between TP and MRP.

Chloride, nitrate and sulphate were determined by ion chromatography (Dionex DX100). Organic carbon (OC) and total dissolved nitrogen (TDN) were simultaneously analysed on a Shimadzu TOC-V CPH analyser. Samples were pre-acidified on the instrument’s autosampler and aspirated to purge off most of the inorganic carbon and volatile compounds. The acidified sample was combusted and a conductivity detector determined C while the total dissolved nitrogen (TDN) was determined by chemiluminescence. Organic nitrogen (ON) was calculated as the difference between the TDN and the inorganic nitrogen species (IN: NH_4-N + NO_2-N + NO_3-N) in mg-N/l units.

Instruments were calibrated for each batch of samples using a range of standard solutions. Values exceeding the top calibration standard were diluted and the analysis repeated. The measurements were validated using values from the analysis of internal QC samples, certified reference materials and regular proficiency testing samples supplied by Aquacheck Ltd. The analysis was conducted using methods which were mainly accredited by United Kingdom Accreditation Service to ISO 17025.

3.4 Validation of ultrafiltration membrane performance and mass balance

To provide an initial validation test for the CFUF performance, two molecular probes (KH_2PO_4, MW 0.136 kDa, and Vitamin B12, MW 1.3 kDa), were employed. The KH_2PO_4 standard (16 µM) was used to determine how much of the macronutrient, P, might be being retained by the membrane and CFUF apparatus. A mass balance P recovery coefficient of 0.97 (corresponding with 95% permeation) demonstrated negligible sorption losses of P during the cross-flow ultrafiltration process, a negligible quantity within the retentate fraction and thus excellent permeation efficiency of the membrane.

The Vitamin B12 standard (0.2µM) was use to test for the effectiveness of the membrane to recover colloidal material with a molecular weight just above the nominal pore size of 1 kDa. Very high retention (coefficient of 0.99) was observed as assessed by estimating the retention coefficient (RC), which equalled 1 - (C_p / C_r), where C_p and C_r are the concentrations of standard colloid molecules in the permeate and retentate, respectively.

<Table 1>

For the CFUF survey, mass balance recovery coefficients (M_r) for each of the analytes is shown in Table 1. A loss of material occurs when M_r <1; contamination occurred when M_r > 1. For most analytes, M_r ranged from 0.85-0.98 (mean, M_r, 0.93±0.1), demonstrating good recovery of macronutrients, metals and trace elements during the cross-flow ultrafiltration process. There appeared to be a 15% contamination of Si which may have arisen from the regenerated cellulose membrane, and around 30% loss for Ce, Fe and Al during cross-flow ultrafiltration (see Discussion section for further details).

3.5 Partitioning of macronutrients, metals and trace elements between dissolved, colloidal and macroparticulate phases

Empirical partition coefficients are a widely-used means of relating dissolved and solid-phase concentrations of metals, trace elements and macronutrients to the concentrations of suspended particular matter in aquatic systems (Benoit et al., 1994; Neal et al., 1997; Turner and Millward, 2002; Turner et al., 1993). These are not true equilibrium coefficients as they are dependent on factors such as pH, temperature and the concentrations of suspended solids (Benoit and Rozan, 1999; Pankow and McKenzie, 1991; Shafer et al., 1997). In their basic form, the effective of use has been questioned previously on the basis both on the meaningfulness of the AAP fraction and the presence of colloidal material (Gustafsson and Gschwend, 1997; Neal et al., 1997). However, for this study, partition coefficients provide us with a simple empirical method for understanding partitioning of macronutrients and metals. By using the CFUF data, we were able to evaluate the influence colloids on partition coefficients. Here, three types of partition coefficients were examined:

1. K_{oc}, a distribution coefficient normalised to organic carbon was used to assess the distribution of macronutrients and metals between organic C in colloidal and truly dissolved fractions (Martin et al., 1995):

$$K_{oc} = (M_c/COC) / (M_{<1kDa}/UOC)$$

Where M_c is the colloidal determinand concentration, $M_{<1kDa}$ is the truly dissolved (<1 kDa) determinand concentration, COC is the colloidal organic carbon concentration and UOC is the truly dissolved (‘ultrafiltered’, <1 kDa) organic carbon concentration. K_{oc} is dimensionless.

This approach allowed us to explore the complexing capability of colloidal organic C relative to truly dissolved (macromolecular) organic C.

2. K_{d_std} , simple partition coefficient between the acid-available particulate fraction and the filtered (<0.45µm fraction), expressed in units of L kg^{-1}:

$$K_{d\_std} = (M_{aap} / SPM) / M_f$$

Where M_{aap} is the acid-available particulate concentration, SPM is the suspended particulate matter concentration and M_f is the concentration in the filtered (<0.45 µm) fraction.

This is a standard partition coefficient employed in routine water quality studies which use an operational (0.45 µm) separation between dissolved and labile particulate fractions.

3. K_{d_cfuf}, a refined partition coefficient, expressed in units of L kg^{-1}, derived using the cross-flow ultrafiltration data. Unlike K_{d_std}, K_{d_cfuf} accounts for the colloidal concentration along with the acid-available particulate concentration within the 'solid' phase and the <1kDa fraction (rather than <0.45µm fraction) as the truly dissolved phase:

$$K_{d\_cfuf} = (M_{solid}/SPM)/M_{<1kDa}$$

Where M_{solid} is the sum of the acid-available particulate concentration and the colloidal concentration ($M_{aap} + M_c$)

3.6 Terminology for the chemical fractions measured

Within this study, the following terminology is used for the chemical fractions reported:

- *filtered* is the concentration in river water which passes through a 0.45 µm filter membrane;

- *colloidal* is the concentration within the filtered river water fraction which is retained by the cross-flow ultrafiltration membrane within the ‘retentate’ fraction (i.e. >1kDa <0.45 µm)
- *truly dissolved* is the concentration within the filtered river water fraction which passes through the cross-flow ultrafiltration membrane into the ‘permeate’ fraction (i.e. <1kDa fraction)
- *acid–available particulate (AAP)* is the acid-leachable fraction of the suspended particulate matter in the >0.45 µm fraction, derived from subtracting the filtered concentration from the concentration derived from an acid digest on an unfiltered sample. *AAP* is not a measure of the total element associated with the solid phase and the measure is an operational semi-quantitative one, that might be considered as the acid labile component of suspended particulate matter. Its inclusion here is simply to provide an initial estimate of measure of the labile particulate fraction.
- *labile solids (LS)* is the sum of the acid-available particulate and colloidal concentrations

4. Results

The results presented here represent the first assessment of the colloidal component for five samples taken from rivers draining a range of clean to polluted environments. They cover the baseflow/near-baseflow component and not high-flows as this was beyond the capability of this study; the findings must be viewed in this light.

4.1 Concentrations of macronutrients, metals and trace elements within the filtered and colloidal fractions

<Table 2a>

The concentrations of metals, trace elements and macronutrients within the filtered (<0.45µm) fraction for the CFUF survey are shown in Table 2a, along with averages and ranges in concentrations from longer-term monitoring at the same sites under the Ribble/Wyre Source to Sea programme. The results showed that the samples collected during the CFUF survey are highly representative of wider longer-term water quality conditions within the rivers over the two year monitoring period. For many of the analytes which were identified by Neal et al (2011b) as having predominantly diffuse catchment sources (e.g. Fe, Ce, Ti, Ni, Al, Cr, dissolved organic carbon (DOC) and Si), the concentration during the CFUF survey was higher than the mean long-term value. This may correspond with the slightly higher than average flow conditions during the survey and some greater diffuse source mobilisation during the time of the survey. In contrast, other analytes linked to effluent or groundwater (e.g. Ca, Sr, Mg, SO_4, K, Rb, Na and Cl) were generally lower than long-term mean values during the CFUF survey, reflecting a small dilution effect. However, the samples collected during the CFUF survey were well within the long-term ranges sampled in the Source-to-Sea study.

Overall, there was a separation in filtered macronutrient and metal concentrations between the rural upland moorland, and the lowland sites which have greater anthropogenic influence. For most determinands, concentrations were higher in the lowlands due to pollutant inputs from effluents and/or contaminated land. Only Al, Ce, Fe and Mn had higher concentrations in the moorland rivers (Dunsop and Tarnbrook), reflecting leaching of lithogenic minerals from the organic-rich acidic soils in the moorlands. Despite this, the upland streams were circum-neutral as a result of buffering by groundwater inputs enriched with base cations. There were much higher concentrations of TP, MRP and major anions and cations in the lowland urban river (Douglas) resulting from proximity to sewage effluent inputs. The industrial river (Hyndburn) had very high concentrations of certain trace elements such as As and Ce, linked to contaminated waterways and the legacy of heavy industry within the catchment (Neal, 2007; Rowland et al., 2011). The agricultural river (Eller) had elevated concentrations of suspended solids, TDN and DOC, linked to farming activities and high concentrations of many of the base cations and Si associated with greater weathering rates within tilled agricultural soils (Jarvie et al., 1997; Jarvie et al., 2008; Neal et al., 2005; Neal et al., 2011b).

<Table 2b>

The percentage contributions of colloids within the filtered river water are shown in Table 2b. Bringing together the filtered (<0.45 µm) concentrations and colloidal percentages in Tables 2a and 2b, several key groupings of elements were identified:

- **Elements found predominantly in colloidal form (i.e. average > 50% colloidal; Fe, Ce, OC, OP, ON, Ni, Cd and Ti)**. Elevated filtered (<0.45 µm fraction) concentrations of Fe, Ce and Cd were found in moorland rivers (Fe and Ce in the Tarnbrook), Cd (in the Dunsop), although there is also an industrial source of both Fe and Ce, given the high concentrations in the industrial river (Hyndburn). Highest filtered concentrations of Ni and Ti occurred in the urban river (Douglas) and the agricultural river (Eller). OP and ON had highest filtered concentrations in the urban river (Douglas), whereas OC was highest in the agricultural river (Eller).

- **Elements in largely truly dissolved form (average <20 % colloidal; Cl, IN, B, Si, Na, Rb, K, Ca, Sr, Mg, SO_4)**. Most of these elements showed a strong increase in concentrations between the upland and lowland rivers, linked to sewage, agricultural and weathering sources from tilled soils. Cl, B, Na, Rb, K, SO_4, Mg, Sr, Ca had highest concentrations in the urban river (Douglas), whereas inorganic nitrogen and Si had highest concentrations in the agricultural river (Eller). Given the very low colloidal percentages, these high-solubility elements are not considered in detail here, as focus is placed on the wide range of macronutrients and metals which partition between dissolved, colloidal and AAP phases.

- **Elements with intermediate colloidal percentages (Ba, Mn, V, TDN, Mo, MRP, Se, As, Sb, Cr, TP and Al)**. Highest filtered concentrations of these elements occurred in the anthropogenically-impacted lowlands (with the exception of Al). Mn, Mo, MRP, Se, Cr, TP had highest filtered concentrations in the urban river (Douglas), suggesting a dominant sewage source. Ba, V, TDN, Sb had highest filtered concentrations in the agricultural river (Eller). Highest filtered concentrations of As were found in the industrial river (Hyndburn). The percentage colloidal contributions of these elements tended to be lower in the lowlands, compared with the uplands.

4.2. Relationships between filtered, colloidal and truly dissolved fractions

<Table 3>

Table 3 shows the regression relationships between colloidal vs filtered and truly dissolved vs filtered fractions and plots for example relationships are shown in Figure 1. A “cross-over” point (C_e) between these two relationships is identified as the intersection where a switch occurs between either colloidal or truly dissolved concentrations dominating the filtered fraction.

For most determinands (TP, MRP, OP, TDN, ON, Ti, V, Cr, Mn, Ni, As, Se, Mo, Sb and Ba), the gradient was higher for the truly dissolved vs filtered fractions than for the colloidal vs filtered fractions. In most cases, colloidal fractions dominated under the lower filtered concentrations in the upland moorland rivers (Dunsop and Tarnbrook), but truly dissolved fractions dominated at the higher filtered concentrations in the lowland rivers. Only TDN, V, As and Ba have no intersection between the colloidal and truly dissolved regression lines (i.e. C_e is less than the lowest measured filtered concentration); this demonstrates that, for TDN, V, As and

Ba, the truly dissolved fraction dominated right along the continuum between upland and lowland river sites.

The remaining determinands (Al, OC, Fe, Ce and Cd) all had higher gradients for the relationship between colloidal vs filtered fractions. The C_e for Al, Ce and Cd, showed that truly dissolved fractions dominated at lower concentrations in the lowland urban (Douglas) and agricultural (Eller) rivers. Colloidal fractions dominated under the higher concentrations in the rivers draining the upland moorlands (Dunsop and Tarnbrook). For Ce and Cd, higher concentrations were also found in both the filtered and colloidal fractions in the industrial river (Hyndburn). There was no cross-over point in the colloidal and truly dissolved regression relationships for OC and Fe, since colloidal forms of OC and Fe were dominant right along the continuum between upland and lowland river sites.

4.3. Partitioning of macronutrients, metals and trace elements between colloidal and truly dissolved organic carbon fractions

<Table 4>

The partitioning of macronutrients, metals and trace elements between colloidal and truly dissolved organic carbon fractions was examined using K_{oc} values (Table 4). The affinity of macronutrients and metals for colloidal and truly dissolved organic carbon was highly variable between determinands and sites. For the majority of the determinands, K_{oc} values were lower than 1, indicating that the truly dissolved organic carbon generally had a higher affinity for macronutrients and metals than the colloidal organic carbon. The monitoring site on the urban river (Douglas), which was located immediately downstream of a major sewage effluent discharge, had the lowest K_{oc} values for many determinands, suggesting that the organic carbon in the truly dissolved fraction from sewage effluent may have a high capacity for complexing macronutrients and metals.

K_{oc} values > 1 indicate a greater affinity for colloidal rather than truly dissolved organic carbon. Fe had a greater a greater affinity for colloidal organic carbon in the moorland river (Dunsop), the agricultural river (Eller) and the industrial river (Hyndburn) (K_{oc} values for Fe in these rivers ranged from 1.27 to 3.84). Ce had a greater affinity for colloidal organic in the moorland river (Dunsop) and the industrial river (Hyndburn), where K_{oc} values for Ce were 1.76 and 2.34, respectively. Total P and OP in the industrial river (Hyndburn) also had higher affinity for colloidal organic carbon rather than truly dissolved organic carbon (K_{oc} 1.06 and 1.89 respectively). In the agricultural river (Eller), OP also had a higher affinity for colloidal organic carbon (K_{oc} 5.05). In the moorland river (Tarnbrook) and agricultural river (Eller), ON also had a higher affinity for colloidal than truly dissolved organic carbon (K_{oc} 1.44).

4.4. Acid-available particulate fractions and the effects of including colloids within the particulate fraction

<Table 5>

The concentrations of acid-available particulate fractions expressed as a percentage of the total acid leached concentration (%AAP) are shown in Table 5. Analytes with the highest average %AAP were Al (55%), Fe (46%), and MRP (44%); in contrast Rb and Ba had less than 10% AAP. The agricultural river (Eller) had the highest % AAP for most analytes, reflecting a much higher suspended solids concentration in river water draining largely arable land (Table 2a). Lowest % AAP for most analytes were found in the moorland river (Dunsop).

<Table 6>

Table 6 shows the AAP concentrations normalised to suspended solids concentrations (AAP/g-SS). Highest AAP/g-SS values for P, Fe and Ce were found in the moorland river (Dunsop);. Highest AAP/g-SS for Al, Ti, V, As, Rb, Cd and Ba were found in the industrial river (Hyndburn). Highest AAP/g-SS for P, Cr and Mn were found in the urban river (Douglas).

The labile solids (LS/g-SS) is defined here as the sum of the colloidal and acid-available particulate concentrations normalised to the suspended solids concentration. A higher proportion of analytes had highest LS/g-SS values in the moorland river (Dunsop) (Al, Fe, V, Cr, Se, Cd, Ba). LS/g-SS values for Ti, Ce, As and Rb were highest in with the industrial river (Hyndburn) with LS/g-SS for P and Mn highest in the urban river (Douglas). Despite the agricultural river (Eller) having the highest %AAP values, none of the analytes considered here had highest AAP/g-SS or LS/g-SS in the Eller. The greatest increases between AAP/g-SS and LS/g-SS (as a result of inclusion of colloidal concentrations), were for P, Ce and Cr in the industrial river (Hyndburn), For all other analytes, the greatest increases as a result of including colloidal concentrations occurred in the moorland rivers (Dunsop and Tarnbrook).

4.5 Use of cross-flow ultra-filtration data to refine solid-solution partition coefficients

<Table 7>

The affinity of each of the analytes for solid and solution phases was assessed using two empirical partition coefficients (Table 7). K_{d_std} is a standard and widely-used coefficient which simply evaluates the partitioning between AAP and filtered (<0.45 µm) concentrations. K_{d_cfuf} , which is based on the cross-flow ultrafiltration data and uses the *truly* dissolved (<1 KDa) concentrations, accounting for the colloidal concentrations within the solid phase, along with AAP. Highest K_{d_std} values were found in the moorland river (Dunsop) for all analytes, apart from Al, Ti and Cd, which had highest K_{d_std} values in the industrial river (Hyndburn) and Ce , which had highest K_{d_std} in the urban river (Douglas). Lowest K_{d_std} values were for Rb in the agricultural river (Eller) and the urban river (Douglas).

Accounting for colloids within the solid phase, K_{d_cfuf} resulted in an increase in the apparent affinity of most analytes for the solids phase. The greatest increases between K_{d_std} and K_{d_cfuf}

were for Ce in the moorland river (Dunsop) and Cd in the other moorland river (Tarnbrook), with a 70 times and 48 times increase between K_{d_std} and K_{d_cfuf}, respectively. In general, the greatest increases between K_{d_std} and K_{d_cfuf} were for the moorland rivers: Al, Ti, Ce, As and Ba in the Dunsop; Mn, Se, Cd and Ba in the Tarnbrook. For MRP, Fe and Cr, greatest increases between K_{d_std} and K_{d_cfuf} were in the industrial river (Hyndburn) and for Rb in the urban river (Douglas). Once colloids are taken into account, most analytes had highest partition coefficients in the Dunsop and all analytes had lowest partition coefficient in the agricultural river (Eller).

<Figures 2a & 2b>

Figures 2a and 2b show inter-element correlation matrices for K_{d_std} and K_{d_cfuf}. For the K_{d_std} correlation matrix, there was a high degree of data scatter in inter-element relationships, with the only positive correlations in K_{d_std} occurring between As, Se and V. In contrast, by accounting for colloids and the truly dissolved fraction, the K_{d_cfuf} showed a dramatic increase in inter-element correlations, demonstrating the importance of colloids in controlling a wide range of metal partitioning along the upland-lowland land-use continuum.

5. Discussion

5.1 Cross-flow ultrafiltration to quantify colloids and truly dissolved fractions in macronutrient transport

The suitability of cross-flow ultrafiltration as a technique for separating and quantifying colloidal and truly dissolved macronutrient fractions has been demonstrated by a combination of molecular probes and mass balance recoveries. The molecular probes showed excellent separation between permeate and retentate either side of the 1 kDa membrane pore size, with 99% recovery of Vitamin B_{12} (MW 1.3 kDa) in the retentate and 97% recovery of KH_2PO_4 (MW 0.136 kDa) in the permeate. Mean mass balance recoveries were 94% for P, 99% for N and 95% for OC demonstrating minimal contamination or losses of these macronutrients during the cross-flow ultrafiltration process.

Nitrogen and phosphorus concentrations in all fractions (filtered, colloidal and truly dissolved) were consistently highest in the lowland rivers of the Ribble/Wyre catchment. Nitrogen fractions were highest in agricultural river (Eller), linked to fertiliser sources. Phosphorus fractions were highest in the urban river (Douglas), as a result of large sewage effluent discharges from Wigan and Skelmersdale STWs. Very little of the inorganic N in the rivers (5-8%) was colloidal, owing to the high solubility of nitrate as the dominant N fraction. In contrast, MRP had much higher colloidal percentages (11-52%), with highest percentages (>40%) in the moorland rivers (Dunsop and Tarnbrook) and the industrial river (Hyndburn). These percentages are consistent with wider observations of colloidal P within surface freshwaters (Cai and Guo, 2009; Haygarth et al., 2006; Haygarth et al., 1997; Hilger et al., 1999). Colloidal material constituted a much higher proportion of the organic forms N and P, compared with the inorganic forms. Between 41 and 72% of organic nitrogen was colloidal, with highest colloidal ON percentages in the moorland rivers (Dunsop and Tarnbrook) and in the agricultural river (Eller). Between 26 and 87% of OP was colloidal, with highest colloidal OP percentages in the agricultural river (Eller) and industrial river (Hyndburn). Between 56 and 80% of OC was colloidal with highest colloidal percentages in the moorland rivers (Dunsop and Tarnbrook). Colloidal fractions dominated the OC loads in all of the rivers. In general, colloids were more important for macronutrient transport in the uplands than the lowlands. For TP, MRP and ON, colloids dominated at lower concentrations in the upland moorland rivers (Dunsop and Tarnbrook), with truly dissolved fractions dominating at higher filtered concentrations in the lowland rivers. This is shown by the intersection between colloidal and truly dissolved concentrations when plotted against the filtered (<0.45µm) fraction and the higher gradient for the truly dissolved concentrations of all macronutrient fractions, except OC

5.2 Controls on macronutrient partitioning between colloidal, acid-available particulate and truly dissolved phases

Substantial concentrations of filtered P and N were as organic fractions (up to 429 µg-P L^{-1} as organic P and 1.4 mg-N L^{-1} as organic N). Therefore, distribution coefficients normalised to organic C (K_{oc}) provided a means of exploring the partitioning of N and P fractions between organic C in colloidal and truly dissolved phases. The K_{oc} values revealed that most P and N fractions had a greater affinity for the truly dissolved (<1 kDa) organic C than colloidal organic C. This is most pronounced in the urban river (Douglas), which had the lowest K_{oc} value. However, it is likely that a high proportion of the truly dissolved MRP in the Douglas is orthophosphate in addition to any organic-P complexes from sewage effluent. With the exception of the upland moorland river (Tarnbrook), K_{oc} values for OP were higher than for MRP and TP and K_{oc} values for ON were higher than TDN. This indicated that organic P and N fractions generally have more affinity for colloidal organic C than the inorganic fractions. Only in a few situations did the macronutrient affinity for colloidal organic C exceed the affinity for truly dissolved organic C (i.e. $K_{oc} > 1$): ON in the moorland river (Tarnbrook) and the agricultural river (Eller) and OP in the agricultural river (Eller) and the urban river (Hyndburn). These were also the sites which had the highest colloidal percentages of ON and OP, as discussed above.

Here, discussion of partitioning with respect to labile acid-available particulate fractions is restricted to P (the acid-available MRP fraction, which is also regarded as the most readily available particle-bound fraction (Ekholm, 1994)), as there were no corresponding labile particulate measurements were available for N. The proportion of MRP transported as acid-available particulate P was higher in the uplands, where up to 62% of MRP was as AAP in the moorland river (Dunsop). The percentage of AAP as MRP declined from uplands to lowlands, falling as low as 27% in the industrial river (Hyndburn). Highest values of K_{d_std} showed that the highest suspended particulate affinity for MRP was in the upland moorland river (Dunsop). Lowest suspended particulate affinity for MRP was in the agricultural (Eller) and urban (Douglas) rivers: these sites are dominated by sewage with very high MRP concentrations that may exceed the P-sorption capacity of the suspended particulate matter. By accounting for colloids within a wider 'solids phase', the K_{d_cfuf} partition coefficient used the results of cross-flow ultrafiltration to quantify partitioning between solids (both macroparticulates and colloids) and the truly dissolved fraction. There was no significant change between K_{d_std} and K_{d_cfuf} for the Eller and Douglas, indicating that colloidal fractions had little impact on the partitioning of MRP between dissolved and particulate phases. However, for the Hyndburn, there was a dramatic (5-fold) increase in K_{d_cfuf} above K_{d_std}, demonstrating the importance of colloids in P transport in this lowland industrial river system. Accounting for colloids as solids also resulted in a 3 fold increase in K_{d_cfuf} above K_{d_std} in the Dunsop, with K_{d_cfuf} in the Dunsop 6 times higher than in the Hyndburn and c.150 times higher than in the Eller.

Whilst suspended solids concentrations were higher in the lowlands, the affinity of P for suspended solids was considerably lower in the lowlands than in the uplands, potentially resulting from (a) lower P sorption capacity linked to a greater history of exposure to P and fewer available P sorption sites per unit mass (particularly in the urban Douglas, linked to very high AAP/g-SS concentrations and very high MRP concentrations in the truly dissolved phase) and/or (b) higher concentrations of larger particles, with lower specific surface area and thus lower P sorption capacity per unit mass (in the agricultural Eller).

Colloids play a much greater role in P transport within the filtered (<0.45 µm) fraction the upland moorland rivers (Dunsop and Tarnbrook) and the industrial river (Hyndburn). In the uplands, links between the high proportion of the filtered (<0.45µm) P fraction being transported as colloids and the high % AAP may indicate that colloidal aggregation may result in formation of macroparticulates, via the process of colloidal ‘pumping’. Colloidal pumping is the process by which particle-reactive species are rapidly adsorbed onto colloidal particles, which in turn coagulate into macroparticulates (Honeyman and Santschi, 1991; Stordal et al., 1996; Wen et al., 1999). Uptake of P into/onto these colloids and their subsequent aggregation may play a role in reducing P bioavailability relative to more readily bioavailable truly dissolved fractions which dominate in the sewage dominated lowland urban and agricultural rivers. In the Hyndburn, the high proportion of the <0.45µm P fraction as colloids was not linked to a high % AAP value, suggesting a decoupling of colloidal and AAP fractions and perhaps greater colloidal stability in the Hyndburn.

In the Douglas, there also appears to be a decoupling of P between colloidal and AAP fractions, albeit via a different source. The combination of very low colloidal percentages for P in the <0.45 µm fraction, low %AAP but very high AAP/g-SS (which is not substantially increased from AAP/g-SS to LS/g-SS, i.e. when colloids are included within the solids phase) suggests a different source of suspended particulate P: either P-rich suspended solids from sewage or sorption of phosphate to suspended solids, i.e. with colloidal intermediates being of lesser importance than in the uplands.

5.3 Cross-flow ultrafiltration to quantify colloids and truly dissolved fractions in metal and trace element transport

Mean mass balance recoveries after CFUF for most metals and trace elements exceeded 85%. The exceptions were Al, Fe and Ce, where slightly lower recoveries (mean 70-75%) indicated losses during cross-flow ultrafiltration, possibly as a result of precipitation of oxyhydroxides and sorption/deposition within the ultrafiltration equipment; this is consistent with results reported elsewhere (Guo and Santschi, 2007; Wilding et al., 2004; Wilding et al., 2005).

The upland moorland streams (Dunsop and Tarnbrook) had high filtered concentrations of Fe, Ce, Cd and Al concentrations linked to mobilisation in acid runoff from peaty soils, although there was also a clear industrial source of Fe, Ce and Cd in the Hyndburn. There was also a strong industrial source of As in the industrial river (Hyndburn). For the other elements, there was a strong upland-lowland transition with lower concentrations in the upland moorland rivers (Dunsop and Tarnbrook) and highest concentrations in the sewage-impacted urban river (Douglas) and agricultural river (Eller).

For many metals, colloids dominated the filtered (<0.45µm) river water in the uplands, whereas truly dissolved fractions were proportionally greater in the lowland rivers. In the uplands, mixing of acid-runoff with much higher alkalinity groundwater and resultant buffering of the runoff from acid moorlands may well result in rapid oversaturation with respect to easily hydrolysable metals of low solubility under near neutral conditions and the production of colloidal forms (Neal et al., 2011a,b). Fe was the only metal which was found predominantly in colloidal form along the entire upland-lowland transition.

5.4 Controls on metal partitioning between colloidal, acid-available particulate and truly dissolved phases

Many easily hydrolysable metals, such as Fe, Al Ce, Ti, Cr and Cd, had high concentrations in the truly dissolved phase. These easily hydrolysable metals might be expected to have very low solubility at the pHs encountered, and therefore it a major part of the truly dissolved loads may be associated with complexation by macromolecular organic ligands which stabilise these metals in solution (Neal et al., 2011a; Neal et al., 2008, Lofts et al, 2008). There are other ions such as sulphate, fluoride, hydroxyl and bicarbonate that may complex with particular metals, but this aspect is beyond the scope of the work. Indeed, higher truly-dissolved metals concentrations occur in the lowlands where the pHs are higher, but where there are industrial and sewage effluent sources. Thus, it seems that source controls (possibly with increased complexation by pollutants that are at their highest concentrations under low-flow conditions at the time of CFUF sampling) override pH controls in these systems.

The higher concentrations of easily hydrolysable metals in the truly dissolved fractions within the sewage-impacted urban river (Douglas) were reflected in the very low K_{oc} values. These K_{oc} values indicated a markedly higher affinity of metals for the truly dissolved organic C fraction in the lowlands, compared with the upland river sites. In contrast, Fe and Ce had greater affinity colloidal than truly dissolved organic carbon in the upland moorland river (Dunsop), lowland agricultural river (Eller) and lowland industrial river (Hyndburn). The upland moorland rivers (Dunsop and Tarnbrook) and lowland industrial river (Hyndburn) tended to have higher K_{oc} values, yet there was no correlation across the sites between K_{oc} values and DOC concentrations. This suggests that differences in the chemistry of the organic carbon in truly dissolved and colloidal phases between upland moorland, lowland, agricultural, urban and industrial rivers are more important than organic carbon concentrations *per se* in controlling the complexation or chelation of metals. For example, in the case of Fe, concentrations were found to increase over many years for an upland site in mid-Wales and this followed increases in DOC concentrations. In this case, although there was a correlation between Fe and DOC, the relationship occurred because the DOC promoted colloidal Fe formation rather than just incorporation of Fe into or onto to the DOC macromolecules (Neal et al., 2008).

The agricultural river (Eller) had the highest concentration of suspended particulate matter, linked to higher rates of soil erosion from arable land. This corresponded with the highest metal % AAP values in the Eller, as a result of erosion of detrital soil-derived particulates. In general, there was an increase in the percentage of total acid-available metals as AAP going from the uplands to the lowlands, linked to higher suspended solids loads in the lowland rivers. However, the agricultural river (Eller) had consistently low AAP/g-SS values. This indicates that suspended solids derived from soil erosion had low metal concentrations, likely as a result of larger particle sizes, with a lower specific surface area for metals sorption.

The upland moorland river (Dunsop) and the industrial river (Hyndburn) had consistently higher AAP/g-SS values, demonstrating much higher levels of metal contamination per unit mass. When colloids are included within the solids phase, the increase in concentration from AAP/g-SS to LS/g-SS was greatest in the upland moorland rivers (Dunsop and Tarnbrook) and the industrial river (Hyndburn). This corresponded with increases in the affinity of metals for particulates, as seen by the large increases from K_{d_std} to K_{d_cfuf} in the uplands and in the Hyndburn. There was an important difference between the detrital suspended solids derived from soil erosion in the agricultural river (Eller), which have relatively low affinity for metals compared with the organic-rich colloids in the uplands and metal oxide precipitates in the industrial rivers, which appear to have a high capacity for binding metals. Aggregation of these highly contaminated colloids may provide an important mechanism for formation of macroparticulates (>0.45 µm), via the colloidal pumping mechanism, with wider implications for metal and trace element transport and bioavailability (Honeyman and Santschi, 1991; Koukal et al., 2007; Vignati et al., 2009). The high concentrations of metals in truly dissolved form immediately downstream of the sewage works on the urban river (Douglas) indicate that macromolecular organics in the truly dissolved (<1 kDa) fraction may play an important role in chelating metals in sewage effluent discharges. Companion studies (Neal et al., 2011a) examined the behaviour of Ti along the river further downstream of these sewage discharges and saw marked losses of filtered (<0.45µm) Ti downstream. This likely resulted from transfer of the dissolved species to larger (>0.45µm) aggregates via colloidal intermediates. Indeed, the colloidal intermediates and colloidal pumping mechanism may provide an important mechanism for in-stream changes in the fractionation and bioavailability of metals during their transport through the fluvial system.

The weak inter-element correlations for K_{d_std} values and the dramatic improvement in inter-element correlations for K_{d_cfuf} demonstrates that partition coefficients derived from CFUF datasets (which account for colloids in the solids phase and use the <1kDa truly dissolved fraction) provide a clearer description of the chemical controls on metal and P partitioning along the upland-lowland land-use continuum. Accounting for colloids and truly dissolved concentrations does not result in a convergence of K_{d_cfuf} values between sites, so there is no clear evidence of a true equilibrium partition coefficient across the sites for any elements. This is because these are empirical partition coefficients, which depend on a range of factors such as pH, temperature and suspended solids concentration (Neal et al., 1997). However, the strong inter-element correlations for K_{d_cfuf} demonstrate (i) simple patterns in metal partition coefficients along the upland-lowland land-use continuum, (ii) the importance of colloids in controlling a wide range of metal partitioning and transport and (iii) the value of CFUF as a technique to separate and quantify the colloidal and truly dissolved components in the filtered (<0.45 µm) fraction which is operationally defined as the 'dissolved' fractions in routine water quality monitoring studies. The simple patterns and strong inter-element correlations in partition coefficients which emerge along the upland-lowland land use continuum is all the more remarkable, given the large differences in metal and macronutrient sources, concentrations and background hydrochemistry between the upland moorland, lowland agricultural, urban and industrial rivers sampled here. Indeed, these results points to the critical role of colloids in controlling partitioning of a wide range of metals across the diversity of land-use types covered by this study.

5.4 Colloids as biogeochemical 'nuclei' linking macronutrient and metals cycling in rivers

The results of this study have shown the importance of colloids for macronutrient and metal transport in the filtered (<0.45μm) fraction, which is classified as "dissolved" in routine water quality monitoring. In general, colloids were more important for macronutrient and metal transport in the filtered fraction of river water in the upland moorland rivers, than in the lowlands. A higher proportion of the filtered loads of macronutrients and metals were in truly dissolved form in the lowland rivers.

There appears to be a significant difference between the lowland sewage-impacted and agricultural sites (where relatively high detrital suspended solids concentrations arise from soil erosion and sewage-derived solids), compared with the upland moorland streams and the industrial rivers where the AAP/g-SS concentrations are considerably higher. This may be linked to a higher proportion of the suspended solids being derived from aggregation of colloids via the 'colloidal pumping' mechanism. Along the transition from upland moorlands to the lowland agricultural, urban and industrial rivers, natural organic carbon played a key role in chelation of metals in dissolved phase, colloid formation and colloid stability/aggregation and thus a wider role in the their transport and bioavailability. Differences in the chemistry of natural organic matter from moorland peat sources in the upland to sewage effluent in the lowlands is likely responsible for clear differences in partitioning of metals and macronutrients between truly dissolved and colloidal phases. Indeed, there were no significant correlations between organic C concentrations and colloidal or truly dissolved concentrations, or partition coefficients across the sites, suggesting that it is not simply the total concentrations of organic C that provide a major control on metal and macronutrient partitioning and that further information on the speciation, chemistry and nature of the organic matter from uplands to lowlands is required to establish process controls (Worsfold et al., 2008). Techniques such as NMR, FTIR and fluorescence spectroscopy offer new possibilities to probe the role of organic compounds in metal partitioning within the truly dissolved and colloidal phases (Chen et al., 2002; Lead et al., 2006; Liu et al., 2007; McKnight et al., 1997; Simpson et al., 2011). Flow field-flow fractionation also allows more detailed insight into the chemical composition associated with size distributions across the colloidal and subcolloidal continuum (Gimbert et al., 2008; Gimbert and Worsfold, 2009; Hassellov et al., 1999; Stolpe et al., 2010)

In the heavily sewage-impacted lowlands, unexpectedly high concentrations and proportions of metals in the in the truly dissolved phase indicate that the organic matter in effluent has a high capacity for chelating easily hydrolysable metals. However, further work is now required to establish whether the very high truly dissolved concentrations measured for the urban sewage-impacted river (Douglas) may be an artefact of the very close proximity of the sampling site to the effluent discharge and that the macromolecular organic-metal and macronutrient complexes entering via sewage effluent may act as pre-cursors to colloid and larger aggregate formation during downstream transport within the river. This may explain the differences observed between the urban river (Douglas) and industrial river (Hyndburn). The Hyndburn sampling site, while subject to effluent discharges, is not within immediate downstream proximity of any sewage treatment works. Moreover, further work is now needed to establish the role of macromolecular organic metal and macronutrient complexes in colloid formation and aggregation of intermediates for macroparticle formation during downstream transport. For example, river reach ‘spiralling’ studies could be augmented using CFUF methods to allow more detailed evaluation of the role of colloids in transforming bioavailability and fluxes of metals and macronutrient during downstream transport.

6. Conclusions

This study has demonstrated the value of cross-flow ultrafiltration for separating and quantifying the contributions of colloidal and truly dissolved fractions for macronutrient and metals transport across a range of rivers and along a continuum from upland moorland to lowland agricultural, urban and industrial land-use types. Clear differences in the partitioning and transport of N, P, C and metals between were observed between the colloidal, truly dissolved and acid-available (labile) particulate fractions, according to different land uses along the upland-lowland continuum. Colloidal components were generally more important for both macronutrient and metal/trace element transport in the filtered (<0.45 µm) fraction in the uplands than in the lowlands. The generally high concentration of many easily hydrolysable metals (Fe, Al Ce, Ti, Cr and Cd) in truly dissolved form, above saturation levels for their inorganic metal ions, in the most heavily sewage impacted river particularly in the lowland rivers, is indicative of the role of macromolecular organic ligands from sewage effluent in chelation of metals,

The study indicates important differences in the origin and nature of metal and trace element transport along the upland-lowland continuum under baseflow/near-baseflow. In the lowland agricultural and urban rivers, suspended solids were derived from soil erosion and runoff from urban surfaces, with a relatively low degree of metal enrichment compared with the upland and industrial rivers. The organic-rich colloids in the uplands and metal oxide colloidal precipitates in the industrial rivers have a much higher capacity for binding metals. Subsequent aggregation of these more highly contaminated colloids may provide an important mechanism for formation of macroparticulates with a much higher degree of metal enrichment than in the agricultural and urban rivers. This mechanism of transfer of contaminants to larger aggregates via colloidal intermediates, known as colloidal pumping, may also provide a mechanism for particulate P formation and the high proportion of P being transported in the acid-available particulate fraction in the uplands.

Cross-flow ultrafiltration has allowed us to refine standard empirical partition coefficients by quantifying colloidal and truly dissolved components. By accounting for colloids within the solids phase and replacing the filtered (<0.45µm fraction) with the truly dissolved (<1kDa) concentrations, simple patterns and strong inter-element correlations in partition coefficients emerged along the upland-lowland continuum, despite the wide range in metal and macronutrient sources, concentrations and background hydrochemistry of the rivers sampled. This points to the important role of colloids in controlling the partitioning of a wide range of metals that are generally of low solubility, across a wide range of rivers and land-use types. It also demonstrates the value of using cross-flow ultrafiltration as a technique to separate and quantify the truly dissolved and colloidal components within operationally-defined <0.45µm "dissolved" fractions. In this study, we have examined one key end member under low-flow conditions, where effluent and groundwater inputs will be maximal. However, there is likely to be large variability in colloidal composition and concentration across the flow range, including hysteresis effects if supplies are limited. A vital next step will be to examine hydrological controls, with a systematic sampling campaign, to apply cross-flow ultrafiltration to river water samples, collected across different flow regimes and antecedent conditions.

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Table 1 Mass balance recovery (M_r) for cross-flow ultrafiltration survey on the Ribble/Wyre.

	Upland moorland		**Lowland agricultural**	**Lowland urban**	**Lowland Industrial**	
Analyte	**Dunsop**	**Tarnbrook**	**Eller**	**Douglas**	**Hyndburn**	**Mean recovery**
Si	1.13	1.14	1.02	1.06	1.02	1.07
Mo	1.3	0.97	0.99	0.98	1	1.05
Sb	1.07	0.96	0.99	0.96	0.99	0.99
Na	1.04	0.99	0.98	0.98	0.98	0.99
N	1.3	0.81	0.85	1.03	0.95	0.99
K	1	0.99	0.99	0.98	0.98	0.99
Cl	1.05	0.96	0.94	1	0.97	0.98
B	0.98	0.99	0.97	0.99	0.98	0.98
Ca	0.97	0.96	0.98	0.98	0.97	0.97
Mn	0.94	0.82	0.93	1.2	0.96	0.97
Mg	0.96	0.93	0.98	0.97	0.98	0.96
As	0.98	0.87	1	0.96	0.96	0.95
Rb	0.94	0.93	0.93	0.96	0.98	0.95
Se	1.1	0.8	1.02	0.93	0.88	0.95
OC	0.94	0.8	0.94	1.09	0.96	0.95
Sr	0.95	0.88	0.95	0.96	0.98	0.94
P	1.09	0.8	0.87	0.96	0.97	0.94
SO_4	0.92	0.88	0.91	1	0.98	0.94
Cd	0.99	0.81	0.91	1.05	0.81	0.91
Cr	0.85	0.81	1.1	0.85	0.94	0.91
Ba	0.9	0.76	0.97	0.96	0.96	0.91
Ni	0.94	0.79	0.89	0.88	0.93	0.89
Ti	1.07	0.79	0.6	0.85	0.92	0.85
V	0.94	0.8	0.93	0.92	0.64	0.85
Al	0.83	0.65	0.68	0.72	0.85	0.75
Fe	0.87	0.58	0.67	0.61	0.86	0.72
Ce	0.87	0.59	0.58	0.64	0.78	0.69

Table 2a: Comparison of the water quality and chemical concentrations in the <0.45µm fraction measured during the cross-flow ultrafiltration (CFUF) survey in September 2008 and the routine long-term (LT) monitoring for the Ribble/Wyre Source to Sea programme from February 2008 to March 2010

		Upland moorland		**Lowland agricultural**	**Lowland urban**	**Lowland Industrial**
Analyte	**fraction**	**Dunsop**	**Tarnbrook**	**Eller**	**Douglas**	**Hyndburn**
pH	CFUF survey	6.89	6.47	7.42	7.66	7.96
	LT mean	7.82	7.1	7.95	7.76	8.37
	(& range)	(6.51-8.66)	(5.94-8.94)	(7.68-8.28)	(7.56-7.95)	(7.76-9.16)
Alkalinity (µEq/L)	CFUF survey	527	87	2118	2954	2107
	LT mean	518	142	3054	2721	2404
	(& range)	(42-890)	(9-426)	(2340-3730)	(2260-3380)	(1060-3380)
Conductivity (µS cm^{-1})	CFUF survey	72.9	48.3	422	620	376
	LT mean	99.5	64.7	548	704	430
	(& range)	(43.9-136)	(45.3-94.4)	(256-921)	(455-1307)	(230-1130)
Suspended solids (mg/L)	CFUF survey	1.3	5.8	56	11	3
	LT mean	2.9	6.3	15.9	14.6	13.2
	(& range)	(0.4-29)	(0.6-61)	(2.2-340)	(5.1-150)	(1.6-102)
Fe (mg/L)	CFUF survey	0.440	0.849	0.155	0.255	0.559
	LT mean	0.195	0.368	0.173	0.201	0.262
	(& range)	(0.028-1.36)	(0.122-1.04)	(0.061-0.45)	(0.102-0.403)	(0.011-1.26)
Ce (µg/L)	CFUF survey	0.4	0.6	0.2	0.101	1.275
	LT mean	0.2	0.3	0.1	0.05	0.1
	(& range)	(0.01-0.6)	(0.1-0.7)	(0.02-0.5)	(0.02-0.2)	(0.002-0.6)
OC (mg/L)	CFUF survey	10.1	14.3	15.1	11.3	9.4
	LT mean	5.22	7.61	12.2	10.6	7.4
	(& range)	(1.46-17)	(2.64-18.8)	(7.11-24.9)	(5.59-19.3)	(3.16-17.3)
OP (µg/L)	CFUF survey	7	12	19	429	58
	LT mean	5	9	10	210	167
	(& range)	(4-13)	(2-39)	(6-72)	(24-850)	(8-480)
ON (mg/L)	CFUF survey	0.4	0.4	0.8	1.4	0.7
	LT mean	0.2	0.3	0.9	1.2	0.5
	(& range)	(0.3-0.7)	(0-0.7)	(0-5.6)	(0-7.4)	(0-1.3)
Ni (µg/L)	CFUF survey	2.11	2.55	3.35	3.38	3.12
	LT mean	1.0	1.6	2.5	2.6	1.9
	(& range)	(0.3-2.3)	(0.8-2.9)	(1.6-4.6)	(0.7-5.4)	(1.1-3.1)
Cd (µg/L)	CFUF survey	0.1	0.05	0.03	0.02	0.1
	LT mean	0.05	0.04	0.03	0.02	0.06
	(& range)	(0.01-0.1)	(0.01-0.08)	(0.01-0.6)	(0.01-0.05)	(0.01-0.2)
Ti (µg/L)	CFUF survey	1.4	1.6	5.1	6.5	2.6
	LT mean	0.9	1.9	3.7	6.5	2.1
	(& range)	(0.2-2.3)	(0.3-12)	(1.3-14)	(0.5-13)	(0.4-17)
Al (mg/L)	CFUF survey	0.18	0.22	0.13	0.06	0.051
	LT mean	0.09	0.14	0.08	0.04	0.04
	(& range)	(0.001-0.25)	(0.02-0.34)	(0.01-0.47)	(0.01-0.18)	(0-0.37)
TP (µg/L)	CFUF survey	15	24	138	1080	131
	LT mean	9	15	450	1460	62
	(& range)	(0-18)	(3-54)	(129-1250)	(404-3000)	(15-170)
Cr (µg/L)	CFUF survey	0.5	0.4	1.67	1.73	1.5
	LT mean	0.2	0.3	0.8	0.6	0.5
	(& range)	(0-0.6)	(0.5-0.8)	(0.3-1.6)	(0.2-1.3)	(0.2-1.2)
Sb (µg/L)	CFUF survey	0.1	0.1	2.1	1.2	1.46
	LT mean	0.1	0.1	1.2	0.8	0.9
	(& range)	(0-0.3)	(0-0.3)	(0.2-1.9)	(0.1-1.3)	(0.6-1.7)
As (µg/L)	CFUF survey	0.5	0.483	1.94	2.52	3.17
	LT mean	0.3	0.338	1.92	2.34	3.77
	(& range)	(0.2-0.6)	(0.149-0.603)	(0.604-4.42)	(0.395-3.22)	(0.25-7.75)
Se (µg/L)	CFUF survey	0.3	0.3	0.6	0.772	0.601
	LT mean	0.3	0.3	0.7	0.6	0.5
	(& range)	(0.2-0.5)	(0.1-0.3)	(0.4-1.2)	(0.3-1.2)	(0.1-0.8)
MRP (µg/L)	CFUF survey	8	12	119	651	73
	LT mean	4	6	340	1251	65
	(& range)	(0-12)	(0-29)	(110-964)	(212-2600)	(4-122)

Mo (µg/L)	CFUF survey	0.1	0.04	2.0	2.2	1.0
	LT mean (& range)	0.16 (0.05-0.63)	0.08 (0-0.51)	1.8 (1.1-3.1)	1.9 (0.8-3.9)	0.9 (0.6-1.7)
TDN (mg/L)	CFUF survey	0.8	0.7	7.6	5.3	1.9
	LT mean (& range)	0.6 (0.4-1.1)	0.6 (0.3-1.2)	6.1 (3.6-9.9)	9.6 (5.2-16)	1.7 (0.9-2.6)
V (µg/L)	CFUF survey	0.3	0.4	2.6	1.0	0.6
	LT mean (& range)	0.2 (0.1-0.4)	0.3 (0.1-0.9)	1.8 (0.3-2.5)	0.9 (0.2-2.5)	0.5 (0.2-1.3)
Mn (µg/L)	CFUF survey	13	30	50	57	29
	LT mean (& range)	9 (2-35)	21 (5-47)	23 (5-55)	81 (4-172)	39 (9-102)
Ba (µg/L)	CFUF survey	16	22	66	37.4	52.6
	LT mean (& range)	17 (11-24)	24 (17-34)	62 (43-98)	36 (24-58)	58 (23-83)
Ca (mg/L)	CFUF survey	7.1	2.8	45	57	42
	LT mean (& range)	10 (2.7-15)	3.9 (1.9-6.3)	63 (47-75)	57 (46-66)	45 (3.7-58)
Sr (µg/L)	CFUF survey	18	11	130	176	138
	LT mean (& range)	24 (8-38)	15 (9-26)	182 (123-269)	195 (138-258)	166 (14-279)
Mg (mg/L)	CFUF survey	1.6	0.8	8.36	13.3	6.17
	LT mean (& range)	2.4 (0.7-3.7)	1.3 (0.7-2.1)	13 (4.1-16)	15 (3-20)	7.6 (1.2-12)
SO4 (mg/L)	CFUF survey	2.0	1.5	11	30.5	13
	LT mean (& range)	2.5 (0.9-3.6)	1.9 (1-2.9)	15 (10-32)	33 (21-45)	15 (4.5-25)
K (mg/L)	CFUF survey	0.6	0.5	6.1	12.5	3.99
	LT mean (& range)	0.8 (0.4-1)	0.7 (0.5-1.3)	7.6 (2.5-13)	13 (1.5-23)	4.2 (0.7-5.5)
Rb (µg/L)	CFUF survey	1.0	1.05	2.62	7.55	3.23
	LT mean (& range)	1.0 (0.8-1.5)	1.3 (0.8-2.4)	3.5 (1.9-7.6)	8.0 (1.1-12)	3.2 (1.0-4.6)
Na (mg/L)	CFUF survey	4.5	4.03	9.59	45	21
	LT mean (& range)	5.1 (3.5-6.1)	5.6 (3.8-7.9)	25 (12-91)	56 (12-171)	38 (5.5-154)
Si (mg/L)	CFUF survey	2.5	1.91	5.33	5.04	4.27
	LT mean (& range)	2.1 (4.8-12)	1.7 (0.38-2.9)	4.6 (0.81-6.0)	4.1 (0.7-5.4)	3.3 (0.53-4.6)
B (µg/L)	CFUF survey	9	8	53.6	103	59.8
	LT mean (& range)	9 (5-12)	9 (5-15)	54 (2-84)	95 (13-140)	67 (7-106)
Inorganic N (mg/L)	CFUF survey	0.4	0.3	6.8	3.9	1.2
	LT mean (& range)	0.4 (0.2-0.8)	0.4 (0.7-0.8)	5.2 (1.3-9.9)	8.4 (2.0-18)	1.3 (0.3-2.5)
Cl (mg/L)	CFUF survey	6.0	5.9	29	37	23
	LT mean (& range)	8.2 (5.8-11)	9.4 (6.31-14)	44 (27-171)	63 (24-308)	50 (11-247)

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Table 2b Percentage colloidal concentration within the filtered (<0.45 µm) river water fraction collected during the cross-flow ultrafiltration survey

	Upland moorland		**Lowland agricultural**	**Lowland urban**	**Lowland Industrial**
Analyte	**Dunsop**	**Tarnbrook**	**Eller**	**Douglas**	**Hyndburn**
Fe	88	58	62	55	85
Ce	88	59	55	63	78
OC	80	68	56	66	60
OP	68	38	87	26	74
ON	63	72	65	41	51
Ni	79	67	50	31	58
Cd	71	65	37	42	51
Ti	79	60	34	28	57
Al	55	64	26	45	43
TP	59	48	24	17	61
Cr	54	61	42	22	24
Sb	73	67	19	15	13
As	56	48	20	14	37
Se	45	45	36	17	30
MRP	52	42	13	11	51
Mo	40	71	12	9	12
TDN	33	43	13	15.	23
V	33	27	15	14	35
Mn	34	38	13	8	17
Ba	31	37	11	9	13
Ca	25	42	11	7	10
Sr	24	36	10	8	10
Mg	20	32	10	7	9
SO4	21	23	11	8	11
K	13	17	10	7	8
Rb	12	15	10	7	8
Na	11	15	9	7	8
Si	9	8	10	10	9
B	7	5	9	6	8
Inorganic N	8	5	7	6	7
Cl	6	3	7	6	7

Table 3 Relationships between colloidal or truly dissolved concentrations and concentrations in the filtered (<0.45µm) river water fraction. C_e is the "cross-over" point i.e. the filtered concentration where a switch occurs between dominance of either colloidal or truly dissolved fractions; see text and Figure 1

			Truly dissolved vs filtered fraction		Colloidal vs filtered fraction	
	Cross-over filtered concentration (C_e)	Concentration range for filtered range	gradient	r^2	gradient	r^2
TP (µg/L)	60	15-1080	0.87	0.966	0.15	0.904
MRP (µg/L)	26	8-651	0.90	0.998	0.10	0.836
OP (µg/L)	42	7-429	0.76	0.994	0.24	0.940
TDN (mg/L)	0.6	0.7-7.6	0.90	1.00	0.11	0.997
ON (mg/L)	0.9	0.4-1.4	0.69	0.985	0.36	0.82
OC (mg/L)	NA	9.4-15	0.47	0.602	0.53	0.658
Al (mg/L)	0.13	0.05-0.22	0.33	0.64	0.67	0.879
Fe (mg/L)	NA	0.155-0.849	0.37	0.627	0.63	0.833
Ti (µg/L)	2.5	1.4-6.5	0.84	0.994	0.16	0.87
Ce (µg/L)	0.1	0.1-1.3	0.21	0.737	0.79	0.975
V (µg/L)	0.2	0.3-2.6	0.88	0.997	0.12	0.845
Cr (µg/L)	0.6	0.5-1.7	0.83	0.938	0.18	0.406
Mn (µg/L)	13	13-57	1.00	0.972	-1.0	0.001
Ni (µg/L)	3.1	2.1-3.4	1.22	0.86	-0.22	0.164
As (µg/L)	0.2	0.5-3.2	0.75	0.929	0.25	0.59
Se (µg/L)	0.3	0.3-0.7	0.94	0.964	0.06	0.098
Mo (µg/L)	0.06	0.04-2.2	0.91	1	0.09	0.968
Sb (µg/L)	0.11	0.09-2.1	0.85	0.997	0.15	0.896
Cd (µg/L)	0.03	0.02-0.1	0.06	0.098	0.94	0.964
Ba (µg/L)	11	16-66	0.98	0.992	0.02	0.07

Table 4: Organic carbon partition coefficients, K_{oc}.

	Dunsop	**Tarnbrook**	**Eller**	**Douglas**	**Hyndburn**
TP	0.36	0.42	0.24	0.10	1.06
MRP	0.27	0.34	0.12	0.06	0.71
OP	0.53	0.28	5.06	0.18	1.89
TN	0.13	0.34	0.12	0.09	0.19
ON	0.43	1.20	1.44	0.35	0.69
Al	0.30	0.81	0.27	0.42	0.51
Fe	1.90	0.65	1.27	0.63	3.84
Ti	0.92	0.70	0.41	0.20	0.87
Ce	1.76	0.67	0.96	0.87	2.34
V	0.12	0.17	0.14	0.08	0.36
Cr	0.30	0.71	0.57	0.14	0.22
Mn	0.13	0.28	0.12	0.05	0.13
Ni	0.92	0.92	0.78	0.23	0.91
As	0.32	0.42	0.19	0.09	0.40
Se	0.20	0.38	0.43	0.11	0.29
Mo	0.17	1.15	0.11	0.05	0.10
Sb	0.67	0.93	0.19	0.09	0.10
Cd	0.63	0.85	0.45	0.37	0.71
Ba	0.11	0.27	0.10	0.05	0.10

Table 5: Acid-available particulate concentrations, expressed as a percentage of the total acid leached concentration (%AAP)

	Upland moorland		**Lowland agricultural**	**Lowland urban**	**Lowland Industrial**
	Dunsop	**Tarnbrook**	**Eller**	**Douglas**	**Hyndburn**
MRP	62	52	51	26	27
Al	14	35	87	75	67
Fe	52	18	79	56	26
Ti	12	47	52	35	36
Ce	10	19	84	59	5.7
V	11	18	35	20	16
Cr	6.3	12	29	29	1.3
Mn	14	9.3	40	46	21
Ni	3.2	1.5	26	15	5.7
As	8.1	8.7	39	10	8.6
Se	32	56	42	38	6.0
Rb	2.9	7.9	4.4	0.9	2.7
Cd	28	15	40	59	40
Ba	3.5	4.3	18	8.1	5.9

Table 6: Acid available particulate concentrations normalised to suspended solids concentration (AAP/g-SS); labile solids (LS/g-SS; i.e. acid-available particulate + colloidal concentrations, normalised to suspended solids concentrations) [Units are μg/g-SS, apart from Fe and Al, which are expressed as mg/g-SS]. Increase (x) denotes the concentration increases between AAP/g-SS and LS/g-SS, as a result of including colloids in the labile solids concentration.

	Upland moorland						**Lowland agricultural**			**Lowland urban**			**Lowland industrial**		
	Dunsop			**Tarnbrook**			**Eller**			**Douglas**			**Hyndburn**		
	AAP/g-SS	**LS/g-SS**	**Increase (x)**	**AAP/g-SS**	**LS/g-SS**	**Increase (x)**	**AAP/g-SS**	**LS/g-SS**	**Increase (x)**	**AAP/g-SS**	**LS/g-SS**	**Increase (x)**	**AAP/g-SS**	**LS/g-SS**	**Increase (x)**
MRP	10000	13212	1	2241	3116	1	2196	2482	1	20727	27237	1	9000	21488	2
Al	22	97	5	20	44	2	15	16	1	15	17	1	34	41	1
Fe	365	664	2	33	118	4	10	12	1	30	42	1	67	225	3
Ti	146	968	7	240	402	2	97	128	1	309	474	2	480	974	2
Ce	35	312	9	24	85	4	23	25	1	13	19	1	25	356	14
V	34	121	4	15	34	2	25	32	1	22	34	2	40	114	3
Cr	27	244	9	11	62	6	12	25	2	63	97	2	7	129	19
Mn	1538	4843	3	534	2525	5	588	702	1	4436	4870	1	2500	4100	2
As	33	242	7	7.9	47.7	6	22	29	1	26	59	2	100	492	5
Se	13	131	10	2.2	24.2	11	2	5	4	2	14	8	10	70	7
Rb	22	113	5	15.5	43.4	3	2	7	3	6	55	9	30	121	4
Cd	5	52	11	0.3	5.8	17	1	1	1	1	2	2	9	26	3
Ba	462	4350	9	172	1566	9	261	395	2	300	621	2	1100	3350	3

Table 7. Empirical partition coefficients: K_{d_std} (a standard simple partition coefficient between the acid-available particulate fraction and <0.45 µm fraction) and K_{d_cfuf} (a refined partition coefficient, derived from the cross-flow ultrafiltration data, which accounts for the colloidal and truly dissolved concentrations within the <0.45 µm fraction, see text for details). Units: L kg^{-1}. Increase (x) denotes increases between K_{d_std} and K_{d_cfuf}.

	Upland moorland						Lowland agricultural			Lowland urban			Lowland industrial		
	Dunsop			Tarnbrook			Eller			Douglas			Hyndburn		
	K_{d_std}	K_{d_cfuf}	Increase (x)	K_{d_std}	K_{d_cfuf}	Increase (x)	K_{d_std}	K_{d_cfuf}	Increase (x)	K_{d_std}	K_{d_cfuf}	Increase (x)	K_{d_std}	K_{d_cfuf}	Increase (x)
MRP	1.25 x 10^{6}	3.46 x 10^{6}	3	1.87 x 10^{5}	4.50 x 10^{5}	2	1.85 x 10^{4}	2.41 x 10^{4}	1	3.18 x 10^{4}	4.70 x 10^{4}	1	1.23 x 10^{5}	6.05 x 10^{5}	5
Al	1.20 x 10^{5}	1.19 x 10^{6}	10	9.13 x 10^{4}	5.52 x 10^{5}	6	1.22 x 10^{5}	1.69 x 10^{5}	1	269 x 10^{5}	5.62 x 10^{5}	2	6.7 x 10^{5}	1.42 x 10^{5}	2
Fe	8.29 x 10^{5}	1.29 x 10^{7}	16	3.88 x 10^{4}	3.34 x 10^{5}	9	6.6 x 10^{4}	2.03 x 10^{5}	3	1.16 x 10^{5}	3.69 x 10^{5}	3	1.19 x 10^{5}	2.70 x 10^{5}	23
Ti	1.07 x 10^{5}	3.33 x 10^{6}	31	1.53 x 10^{5}	6.41 x 10^{5}	4	1.90 x 10^{4}	3.81 x 10^{4}	2	4.78 x 10^{4}	1.02 x 10^{5}	2	1.83 x 10^{5}	8.55 x 10^{5}	5
Ce	8.62 x 10^{4}	6.07 x 10^{6}	70	3.95 x 10^{4}	3.44 x 10^{5}	9	9.44 x 10^{4}	2.33 x 10^{5}	2	1.33 x 10^{5}	5.12 x 10^{5}	4	2.0 x 10^{4}	1.25 x 10^{5}	63
V	9.73 x 10^{4}	5.15 x 10^{5}	5	3.69 x 10^{4}	1.14 x 10^{5}	3	9.47 x 10^{3}	1.42 x 10^{4}	2	2.31 x 10^{4}	4.15 x 10^{4}	2	6.16 x 10^{4}	2.72 x 10^{5}	4
Cr	5.19 x 10^{4}	1.03 x 10^{6}	20	2.33 x 10^{4}	3.25 x 10^{5}	14	7.38 x 10^{3}	2.57 x 10^{4}	3	3.63 x 10^{4}	7.12 x 10^{4}	2	4.44 x 10^{3}	1.14 x 10^{4}	26
Mn	1.21 x 10^{5}	5.76 x 10^{5}	5	1.76 x 10^{4}	1.34 x 10^{5}	8	1.18 x 10^{4}	1.62 x 10^{4}	1	7.76 x 10^{4}	9.29 x 10^{4}	1	8.65 x 10^{4}	1.70 x 10^{4}	2
As	6.79 x 10^{5}	1.12 x 10^{6}	16	1.64 x 10^{4}	1.89 x 10^{5}	12	1.13 x 10^{4}	1.84 x 10^{4}	2	1.05 x 10^{4}	2.72 x 10^{4}	3	3.15 x 10^{4}	2.46 x 10^{4}	8
Se	3.81 x 10^{4}	6.93 x 10^{5}	18	7.93 x 10^{3}	1.58 x 10^{5}	20	2.39 x 10^{4}	1.36 x 10^{4}	6	2.24 x 10^{4}	2.14 x 10^{4}	10	1.66 x 10^{4}	1.65 x 10^{4}	10
Rb	2.32 x 10^{4}	1.34 x 10^{5}	6	1.48 x 10^{4}	4.89 x 10^{4}	3	8.18 x 10^{2}	2.79 x 10^{3}	3	8.43 x 10^{2}	7.82 x 10^{3}	9	9.3 x 10^{4}	4.08 x 10^{4}	4
Cd	5.31 x 10^{4}	2.11 x 10^{6}	40	7.04 x 10^{3}	3.36 x10^{5}	48	2.52 x 10^{4}	5.0 x 10^{4}	2	2.77 x 10^{4}	1.13 x 10^{5}	4	8.75 x 10^{4}	5.32 x 10^{5}	6
Ba	2.81 x 10^{4}	3.83 x 10^{5}	14	7.80 x 10^{3}	1.12 x 10^{5}	14	3.94 x 10^{3}	6.72 x 10^{3}	2	8.02 x10^{3}	1.83 x 10^{4}	2	2.09 x 10^{4}	7.31 x 10^{4}	3

Figure 1 Example relationships between colloidal and truly dissolved concentrations vs filtered (<0.45µmconcentrations, showing linear regression lines. The dotted line and open squares denote the relationship between the truly dissolved (<1kDa) and the filtered fractions; the solid line and solid diamonds denote the relationship between the colloidal and the filtered fractions. For further information, see text and Table 3.

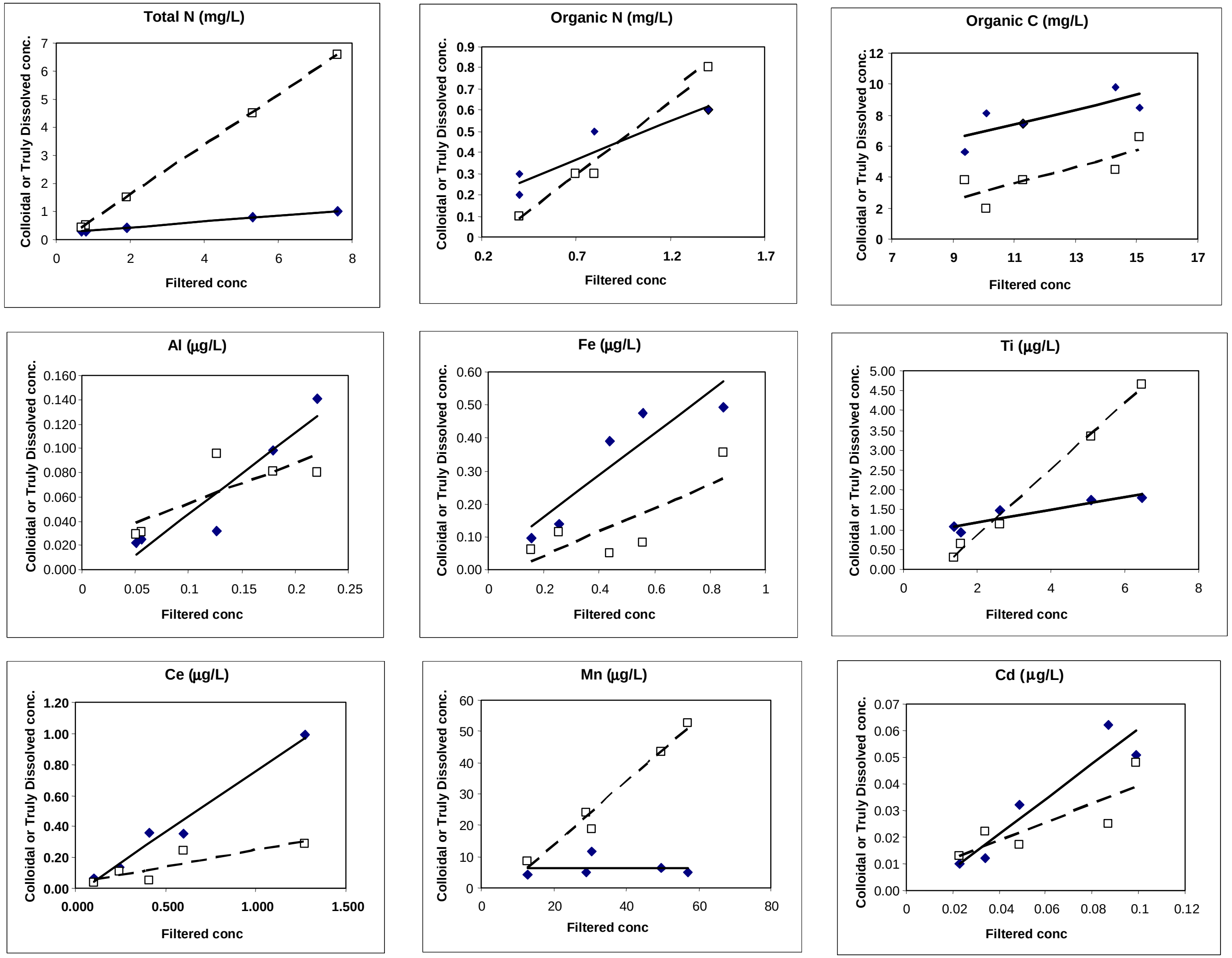
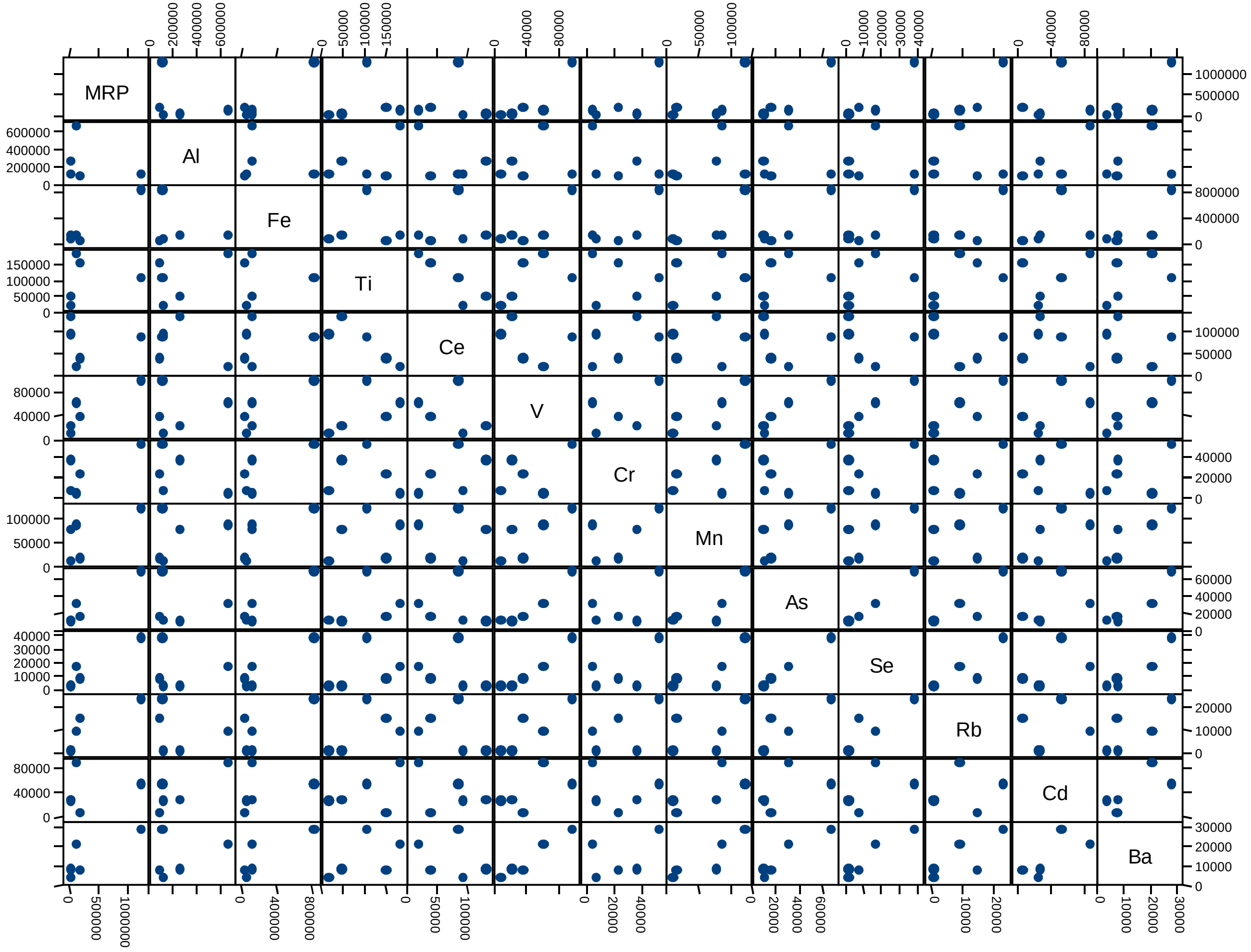
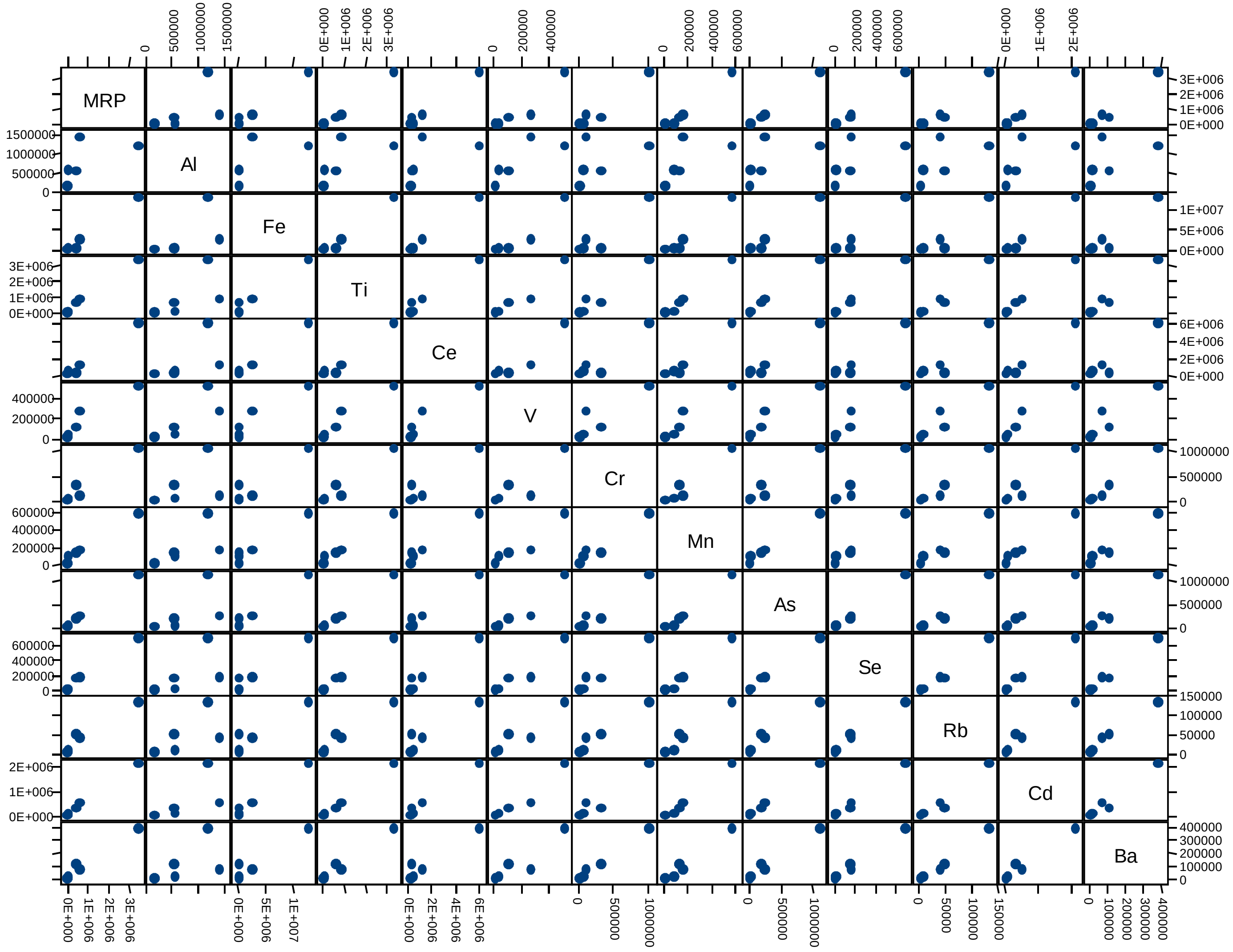


Figure 2: Inter-element correlation matrix plots for (a) K_{d_std} (a standard empirical partition coefficient between the acid-available particulate fraction and <0.45 µm fraction) and (b) K_{d_cfuf} (derived from the cross-flow ultrafiltration datasets and which accounts for the colloidal and truly dissolved concentrations within the filtered (<0.45 µm) fraction); see text for details.

(a)



(b)


MRP
Al
Fe
Ti
Ce
V
Cr
Mn
As
Se
Rb
Cd
Ba
0
500000
1000000
1500000
0E+000
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2E+006
3E+006
0
200000
400000
0
200000
400000
600000
0
200000
400000
600000
0E+000
1E+006
2E+006
3E+006
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1E+006
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1500000
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500000
0
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5E+006
0E+000
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2E+006
1E+006
0E+000
6E+006
4E+006
2E+006
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2E+006
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400000
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100000
0
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1E+006
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3E+006
0E+000
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1000000
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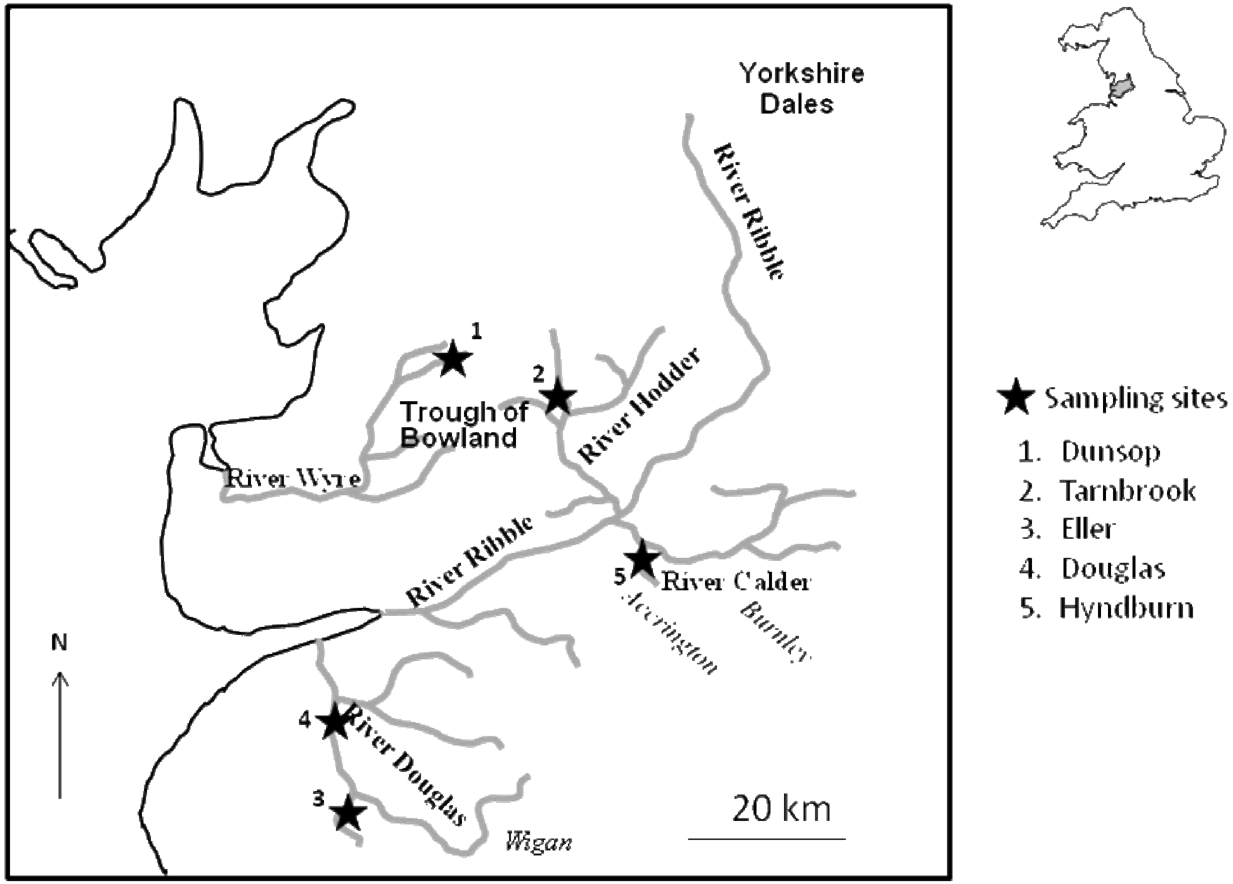
Supporting Information

SI Table 1 Overview of chemical analysis for the fractions sampled during the cross-flow ultrafiltration (CFUF) survey on the Ribble/Wyre

Fraction	pH, alkalinity	Suspended solids	MRP	Total P	Total Dissolved N	Dissolved Organic C	Major anions	Major cations & boron	Trace metals
Unfiltered river water	X	X	X	X				X	X
Filtered<0.45 µm river water			X	X	X	X	X	X	X
CFUF Retentate: colloidal fraction (>1kDa<0.45 µm)			X	X	X	X	X	X	X
CFUF Permeate: truly dissolved fraction (<1kDa)			X	X	X	X	X	X	X

SI, Fig 1: Map of the Ribble/Wyre catchment showing the river network, location of sampling sites and major urban centres



SI, Fig 2: Hydrograph showing flow conditions in the River Douglas at the time of the cross flow ultrafiltration survey, relative to the flow time series for the wider Ribble/Wyre Source to Sea project.