Can sediment data be used to predict alkalinity and base cation chemistry of surface waters?

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Abstract

We hypothesise that stream sediment elemental composition can predict mean and minimum concentrations of alkalinity, Ca and Mg in the river water throughout a river network. We tested this hypothesis for the River Derwent catchment in North Yorkshire, England, by using 6 years of water chemistry data from the Environment Agency and a digital elevation model to flow path-weight British Geological Survey (BGS) sediment element concentration data. The predictive models for mean concentrations were excellent for Ca and alkalinity, but less good for Mg, and did not require land use data inputs as stream water sediment composition seems to reflect all aspects of the riparian zone soil system. Predictive model forms were linear. Attempts to predict minimum values for Ca and alkalinity also were less satisfactory. This probably is due to variations in hydrological response times to individual precipitation events across the catchment.

Key words: Alkalinity, calcium, magnesium, river sediment, predict, flow accumulation, River Derwent

1. Introduction

One positive aspect of concerns over acid deposition impacts upon terrestrial and aquatic ecosystems was the interest stimulated in the quantification of weathering rates and alkalinity generation within soil systems. In acidification-sensitive drainage basins, acid neutralization capacity of river waters approximately equates to Gran

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alkalinity (Neal, 2001). Consequently there is a need for reliable methods that can predict the amounts of alkalinity generated in soils and, potentially, transferable to surface waters. In the present study we have tested the hypothesis that alkalinity is predictable from sediment total Ca or Ca plus Mg concentrations as such data are readily available in many countries from past geological surveys. Alkalinity fluxes determine critical loads of acidity for freshwaters and soils. A robust and verifiable method for predicting alkalinity generation over regional and national scales therefore should be extremely useful in planning strategies for integrated catchment management and managing acid deposition effects (Cresser et al., 2006). Moreover, in the context of the ameliorative role of soil C storage in climate change, currently there is much interest in losses of both inorganic and organic carbon from soils.

Biochemical processes in the terrestrial environment strongly influence the hydrochemical response of small catchments, as stream water is largely made up of drainage from soils (Moldan and Cerny, 1994). A recent study of spatial and seasonal variations in water chemistry across North West England very effectively highlighted the diversity of factors influencing water chemical quality at regional scales (Rothwell et al., 2010). In spite of this complexity, numerous successful hydro-chemical models have been developed over recent decades for predicting, for individual streams, the temporal changes in water chemical quality during and following precipitation events (e.g. Christopherson et al., 1982; Gherini et al., 1985; Nikolaidis et al.,1988; Christopherson et al., 1994). Process-based models may be applied over longer time scales too (Cosby et al., 1985; Whitehead et al., 1988), although care is then needed to ensure that the model encompasses all key parameters driving water chemistry if extrapolation is made significantly beyond the calibration period. Cresser et al. (2000) pointed out, however, that most such models are not transferrable between catchments, which limits their use at regional or national scales. More recently, in a review of benchmarks for ecological and water quality assessments, Hawkins et al. (2010) highlighted the dominance of site-specific modelling approaches, and the crucial importance of better characterization of freshwater environments at a more general level.

Generation of site-specific models based upon data collection is generally prohibitively expensive for regional or national scale use. Billett and Cresser (1992) therefore aspired to be able to predict spatial and temporal variations in water chemistry over a regional scale from readily available soil maps and associated,

already published, soil chemical data. They postulated that it should be possible to predict stream water chemistry under high and low flow conditions from the characteristics of the surface and sub-surface soils in the riparian zone. They further hypothesised that the relative proportions of different soil types immediately adjacent to streams in the Scottish highlands should affect stream water chemistry far more than the total proportional coverage of soil types in each stream's catchment. They therefore used catchment topography to predict flow paths for each catchment to work out the relative proportions of precipitation falling on the catchment likely to drain through each riparian zone soil type. This provided an appropriate flow path weighting for each soil type in their predictive model. Using % Ca saturation of the cation exchange capacity (CEC) for surface and sub-surface soil horizons, flow path-weighted as described above, they obtained excellent predictive relationships for mean and maximum (base flow) Ca concentrations (Billett and Cresser, 1992). However, prediction of minimum Ca concentration for their 10 upland catchments was appreciably poorer. The model later became known as the Aberdeen Soil Horizon (ASH) model (Cresser et al., 2000).

The above results were based upon detailed soil surveys and chemical analyses for 10 upland moorland catchments(Billett and Cresser, 1992). There was no agricultural land use other than rough grazing, and no, or minimal, forestry in any of the catchments. Hooper et al. (1998) later demonstrated the importance of riparian water at the Panola Mountain Research Watershed, Georgia, to base flow and storm flow chemistry, consistent with the concepts of the ASH model.

Johnson et al. (1997) showed that riparian zone soils and land use strongly influenced stream water chemistry in summer at Saginaw Bay in the USA. Land use was not incorporated in the ASH model, because soil management practices associated with diverse types of land use and soil management would cause appropriate changes to the Ca saturation of the CEC of upper and lower soil horizons, so should be incorporated automatically within the model.

ASH utilised the flow path-weighted cation exchange chemistry of the mineral sub-soil (B/C horizon) to predict the base flow chemistry, and that of the organic-rich surface horizons (O and A horizons) to predict chemistry at high-flows. However, the need for reliable high-resolution soil maps was subsequently found to severely restrict the widespread applicability of the ASH model (Cresser et al., 2000). It was modified therefore by making it geology-based (G-BASH) for predictions of Gran alkalinity

and base cation concentrations in stream waters, the underpinning concept being that soil parent material and topography in combination should be a reliable surrogate for soil type and chemistry (Cresser et al., 2000). The down side of basing predictions upon underlying geology was that it was then essential to incorporate riparian zone land cover type into the G-BASH model because of its potential impact upon the chemistry of riparian zone soils. The predictive equations that successfully emerged for alkalinity and base cation concentrations were based primarily upon flow path-weighted bedrock geological composition and proportions of arable land and improved grazing in the riparian zone (Cresser et al., 2000).

The G-BASH model was subsequently modified and extended with reasonable success to predict Gran alkalinity across the whole River Dee Catchment in North East Scotland using digitized geological maps, published rock chemical composition data, and a simple hydrological flow path model in a geographical information system (Smart et al., 2001). Only the rock chemistry was flow path-weighted because of resolution constraints of the GIS for land cover. It was hoped that the G-BASH model subsequently would be transferable to other regions, though so far this has happened, and only after modification, for north west England.

Acid deposition reduces alkalinity, but landscape characteristics moderate the pollution impacts on water chemical quality (Norton, 1980; Soulsby and Reynolds, 1995). It has long been recognized that the sensitivity of the streams to acidification is predictable from the underlying bedrock geology (Norton, 1980; Bricker and Rice, 1989). In Japan, Asano and Uchida (2005) reported that acid neutralization in soils and/or permeable bedrock was important in the neutralization of hill slope discharge for two hydrologically well-defined, steep, granitic drainage basins in the Tanakami Mountains. Extending the application of G-BASH for predicting alkalinity from north east Scotland to north west England, Cresser et al. (2006) found it was essential to take into account both the extent to which alkalinity had been used up in countering the effects of acid deposition as well as the greater dilution in a region where runoff was higher.

With recent technological advances, especially the improved availability and affordability of Geographic Information Systems (GIS), many GIS-based surface and subsurface water models have been applied in resource and water discharge management (e.g. Djokic and Maidment, 1993; Goodchild et al., 1993; Ross and Tara, 1993; Merchant, 1994; Smith and Vidmar, 1994; Cowen et al., 1995; Greene and

Cruise, 1995; Poiani and Bedford, 1995; Shamsi, 1996; Bennett, 1997; USEPA 2001). Integration of conceptual models with best available technology to overcome the barriers that hinder their use has been strongly recommended (Coroza et al., 1997; Sui and Maggio, 1999).

A potetiable and readily available data resource that does not appear to have been considered in the context of predictive models for stream water chemical quality, even at the individual catchment level, is the British Geological Survey river sediment data. These data are in the public domain as a series of 17 regional geochemistry atlases (e.g. BGS, 1996) and as the NERC G-BASE data resource. Sediment composition, like stream water chemical composition, depends upon riparian zone soils and geology and land use adjacent to, and upstream of, the sampling point, so should be an integrating parameter for all their effects. Sediment composition is known to affect heavy metal concentrations present in waters as a result of prior mining activities (Aston et al., 1974). Plant and Moore (1979) noted that appropriately sampled stream sediments should approximate to a composite sample of the weathering products upstream. The objective of the present research is to test the idea that such sediment data can be used to spatially model stream water chemistry. This assumption is made on the basis that sediment composition should directly reflect riparian zone soil characteristics. If successful, such a relatively simple tool should have many benefits to planners, particularly in terms of assessment and management of catchment systems at regional and national scales. Our study is a preliminary assessment of the potential use of BGS sediment data for the River Derwent in North Yorkshire, England, for assessing the spatial and temporal variations in alkalinity, Ca, and Mg concentrations in river water. It is hypothesised that it will be possible to predict mean and minimum concentrations of these determinants just from flow path-weighted sediment Ca and Mg concentrations, with no reference to land use.

2. Site description, data and methodology

2.1 Study Area

The River Derwent in North Yorkshire, England, is used for water abstraction, leisure and sporting activities, and effluent disposal, and its catchment contains several nature reserves. It is 115 km long and drains 2057 km^2 (Neal et al. 1998). In the Yorkshire

area, its catchment is a significant surface and groundwater resource (NRA, 1992). Although considered a clean river with water quality of class 1a (very good) to class 1b (good) based on chemical indices, it has a poorer biological quality rating, the poorest water occurring in the lowland stretches at the southern end of the River (NRA, 1992).

The drainage basin is predominantly rural, with little industry other than agriculture. The headwater areas are mainly heather/grass moorland, bracken, and coniferous woodland (20%), whereas the lower areas are predominantly arable (40% is mainly cropped with wheat and winter- and spring-barley) along with agricultural pasture and meadowlands (25%) and forestry (5%) (Neal et al., 1998). The catchment has received significant deposition of acidic oxide pollutants from the atmosphere in the recent past (Smith et al., 1997).

As shown in Fig. 1, the area is underlain by Cretaceous Chalk, Jurassic sandstone, limestone and clays, and Triassic sandstones and mudstones (Neal et al., 1998), overlain by recent and Pleistocene alluvium ranging from clay to gravel.

2.2. Data

Water chemical data are from the Environment Agency for eight sites along River Derwent, namely Forge Valley, Sherburn, Yedingham, Malton, Low Hutton, Howsham Bridge, Sutton Lock and Derwent Bridge (Fig. 1), covering January 1998 to January 2004 at approximately monthly intervals. Table 1 shows the Ca, Mg, and alkalinity mean values and ranges for each EA sampling site.

Stream sediment data for 851 samples in the drainage basin are from the British Geological Survey. The ranges, means and standard deviations for Ca% and Mg % of the data are shown in Table 2. The methods used for stream sediment sampling are fully described in BGS (1996), and are those now recommended as international standards for geochemical mapping (Darnley et al., 1995); they were based upon earlier work by Plant and Moore (1979). Samples of active sediments were collected, upstream, if necessary, of any identifiable potential source of local contamination such as housing, industry, or road or track crossings. A layer of oxidised material at the surface was removed prior to sampling the sediment, which then was wet-screened in the field using a minimum quantity of water to collect sediment finer than 150 µm until ca. 100 g of material was obtained. Following preliminary air drying, the samples were freeze-dried at a field laboratory. A sediment

subsample of ca. 50 g, obtained by cone-and-quartering, was ball milled and a further sub-sample of the finely ground material then analysed as a powder by direct reading DC arc atomic emission spectrometry. Details of the analytical methodology and quality control procedures are given elsewhere (BGS, 1996).

2.3 GIS analysis

A Digital Elevation Model (DEM) of the area enclosing the River Derwent drainage basin (50 m x 50 m grid) was produced from the Ordnance Survey PANORAMA dataset based upon 1:50000 contour data. This was used in the GIS to quantify the spatial relationships between stream water chemical variables (alkalinity, Ca, and Mg concentrations) at the eight EA river water sampling stations and upstream drainage-water pathway-weighted sediment sample data (sediment Ca and Mg concentrations). Thus sediment elemental composition data from the British Geological Survey (BGS) were used in ArcGIS to provide spatial distributions of the Ca and Mg concentrations in sediment that were deemed likely to influence the temporal and spatial variations in stream water alkalinity, Ca, and Mg concentrations.

The method used simple algorithms for terrain analysis of gridded-DEM available in most GIS software. These allowed an indication of surface water flow directions to be calculated. Surfaces of flow directions were then used to calculate the upstream contributing area for each DEM grid cell (flow accumulation). Flow accumulation is highest along stream channels and decreases rapidly away from channels. Therefore by using an arbitrary threshold of upstream contributing area, a stream network representation was obtained from the DEM. Sediment sampling point Ca and Mg data were attached to their nearest stream network cell, so that sediment data matched the topography representation of the DEM. Once sediment sampling points were located on the gridded representation of the stream network, each cell on the stream network was then allocated to the closest sediment sampling point on the network. This was calculated using standard GIS cost surface analysis, where stream cells had very low cost in comparison to non-stream cells.

Having allocated segments of the stream network to their closest sediment sampling point, the furthest downstream cell of segments allocated to each sediment sampling point was found. Using these as pour-points, once again, standard GIS algorithms for finding watersheds from DEM data were used to find the watershed

upstream of each of these points. These areas represented "sub-catchments" corresponding to each sampling point.

The Ca or Mg concentration in stream water was modelled for all sampling points on the stream network by finding the watershed for each of these points. These watersheds were overlain with the watershed layers for sediment sampling points. Taking the sum of the appropriate element values for these overlaid areas and dividing by the number of cells in those areas gave "flow-weighted" sediment Ca or Mg values.

For the eight sites along the River Derwent, relationships were then examined between mean and minimum Ca, Mg, and alkalinity concentrations in water and drainage flow path-weighted sediment base cation metal concentrations. For Ca and alkalinity we looked at relationships for the means of the three lowest concentrations in river water to compare with use of single minimum concentrations for each EA site.

Forge Valley is quite different from the other study sites within the River Derwent catchment because of a sea cut, where most of the water is diverted to the North Sea in the interests of flood protection down-stream. Therefore, because its contribution to water quality downstream is small, it was treated throughout as a small independent catchment. Subsequently relationships were investigated with and without Forge Valley data.

3. Results

3.1. Predicting alkalinity from sediment Ca and Mg

Mean alkalinity values at the water sampling sites were plotted against flow-path-weighted Ca (%) in sediment (Fig. 2). The R^2- values for simple linear regressions are 0.989 with Forge Valley and 0.968 without. The significance of coefficients and intercepts of regression equations is shown in Table 3. Inclusion of Forge Valley data had an insignificant effect upon slope or intercept (Table 3).

Both $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$ are likely to be major contributors to alkalinity within the River Derwent because of the calcareous geology of the area, so it was decided to test whether adding Ca and Mg concentrations of the sediment on a moles of charge basis improved the correlation strength. This basis was used to allow

summation of different element concentrations and because HCO_3^- will be predominantly balanced by Ca^{2+} and Mg^{2+} in water samples. Plotting river water alkalinity against sediment Ca+Mg (as $mmol_c/kg$) again produced highly significant linear correlations regardless of whether Forge Valley data were included or excluded (Fig. 2 and Table 3). Changing the linear equation without Forge Valley data to a 2nd order polynomial improved the R^2 value to 0.992, but is not easy to justify, because adding the Forge Valley data did not significantly change either the slope or the intercept of the simpler linear regression line (Fig. 2). The Forge Valley data would not fit on the extrapolated polynomial line.

3.2. Predicting mean Ca or Mg concentrations from sediment % Ca or Mg

The mean Ca concentration in river water was strongly correlated with flow-path weighted sediment Ca concentration ($R^2 = 0.942$ for a linear trend line when the Forge Valley data were included, Fig. 3 and Table 3).

A 2nd order polynomial equation best described the relationship between river water mean Mg concentration and flow path-weighted sediment % Mg, giving an R^2 value of 0.964. This possibly is justifiable to a limited extent on the grounds that there would be a significant input of Mg from the atmosphere even if there was no Mg in sediment, because of the maritime climate of the UK, but the simpler linear regression is also reasonable fit (Fig. 3 and Table 3).

3.3. Predicting lowest Ca and alkalinity concentrations from sediment % Ca

Figure 4 shows the correlations for scatter plots for the means of 3 lowest Ca concentrations in river water against flow path-weighted sediment Ca, both including and excluding the Forge Valley data. The linear equations gave R^2 values of 0.729 and 0.935, respectively (Table 3), but with negative Ca concentrations in the water at very low sediment Ca concentrations.

The relationships between means of three lowest alkalinity values for each site and flow path-weighted sediment Ca concentration were slightly weaker than those for lowest Ca concentrations in water, regardless of whether or not Forge Valley data were included (R^2 0.675 and 0.877 respectively, Table 3). Correlations were even less significant for discrete minimum values for each site.

4. Discussion

4.1. Predicting alkalinity from sediment Ca and Mg

The very high R^2 values of above 0.9 for predictions of mean alkalinity values at the water sampling sites using flow-path-weighted Ca (%) in sediment indicate that this single variable seems to be an excellent predictor for water mean alkalinity. By including data for Forge Valley as an independent catchment, the calibration range was significantly extended by the presence of a catchment highly dominated by heather moorland and mainly coniferous woodland. However, the slopes and intercepts of the regression plots in Fig. 2 differ very little (Table 3); therefore the Forge Valley catchment could be regarded as a validation catchment for the model obtained with Forge Valley excluded. There is no evidence from regression diagnostics that Forge Valley (at the lower end of both the response and predictor variable range) influences the regression model unduly.

Plotting river water alkalinity against sediment Ca+Mg (as $mmol_c/kg$) did not improve the fit of model predictions to observations, regardless of whether Forge Valley data were included or excluded. Although both $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$ will contribute to alkalinity within the river, some Mg emanating from the riparian zone soils will undoubtedly be of maritime origins. Cresser et al. (2000) found that their equations for predicting river water Mg concentrations in River Dee sub-catchments in northeastern Scotland were significantly improved when chloride concentration was included as one of the predictive variables in their model. Green et al. (2008) have shown that road salting can significantly increase the pH of soils lying between roads and parallel river systems. In future work it may be necessary therefore to consider the possible contribution that road salting may make to equations for predicting alkalinity if Mg sediment data are included, as road salt in the UK generally contains substantial amounts of Mg and often Ca as gypsum too.

4.2. Predicting mean Ca or Mg concentrations from sediment % Ca or Mg

The strong linear correlation between mean Ca concentration in river water and flow path-weighted sediment Ca concentration suggests that it should be feasible to predict spatial variations in mean Ca concentrations throughout catchments.

Although a 2nd order polynomial equation best described the relationship between river water Mg concentration and flow path-weighted sediment % Mg,

giving an R^2 value of 0.964, simple linear regression provides a useful predictive relationship. It is highly likely that road salting/road runoff would substantially enhance the river water Mg concentration at some sites. The Sherburn and Yedingham sites gave the highest river water mean Mg concentrations (Table 1), and these are the sites where road runoff would exert the greatest effect because the sea cut reduces dilution from less contaminated and more rural upland areas.

4.3. Prediction lowest Ca and alkalinity concentrations from sediment % Ca

Although the linear regression model based upon means of 3 lowest Ca concentrations in river water against flow path-weighted sediment Ca, excluding the Forge valley site, is good, it is probably not yet adequate for predictive purposes without more calibration data. This is because of the negative intercept and because of the poor R^2 value when Forge Valley data are included. Correlations were even poorer if simple single lowest concentration values were used rather than means of the three lowest values for each water sampling site (plots not shown). Clearly more data are needed before an appropriate predictive model is found, and this might also overcome the problem of negative intercepts.

With hindsight, the relatively poor relationships between means of three lowest alkalinity values for each site and flow path-weighted sediment Ca concentrations are probably to be expected. Alkalinity minima correspond to high or highest discharge conditions (Wade et al., 1999), which are likely to be attained at different times during storms across the catchment and along its length. They will also depend upon the spatial variations in the acidity of near-surface soils. Such variations are caused by variability of natural soil acidification processes coupled with acid deposition impacts, as soil acidity of both organic acid and mineral acid origins will be neutralized to some extent by in-situ alkalinity generation (Cresser et al., 2006). Therefore substantial variations in alkalinity around minimum values are to be expected. Research by Tetzlaff et al. (2007) using fine resolution Gran alkalinity time series data over a hydrological year demonstrated, for the Feugh catchment in Scotland, that there were diverse and subtle changes in stream-water chemistry over the year. When attempting to model stream-water Gran alkalinity at different spatial scales and under different

hydrological conditions using end member mixing analysis (EMMA), Wade et al. (1999) commented on the problems caused by the very limited amount of high discharge data when rivers were sampled only monthly.

5.1 Conclusions

The results of this preliminary study strongly support the hypothesis that stream water sediment elemental composition data are useful for prediction of mean concentrations of alkalinity, Ca and Mg in river water throughout the catchment of the River Derwent in North Yorkshire. This is in spite of the fact that as the river flows across the Corallian limestone, some water is lost from the river to groundwater recharge (Carey and Chadha, 1998). The predictive models did not require land use data inputs. This was as anticipated from the hypothesis that stream water sediment composition would reflect all aspects of the riparian zone soil system, including land use effects. Further work is needed, however, to robustly account for the poorer linear relationships observed for Mg concentration.

Attempts to predict minimum values for Ca and alkalinity using a simple regression approach were, however, slightly less encouraging , which was thought to be primarily due to variations in hydrological response times to individual storm events across the catchment.

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Table.1.

Sample Point	Ca (mg/l)				Mg (mg/l)				Alkalinity (as CaCO$_3$ mg/l)			
	Max	Min	Mean	SD	Max	Min	Mean	SD	Max	Min	Mean	SD
Forge Valley	70.9	19.8	50.7	(12.7)	6.21	2.68	4.9	(0.8)	144	29.8	96.6	(28.5)
Sherburn	147	67.7	109	(16.2)	22.8	7.62	12.3	(2.3)	225	95.5	172.1	(27.6)
Yedingham	149	84	122	(12.4)	15.2	8.77	11.5	(1.3)	234	121	197	(23.3)
Malton	101	20.3	82.3	(14.7)	8.3	2	6.7	(1.1)	191	21.8	150	(30.3)
Low Hutton	98.7	20.6	82.5	(14.0)	8.32	1.92	6.7	(1.1)	224	20.6	152	(30.0)
Howsham Bridge	101	28.5	81.6	(14.9)	8.41	2.61	6.6	(1.2)	194	47.6	149	(30.2)
Sutton Lock	106	26.1	84.1	(15.6)	9.15	2.71	7.2	(1.3)	192	28.2	149	(32.4)
Derwent Bridge	125	36.3	89.1	(15.9)	10.5	3.52	8.0	(1.4)	207	50.4	156	(30.4)

Table.2. Ranges of Ca and Mg in River Water Sediments.

	Range			
	Lowest	Highest	Mean	SD
Ca	2024.4	164204.4	17723.6	(23745.8)
Mg	1073.9	43164.4	5756.8	(5072.4)

Table 2. Ranges and means of Ca and Mg concentrations (%) in river sediments.

Element	Lowest	Highest	Mean	SD
Ca	0.202	16.42	1.77	(2.37)
Mg	0.107	4.32	0.576	(0.507)

| Fig. No.	Dependent (water) variable	+/- Forge Valley	Independent (sediment) variable	Slope			Intercept			R^2
				Value	SE	t	Value	SE	t	
2	Mean alkalinity	-	Ca+mg (mmol$_c$/kg) x^2	.0000151	.000	13.804	112.778	3.668	30.744	0.974
2	Mean alkalinity	-	Ca+mg (mmol$_c$/kg) x	.057	.005	10.485	60.478	9.679	6.248	0.956
3	Mean Mg	+	Mg (%) x^2	14.141	1.398	10.112	2.438	.596	4.092	0.945
3	Mean Mg	+	Mg (%) x	16.614	2.427	6.845	-2.172	1.521	-1.428	0.886
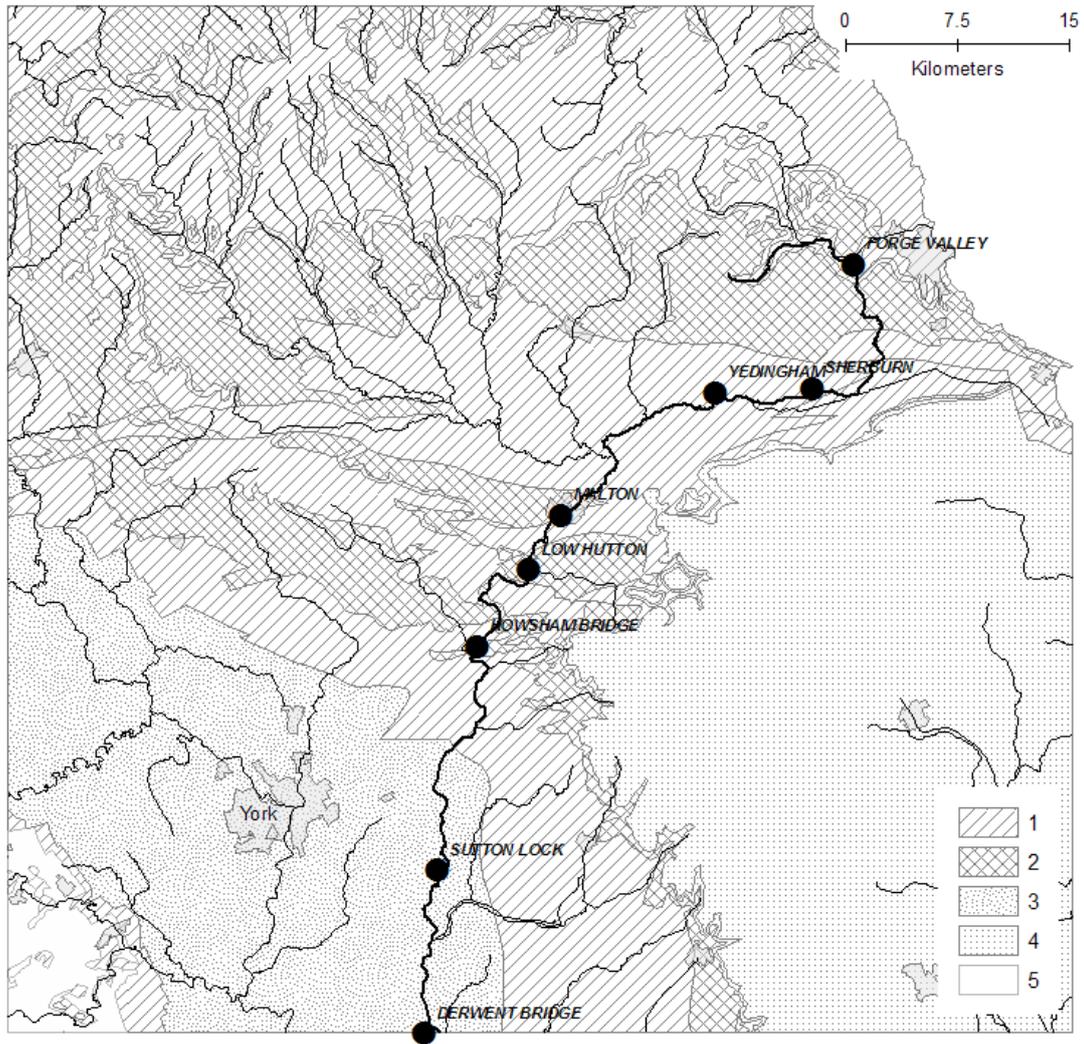
Fig. 1. Simplified bedrock geology around the sampling sites and the distribution of the eight monitoring sites (circles) along the length of the River Derwent (darker line) in North Yorkshire. Geology data are reproduced with the permission of the British Geological Survey ©NERC. All rights reserved. In the key, 1 denotes Mudstones, siltstones and sandstones; 2 Sequences including limestones and associated, mudstones, siltstones and sandstones; 3 Sandstones and conglomerates; 4 Chalk; 5 Miscellaneous other (5 is all outside the Derwent catchment area).
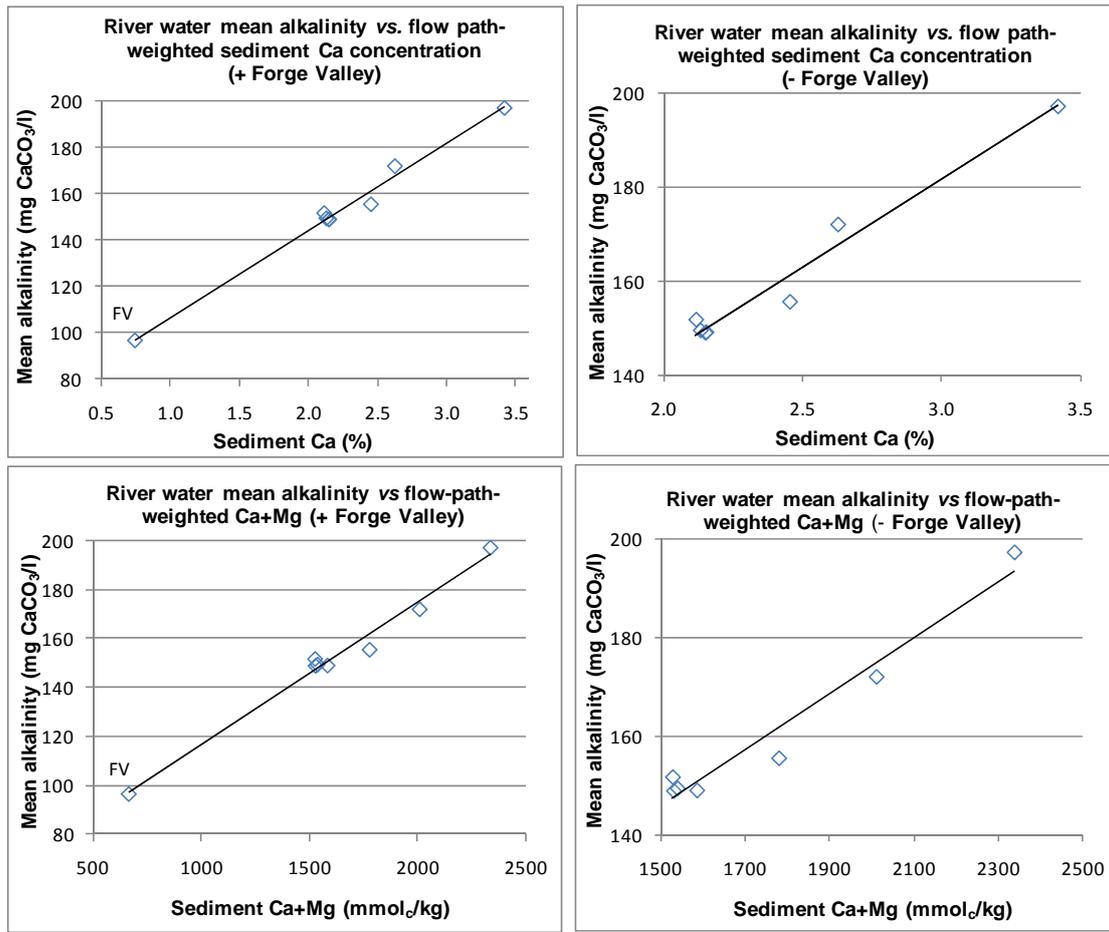
Fig. 2. Linear correlations of mean river water alkalinity with flow-path-weighted Ca concentration (%) in sediment, +/- Forge Valley data (upper left and right respectively), and with flow path-weighted Ca + Mg concentrations in sediment (mmol$_c$/kg) (centre left and right respectively). "FV" denotes the Forge Valley points.
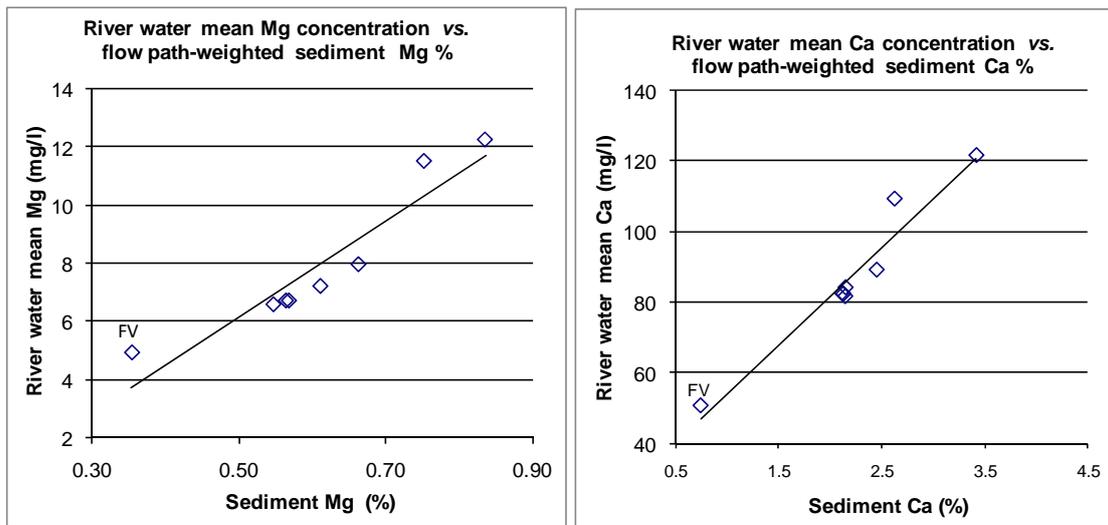
Fig. 3. River water mean Mg (left) and Ca (right) concentration *vs.* flow path-weighted sediment % Mg or % Ca concentration respectively (both including Forge Valley values, denoted by FV).
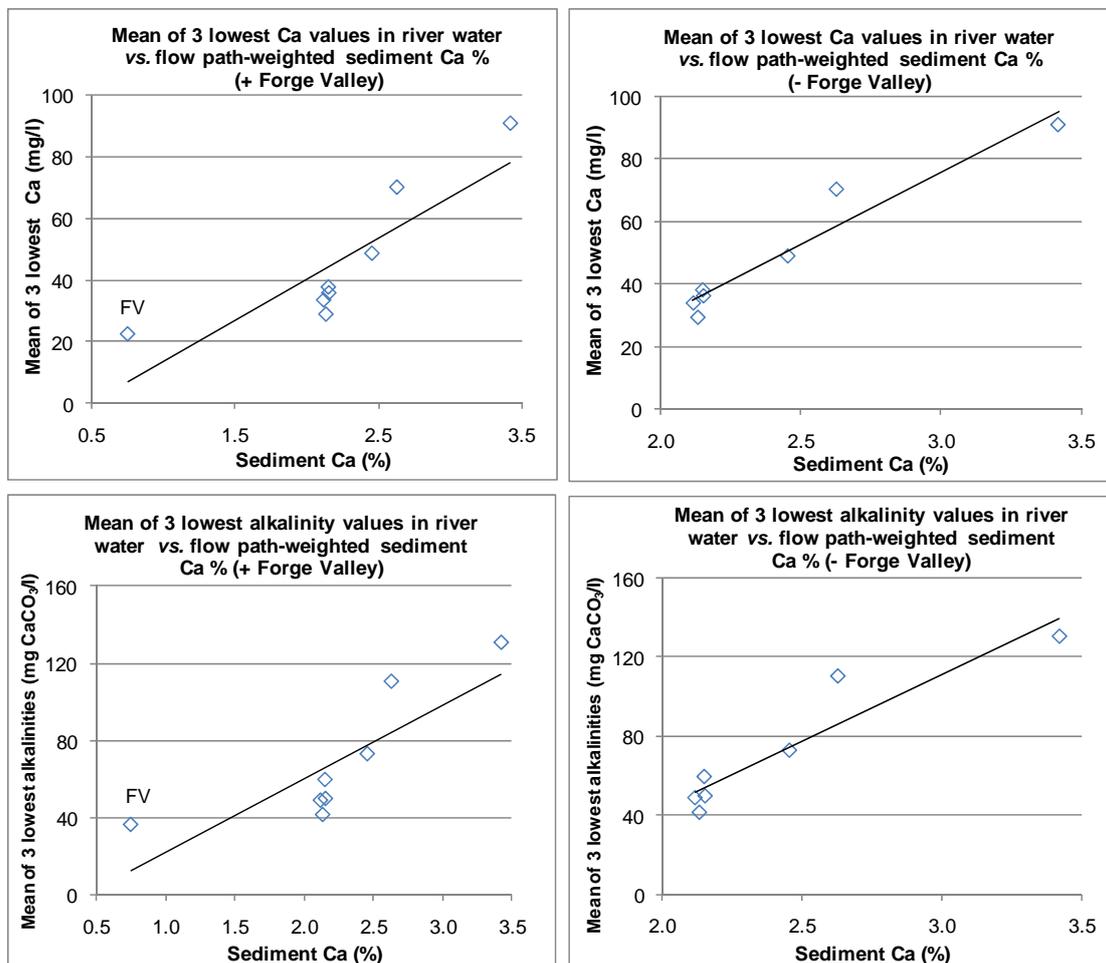
Fig. 4. Correlations of means of three lowest Ca concentrations in river water (upper plots) and alkalinity in river water (lower plots) with flow path-weighted sediment Ca concentration in sediment (%), with (left) and without (right) Forge Valley data, denoted by FV.