Comment on: ‘Multi-element signatures of stream sediments and sources under moderate to low flow conditions’ by M.I. Stutter, S.J. Langan, D.G. Lumsdon, L.M. Clark.

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1. Introduction

In a recent paper on ‘Multi-element signatures of stream sediments and sources under moderate to low flow conditions’, Stutter et al. (2009) presented results of a simple sediment source tracing method based on major and trace elements for a small agricultural catchment in north-east Scotland. The authors reported statistically significant, larger concentrations of four trace elements (Ce, Nd, Th and Y) in bank subsoils (n=5) and stream bed sediments (n=3) compared to topsoils from both pasture (n=5) and arable (n=5) land. They used these differences to aid discrimination between topsoil and subsoil (stream bank erosion) contributions to bed sediment. These elements may be more depleted in topsoil compared to subsoil because the former have been subject to more intense weathering over a longer period. If these naturally occurring trace elements could be used to understand the relative proportions of topsoil and subsoil contributions to headwater bed sediments this approach might be applied more widely to elucidate transport pathways for the transfer of agricultural contaminants such as particulate phosphorus to streams (Walling et al., 2008). This approach warrants further investigation across a range of catchments at different scales with contrasting land use and bedrock types. This can be undertaken using data from regional-scale geochemical surveys (Johnson et al. 2005) which include analyses of both stream bed sediments and subsoil samples. Previous studies have shown that much of lowland central England is at risk of topsoil transfer to watercourses via land drains (Chapman et al., 2003). A geochemical survey across part of central England covering 15 400 km^2 was recently undertaken and these data are well-suited to testing whether three of the four trace elements identified by Stutter et al. might be used to discriminate between topsoil and subsoil in sediments more widely. Specifically, if the concentrations of these elements are significantly smaller in stream bed sediments than in the subsoil, this may be due to mixing with topsoils which have lower concentrations of these elements. Below I describe the regional-scale survey, the methods I used to compare the geochemical data in subsoil and bed sediments, and I discuss my findings and their implications.

2. Regional-scale geochemical survey

The soil and stream sediment sampling was undertaken across the same large region of central England during the summers of 1997, 1998 and 1999 in rural and peri-urban areas; the coordinates of the region are between 400 and 540 km (Easting) and between 235 and 345 km (Northing) on the British National Grid. Elevation across the region is between 20 and 255 m above sea level, with undulating topography. Bedrock in the study region ranges in age from Precambrian to Cretaceous with a wide range of predominantly sedimentary lithologies including limestones, sandstones, siltstones, mudstones, shale, coal measures, marls, ironstones and chalk. There are also extensive superficial deposits including glacial tills, glacial sands and gravels, marine and river alluvium, river terrace deposits, and to the east of the region, peat deposits (Sylvester-Bradley and Ford, 1968). Land use is dominated by agriculture: 48% arable and 21% grassland.

Soil sampling locations (n=7288) were chosen from alternate kilometre squares of the British National Grid by simple random selection within each square, subject to the avoidance of roads, tracks, railways, urban areas and other seriously disturbed ground. At each site, a soil sample was taken from between 35 and 50 cm from five holes augered at the corners and centre of a square with a side of length 20 m by a hand auger and combined to form a bulked sample. All samples of soil were dried and disaggregated and sieved to finer than 150μm.

Mainly first and second order streams sites were selected, either avoiding or located upstream of obvious sources of contamination such as road intersections and farm buildings. Where possible, sediment was collected from central areas of active stream beds after removal of the upper layer of oxidised sediment. Between 15 and 25 kg of sediment was wet-screened on site to collect the fraction finer than 150μm typically yielding a final mineral mass of approximately 500 g. On return to the laboratory, all bed sediment samples were freeze-dried, coned and quartered and a 50-g sub-sample was ground in an agate planetary ball mill. The total concentrations of major and trace elements including Ce, Th and Y were determined in each sample by wavelength and energy dispersive XRFS (X-ray fluorescence spectrometry). From a larger set of stream sediment sites from which bed sediment was collected, I selected a subset of the smallest ($< 10\text{km}^2$ catchments sediment sites (n=1005) comprising only: i) first and second order streams, ii) low to moderate flow conditions (at the time of sampling) and, iii) small channels with widths of between 1 and 3 metres.

3. Estimating subsoil trace element concentrations in each drainage catchment

I examined the distributions of the concentrations of the three elements in the subsoil and stream sediment. Each distribution was positively skewed and so I took natural logarithms of each to transform them to approximately normal distributions.

I used a 5 m resolution digital terrain model (DTM; Intermap, 2009) of the study region and hydrological functions in ArcMap9.3$^{\text{TM}}$(ESRI) to generate drainage networks. I then superimposed on this the locations of each of the 1005 sediment sampling sites and snapped these to the nearest stream, ensuring that where two streams were close together, the correct stream had been selected by reference to positions which had been recorded on hardcopies of Ordnance Survey maps during sample collection. I then used hydrological functions and the DTM to delineate polygons of the

1005 sub-catchment areas draining to each of the sampling sites. I identified the central locations of the drainage catchment polygons using the 'centroids' function in the GIS.

I then used ordinary kriging to make optimal estimates of subsoil concentrations of the three elements at the central positions of the 1005 catchments where bed sediments had been sampled. Using the data on the log transformed concentrations of each element in subsoils across the region (n=7288), I calculated semivariances using lag intervals of 1 km to a maximum lag distance of 40 km and fitted both exponential and spherical functions to them. I checked for any substantial anisotropy by calculating variograms in four directions, but none was apparent in the data so I proceeded by using isotropic variograms. In each case I found an exponential function was optimal when fitted to the semivariances; the models had nugget:sill ratios of between 50 and 52% showing that there was a substantial proportion of spatially correlated variance in the data. I used these functions to make ordinary kriged estimates (Webster and Oliver, 2007) of Ce, Th and Y in subsoil at the centre of each catchment using the log transformed data. The final data were a set of 1005 paired concentrations (log scale) of Ce, Th and Y in subsoil at the centre of each catchment and in its bed sediment.

4. Comparison of subsoil and bed sediment geochemical data

As might be expected the subsoil and sediment concentrations of Ce, Th and Y were linearly related (Pearson correlations coefficients r = 0.5, 0.54 and 0.41, respectively) and each linear relationship was statistically significant (P-value <0.001). I calculated mean and standard deviations for each element in each media. In the case of Ce and Y, their mean log concentrations in stream sediment (4.49 and 3.41) were slightly larger than in subsoil (4.46 and 3.38). In the case of Th, the log mean concentration in subsoil (2.34) was slightly larger than in sediment (2.33). I applied a one-sided, paired t-test to the two Th distributions (n=1005); the mean subsoil Th concentration was not significantly larger then the mean Th concentration in stream sediment at the 95% confidence level (P-value=0.734). The standard deviations of each of the three, paired distributions were very similar.

5. Discussion

Evidence from geochemical surveys across a large area of agricultural central England demonstrate that subsoil concentrations of Ce, Th and Y are not substantially greater than in the same, fine size fraction ($< 150\mu$m) stream bed sediments in many (n=1005) small headwater catchments. The mean concentrations in both media were very similar for each of the three elements. It is therefore unlikely that these elements could be used to discriminate topsoil and subsoil inputs to stream beds across this region. This contrasts strongly with the results of Stutter et al. (2009) who reported significantly higher concentrations of these elements in bank subsoil than in stream bed sediment. Differences in parent material types between the two regions may go some way to explaining this; the study area of Stutter et al. is dominated by igneous bedrock (gabbro to granite) whilst the East Midland region largely comprises sedimentary lithologies. It is conceivable that soil formation processes are different in these two regions. Also, the subsoil samples from the regional survey were from sites across the entire landscape and not from the stream bank locations sampled by Stutter et al., but I would not expect this to cause significant differences between their geochemical compositions. Finally, sediment dynamics in the Scottish study site may be somewhat different resulting in different bed sediment particle size distributions – and by association, geochemical composition – in comparison to the catchments in the East Midlands. In summary, the results of my analysis based on data from 1005 catchments suggest that discrimination of soil-related source contributions to headwater bed sediments based on Ce, Th and Y concentrations is unlikely to be widely applicable.

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References

Chapman AS, Foster IDL, Lees JA, Hodgkinson RJ, Jackson RH. 2003. Sediment and phosphous delivery from field to river via land drains in England and Wales. A risk assessment using field and national databases. Soil Use Mge. 19,347–355.

Intermap (2009). NEXTMap Britain. Intermap. http://www.intermap.com/nextmap-britain . Accessed 6th December 2009.

Johnson, C.C., Breward, N., Ander, E.L., Ault, L. 2005. G-BASE: Baseline geochemical mapping of Great Britain and Northern Ireland. Geochem. Explor. Environ. Anal. 5, 1–13.

Stutter, M. I., Langan, S. J., Lumsdon D.G., Clark, L.M. 2009. Multi-element signatures of stream sediments and sources under moderate to low flow conditions. Appl. Geochem. 24, 800–809.

Sylvester-Bradley, P.C. and Ford, T.D. 1968. *The geology of the East Midlands.* Leicester University Press, 400pp.

Walling, D. E., Collins, A.L., Stround, RW. 2008. Tracing suspended sediment and particulate phosphorus sources in catchments. J. Hydrol. 350, 274–289.

Webster R, Oliver MA. 2007. *Geostatistics for Environmental Scientists,* 2nd edition. John Wiley & Sons, Chichester.