



Controls on the phosphorus content of fine stream bed sediments in agricultural headwater catchments at the landscape-scale

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The concentration and forms of bed sediment phosphorus (BSP) in agricultural headwater catchments has profound implications for water quality. To date there have been no landscape-scale assessments which quantify the relative importance of both organo-mineral properties of BS (bed sediment) and associated catchment characteristics (geology, land cover and topsoil phosphorus (P) content) for BSP. In this study we applied mid infra red diffuse reflectance spectrometry (MIR-DRS) to estimate the quantities of organic matter, dithionite extractable aluminium- (Al_d) and iron (Fe_d), kaolinite, dioctohedral clay and mica (D&M) minerals in 1052 snapshot samples of fine ($< 150 \mu m$) BS. The BS were collected from small to medium-sized ($5-50 km^2$) agricultural headwater catchments during summer months across a large area ($15\ 400 km^2$) of central England. The analysis also included accurate estimates of: i) mineral specific surface area, ii) residual iron, iii) cerium (Ce) concentrations – a rare earth indicator of apatite- or fertiliser-P, and iv) average topsoil catchment P content.

Simple linear regression demonstrated that the proportion of variance in BSP explained by specific components across all catchments declined in the following order: $Al_d > Fe_d > \text{topsoil P} = \text{kaolinite} = \text{residual iron} > \text{organic matter} = \text{Ce} > \text{D\&M} > \text{mineral SSA}$. There was significant correlation amongst them so principal components were taken prior to forming a multiple regression model (MRM) which included a classification of dominant bedrock lithology in each catchment and proportions of arable and grassland by area. The optimum regression model accounted for 61.9% of the variance in BSP including a signature from Ce content, inferred as denoting some combination of input from either apatite or P-fertiliser. The geological classification – and four interactions with other BS predictors – was statistically significant because bedrock type partly accounts for the processes controlling the transport and delivery of P to headwater BS. Although the proportions of arable and grassland by area in each catchment were statistically significant in the MRM, the coefficients were negative for arable and positive for grassland, which was counter-intuitive. This relationship should be explored further based on a detailed examination of hydrological connectivity and sediment delivery. The principal component analysis showed that across this large region – with widely differing geology and soil types – Fe_d in BS is more strongly associated with kaolinite than D&M minerals. This is likely due to the contemporaneous formation and association of iron-oxyhydroxides and kaolinite during pedogenesis. The SSA of fine bed sediments is largely determined by catchment area; this relationship can be fitted accurately by a power function.