

River Colloids: Agents or Reflections of Chemical Weathering in Temperate Uplands?

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Estimates of the extent of chemical weathering are typically based on the composition of river waters which have been filtered at 0.45 μ m. However, 0.45 μ m filtrates contain both truly dissolved elements and also elements associated with sub 0.1 μ m, inorganic and organic colloids. The aim of this work was to examine controls on the composition of colloids in rivers and to infer their potential role in the weathering process.

We used Cross Flow Filtration to determine the pools of fine particulate (0.1–0.45 μ m), colloidal (1000 Dalton ~ 0.1 μ m) and dissolved (< 1000 Dalton) metals in seven upland rivers from an area of northern Britain which is sufficiently small that the pH and composition of rainfall can be assumed to be constant. The regional occurrence of peat means that all the rivers are relatively rich in organic matter but because they drain predominantly calcareous or silicate terrains, they have differing pH, alkalinity and ionic strength. Fine particulate metals contribute less than 10% of the total metal load of < 0.45 μ m filtered waters. The metal contents of < 0.45 μ m filtered river waters primarily reflect two metal pools with differing elemental compositions: a truly dissolved pool and a colloidal pool, which in these rivers is likely to comprise primarily organic matter. Colloidal metals generally comprise at least the following percentages of the metal load of < 0.45 μ m filtered waters: >50% of Fe, Al and trace metals; 30% Mn, 25% Ca and Mg; 15% Na and K; a few % Si. These figures are probably minima because experiments with the CFF apparatus suggest that whilst recoveries of pure metal salt solutions are close to 100%, only 70% of particle reactive metals are recovered from metal salt solutions spiked with humic acid.

Rivers draining calcareous terrains are of course enriched in alkalis and alkaline earths compared to silicate rivers. However, levels of dissolved Al, Fe, Mn and Si are similar in both carbonate and silicate rivers and are approximately in

equilibrium with a kaolinite-quartz-Fe hydroxide-Mn oxide mineral assemblage. In contrast, the composition of colloids in the calcareous and silicate rivers is very different. Compared to the silicate rivers, colloids in the calcareous rivers are enriched in Ca and Mg but depleted in Al, Fe and Mn. The <0.1 μ m fractions of all the rivers, but especially the silicate rivers, thus appear to be highly supersaturated with respect to the suggested mineral assemblage.

We propose that the metal composition of riverine colloids is primarily controlled by element mobility during weathering. In carbonate-rich soils, rapid neutralisation of rainwater by carbonate minerals restricts the dissolution and mobilisation of aluminosilicates and oxides; the occurrence of significant concentrations of colloidal organic matter is unimportant. But in organic-rich soils with low acid neutralising capacity, low pH solutions persist and drive the dissolution of aluminosilicates and oxides. Colloids derived from these soils are enriched in Al, Fe, Mn and trace metals, resulting in high concentrations of these elements in < 0.45 μ m filtered waters. Given the high concentrations of organic matter in these rivers and the fact that the proportions of colloidal metals are quite accurately predicted by Tipping's (1994) humic acid model, it is tempting to conclude that DOM does indeed enhance the extent of chemical weathering of aluminosilicates, by as much as an order of magnitude. However, our chemical data alone do not distinguish inorganic and organic colloids and it is possible that the high abundance of colloidal Al and Fe reflects secondary precipitates rather than organic-bound elements. In this case, the implied driver of chemical weathering would simply be the pH of the rainwater, with a lesser role for colloidal organic matter.

Tipping, E, *Computers and Geoscience*, **20**, 973-1023, (1994).