Defining the chemical and physical length and time scales that control chemical fluxes from landscapes

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As fluids move through the subsurface they acquire solutes at a rate that is controlled primarily by the available surface area, the reaction kinetics of the individual minerals and the thermodynamic departure from chemical equilibrium [1]. As a result, both the physical length scale (or cumulative mineral surface area) and the time available for the fluid to react (or the fluid residence time) should exert a coupled influence on the solute fluxes from a given landscape. For example, if actual fluid residence times exceed the theoretical time required to reach chemical equilibrium, then the solute fluxes are optimized. However, because rivers and streams average over spatial domains that include an array of length scales and fluid residence times, determining the length and time scales that control solute generation has proven difficult. Defining and linking these length and time scales presents a key challenge to fields of geochemistry, geomorphology, biology and hydrology. Yet, if the length and time scales that control solute fluxes could be defined, this knowledge may provide a mechanistic approach for interpreting catchment to global-scale solute fluxes.

A comparison between soil profile solute evolution from stable and eroding landscapes, and concentration-discharge relationships (C-Q) both for small rivers from the U.S. Geological Survey's Hydrologic Benchmark Network (HBN) and large rivers from the Global Environmental Monitoring System (GEMS) database suggests that even with increasing discharge and catchment area, the ratio between the physical and chemical length scales may remain relatively constant. Catchments that show little variability in concentration with discharge (or "chemostatic behavior") are characterized by average fluid residence times that exceed the time required to reach chemical equilibrium. Chemostatic rivers may also represent rivers that are at their optimal solute flux. Conversely, decreases in concentration with increasing discharge are explained by average residence times shorter than required to approach chemical equilibrium, resulting in dilution. In these systems, if fluid residence times increase or chemical equilibration lengths decrease, solute fluxes are expected to increase to the optimum level. The fluid residence time model could provide an alternative framework for assessing both the relationship between discharge and concentration for individual catchments and controls on the solute fluxes of larger rivers. However, more detailed studies of the chemical and physical length and time scales and the development of scaling approaches are necessary to refine the simple model presented here. In particular, the time required to reach chemical equilibrium is perhaps the most poorly constrained variable in the fluid residence time model.

[1] White, A.F., et al. (2008) *Geochim. Cosmochim. Acta*, **73**, 2769-2803.

Assessing limitations for PAH biodegradation in long-term contaminated soils using bioavailability assays

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Polycyclic aromatic hydrocarbons (PAHs) are a class of organic contaminants that are ubiquitous in the environment through the incomplete combustion of organic matter such as diesel, coal and wood as well as being present at industrial sites due to use in a range of industrial processes. Once PAHs enter the environment, the predominant mechanisms for removal are biological via microbial activity, although physiochemical processes such volatilization can reduce the concentration of some PAHs. However, due to their hydrophobic structure, PAHs have the potential to partition onto soil organic matter thereby decreasing their bioavailability to microorganisms and limiting their degradation in the environment. This explanation was felt to be the reason for a lack of evidence of PAH biodegradation in a study of long-term contaminated soils. Instead, natural organic matter was being utilised as a carbon source resulting in the persistence of PAHs at this site [1].

Although biodegradation may be limited by a variety of environmental factors, bioavailability is considered to be a major limitation in contaminated soils. To test the hypothesis that bioavailability was the limiting factor for biodegradation in theses soils, PAH bioavailability was determined using non-exhaustive extraction (propanol, butanol, hydrooxypropyl-β-cyclodextrin) and oxidation (persulfate) methodologies designed to determine the fraction of contaminants within soil which are available for biological uptake [2, 3]. By comparing the initial PAH concentrations to the residual PAH concentrations following each assay, it was determined that the majority of PAHs in the soils were inaccessible to microorganisms which suggested that bioavailability limitations were the primary cause for the lack of observed biodegradation at this site.

These results highlight the importance of bioavailability to PAH degradation as well as the effectiveness of these assays as a rapid, and inexpensive method for determining the endpoints of PAH bioremediation. Such assays have the potential to provide a decision making tool on the suitability of bioremediation for soil treatment with minimal cost and time impacts and high accountability.

[1] Mahmoudi et al. (2011), submitted to *Env Sci & Technol*
[2] Juhasz et al. (2005) *Biorem J* **9**, 99-114.
[3] Dandie et al. (2010) *Chemosphere* **81**, 1061-1068.