Quantifying rates and mechanisms of shale weathering across a continental-scale climosequence

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Both ecosystems and humans are dependent on soil for nutrient and water cycling as well as food, making the loss of soil a major issue facing humanity. However, the rate at which soil forms has not been well quantified. To investigate rates of soil formation as a function of climate, a latitudinal climosequence of forested sites has been established in North America and Wales. The climosequence is bounded by a cold/wet end member in Wales and a warm/wet end member in Puerto Rico. In between, temperature and rainfall increase as sites extend south through New York, Pennsylvania, Virginia, Tennessee and Alabama. All sites, except Puerto Rico, are underlain by an organic-poor, iron-rich (Silurian-age) shale, providing a constant parent material from which soil is forming. Puerto Rico is located on chemically similar, but younger, shale. Soil sampling and geochemical analyses were completed similarly at all sites to allow direct comparisons and modelling of shale weathering. Independent Be^{10} estimates of erosion rates for a few locations along the transect are used to estimate residence times. Initial results show soil depth increases as a function of temperature, with shallow (~30 cm) profiles in Wales and Pennsylvania varying up to 630 cm deep in Puerto Rico. Depletion profiles of Na, a proxy for feldspar dissolution, are less than 20 % depleted at the surface in Wales and Pennsylvania, 50-60% depleted in Virginia and Tennessee, and 100% depleted at the surface in Puerto Rico. Using estimated soil residence times, apparent activation energies for Na depletion were calculated using different assumptions to range from 15-19 kcal mol^{-1}, values that are slightly higher than those reported for Na plagioclase dissolution in the laboratory. Overall, data collected from soils across the transect will promote a better understanding of how climate changes can impact soil formation rates.

CAPRAM mechanism development: Evaluation of prediction methods for aqueous phase rate constants and model results

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Organic compounds are ubiquitos in the tropospheric multiphase system. With either large biogenic and athropogenic sources they play an important role and have thus become a major research topic within the last decades.

Modelling can provide a useful tool to explore the chemical and microphysical processes in the troposphere. However, detailed oxidation mechanisms exist mainly in the gas phase while they are very limited in the aqueous phase. Current studies aim to expand the aqueous phase mechanism CAPRAM 3.0i, which is the currently most comprehensive chemistry mechanism with 777 reactions and 380 species. However, the oxidation scheme is still incomplete for C3 and C4 organic chemistry and higher organics are missing at all.

The huge amount of organic species relevant in the troposphere makes it impossible to determine all the needed kinetic data experimentally. Therefore, estimation methods become necessary. Besides the construction of an up-to-date database of about 600 experimentally determined reaction rate constants of OH and NO_3 radicals with organics, estimation methods for the prediction of missing data have been evaluated. The evaluation led to a new oxidation schemes for C3 organic compounds added to the existing CAPRAM 3.0i mechanism. Furthermore, branching ratios were introduced for already prescribed OH reactions with organics. Model runs have been performed with the multiphase mechanism MCMv3.1 and the extended CAPRAM version for a meteorological scenario with non-permanent clouds under remote and urban conditions.

The addition of new C3 organic compounds led to the modified concentration profiles of many organic and inorganic species. For example, acid production is enhanced although contrations are still lower than measured in the field due to the missing implementation of the oxidation of higher organics. The introduction of branched OH attack to organics let to further refined results.