

# The Effects of Organic Matter and Seasonal Redox Dynamics on Chemical Weathering: Constraints from Natural Wetland Studies

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Several recent studies suggest that the rate of chemical weathering could be higher in swamp zones or wetlands compared to well-drained soils, due to organic matter and vegetation effects (e.g. Viers et al., 1997; Oliva et al., 1999). However, the role played by seasonal bioclimatic processes such as the achievement of temporary reducing conditions and/or the seasonal enhancement of leaching and fragmentation of plant detrital material in the overall process is still a debated issue. In order to study these effects in details, we have analysed the temporal variability of dissolved trace element (REE, Fe, Mn, Al, Cu, Zn, Th, U, Cd and As) and DOC concentrations in wetlands from two small western Europe catchments (Pleine Fougères and Kervidy-Naizin, France). These two sites offer an unique opportunity to study the role of organic matter and seasonal redox dynamics on weathering mechanisms by comparing the chemistry of shallow, organic-rich waters from wetland areas with those of deeper, organic-poor waters collected on the same catchments. Moreover, each site benefits from long, high frequency time series, allowing thorough investigation of the role of short term bioclimatic factors on water chemistry.

The two studied wetlands exhibit comparable soil horizons consisting of a complex assemblage of quartz, kaolinite, Fe and Mn oxi-hydroxides together with plant detrital materials. Results from water analyses are also quite similar, with the two studied wetlands showing the same marked seasonal changes in dissolved concentrations for all elements except Zn and Cu. Concentrations are found to be low until about February or March and then increase abruptly. Mn and Fe show the largest seasonal variations, with concentrations increasing by 1 to 2 orders of magnitude, respectively. For REE, U, Th and Al, concentrations are multiplied by factors ranging from 5 to 2. Ancillary data (i.e. DOC, measured redox potential, temperature) associated with the trace element time series show that the onset of trace element release occurs in phase with a decrease of the redox potential and coincides with large percentage changes of the DOC content of the waters (from ca. 10 to 30-50 mg/l). A comparison of these results with those obtained for organic-poor waters (DOC < 5 mg/l) collected from upland wells installed above the two studied wetlands reveals that wetland waters are systematically strongly enriched in U, Th and Cu compared to their organic-poor counterparts. Moreover, concentrations in the

latter do not vary through time. Finally, another important difference is the occurrence of a permanent deep negative Ce anomaly in upland organic-poor waters ( $0.1 < Ce/Ce^* < 0.7$ ), which is not seen in wetland soil solutions ( $Ce/Ce^* = 1$ ).

The fact that the seasonal build up of dissolved trace element concentrations in wetland waters occurs in phase with a decline of the measured redox potential may suggest that the observed variation in water chemistry is under the control of redox processes. Redox processes could participate to the observed chemical variations through the reductive dissolution of soil-forming iron and manganese oxi-hydroxides. The ability of these phases to accommodate elements such as Al, U, Th, Cd and the REE has been already widely demonstrated, as also the ability of Fe(III) and Mn(IV) to provide alternate electron acceptors for microbial population in wetland soils where the supply of oxygen is greatly reduced. Elements with multiple oxidation states (e.g. As) could be themselves directly involved in reductive dissolution. Alternatively, the observed changes in trace element concentrations could arise from the seasonal build up of DOC which is seen to accompany the trace element variations. Organic matter could participate to this process in two ways: i) dissolved organic acids could enhance dissolution of soil minerals and also favour the mobilisation of insoluble elements such as Fe, Th and REE by chemical complexation; ii) trace elements scavenged into soil particular organic matter could be release into the solution during decomposition by micro-organisms. With the data available, it is impossible to decide which of these different processes play the dominant role in controlling the observed variation in water chemistry. In conclusion, the results presented here underscore the key role of seasonal bioclimatic factors in controlling soil/water exchange processes, and the importance of taking into account this temporal variability when modelling chemical weathering mechanisms and chemical weathering fluxes in organic-rich, waterlogged soils.

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