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# pH : a key control of the nature and distribution of dissolved organic matter and associated trace metals in soil

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Dissolved organic matter is ubiquitous at the Earth's surface and plays a prominent role in controlling metal speciation and mobility from soils to hydrosystems. Humic substances (HS) are usually considered to be the most reactive fraction of organic matter. Humic substances are relatively small and formed by chemically diverse organic molecules, bearing different functional groups that act as binding sites for cations and mineral surfaces. Among the different environmental physicochemical parameters controlling the metal speciation, pH is likely to be the most important one. Indeed, pH affect the dissociation of functional groups, and thus can influence the HS structure, their ability to complex metals, their solubility degree allowing the formation of aggregates at the mineral surface.

In this context, soil/water interactions conducted through batch system experiments, were carried out with a wetland organic-rich soil to investigate the effect of pH on the release of dissolved organic carbon (DOC) and associated trace elements. The pH was regulated between 4 and 7.5 using an automatic pH stat titrator. Ultrafiltration experiments were performed to separate the dissolved organic pool following decreasing pore sizes (30 kDa, 5 kDa and 2 kDa with 1 Da = 1 g.mol-1).

The pH increase induced a significant DOC release, especially in heavy organic molecules (size >5 kDa) with a high aromaticity (>30 %). These were probably humic acids (HA). This HA release influenced (i) directly the trace element concentrations in soil solution since HA were enriched in several trace elements such as Th, REE, Y, U, Cr and Cu; and (ii) indirectly by the breaking of clay-humic complexes releasing Fe- and Al-rich nanoparticles associated with V, Pb and Ti. By contrast, at acid pH, most HS were complexed onto mineral surfaces. They also sequestered iron nanoparticles. Therefore, at low pH, most part of DOC molecules had a size < 5 kDa and lower aromaticity. Thus, the DOC was mostly composed of simple organic compounds little complexing. Consequently, the soil solution was depleted in trace elements such as Th, REE, Y, U, Cr, Cu, Al, Fe, V, Pb and Ti, but also enriched in Ca, Sr, Ba, Mn, Mg, Co, Zn and in a lesser proportion in Rb, Li and Ni. The aromaticity in the fractions <5 kDa was higher than in the fractions <30 kDa or <0.2 $\mu$m. Complementary experiments were performed to understand the HS size distribution and aromaticity according to pH and ionic strength .The molecular size and shape of HS is usually explained by two concepts: (i) the macropolymeric structure with heavy organic molecules considered to be flexible linear polyelectrolytes and (ii) the supramolecular structure with an association of a complex mixture of different molecules held together by dispersive weak forces. Ours results supported the HA supramolecular structure at neutral or basic pH conditions. But, at acid pH, a disruption of the humic supramolecular associations involved the release of small organic molecules with a high aromaticity. Moreover, this aromaticity variation can be due also to the presence of fulvic acids in the fractions <5 kDa and a mixture of heavy organic molecules little complexing in the fractions >5 kDa. These latter molecules displayed a low aromaticity decreasing the global aromaticity of the fractions <30 kDa and <0.2 $\mu$m.

To summarize, these new data demonstrated that the DOC and trace element concentrations of the soil solutions were strongly controlled by pH. This parameter influenced the nature and the size of the DOC as well as, the trace element concentrations in the soil solutions, with a decreasing contribution of HA when pH decreased. This pH dependence is a key issue of concern since local (human pressure) and/or global (climatic) warning result in pH water changes.