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## Adsorption and Retardation of Organic Molecules: Past and new insights on hydrophilicity.

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### Organic Fate in Environment

Organic molecules are widely studied in environmental sciences, marine chemistry and pedo/geosciences. Among them, the anthropogenic organic matter (AOM) corresponds to manmade molecules, potentially released through the geosphere as emerging pollutants. AOM covers massive polymers, solvents and fuels, organic coatings and synthesised compounds such as pharmaceuticals. It includes both ionic and non-ionic molecules, polar and apolar molecules. The ionic polar molecules are highly soluble in water and more mobile in soils and rocks. They play a key role in environmental issues by complexing ions and increasing their solubility, weathering minerals and in some cases driving metal/radionuclides transport. The determination of AOM behaviour is then a key point for containment of wastes, extraction of elements and remediation of soils.

Hydrophobic AOM and its adsorption on Soil Organic Matter (SOM) have been extensively studied in the context of pesticide fate in the environment<sup>[1,2]</sup>. Yet, the behaviour of polar hydrophilic molecules is far less documented than that of apolar hydrophobic molecules. In this study, we tried to highlight a general behaviour during adsorption of polar organic acids on a sedimentary rock.

### From nuclear wastes disposal to gas extraction

Claystone geological formations are considered in several countries for hosting a radioactive waste disposal (Callovian-Oxfordian in France (COx), Opalinus Clay in Switzerland, Wakkanaï formation in Japan, Boom Clay in Belgium). The COx claystone has been extensively studied in the context of the French Underground Retrievable Nuclear Waste Repository project (Cigéo). Our recent study focused on AOM released by radioactive wastes (polymeric waste, bitumen, graphite...) under disposal conditions. Recent achievements were obtained concerning adsorption and transport of AOM in COx claystone<sup>[3,4]</sup> (Figure 1).

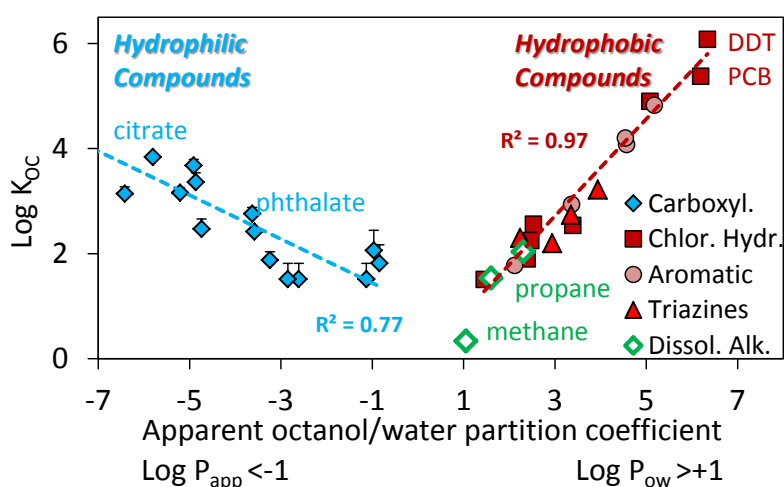


Figure 1: Adsorption of organic molecules as a function of Octanol Water Partition Coefficient. Recent data acquired in this study on hydrophilic carboxylic acids (blue) on COx claystone<sup>[3]</sup>, Bibliographic data on hydrophobic compounds (red) on various soils<sup>[1]</sup>, Recent data on dissolved alkanes (green) extracted from Opalinus claystone<sup>[5]</sup>.

The adsorption of polar carboxylic acids (hydrophilic) was found to exhibit an opposite trend than that of apolar compounds (hydrophobic) :

On one hand, polar hydrophilic acids were found to adsorb on oxides and or clay minerals (Figure 1, blue dots). This affinity is proportional to polarity and hydrophilicity (i.e. inversely proportional to  $P_{ow}$ ). For example in the case of ortho-phthalic acid, it was found to be a reversible adsorption leading to a significant retardation factor during diffusion.

On the other hand, apolar hydrophobic molecules are adsorbed onto, or incorporated into SOM. The affinity per mass of the SOM between the molecules and sorbents,  $K_{oc}$ , is highly soil or sediment independent<sup>[1]</sup> and proportional to hydrophobicity,  $P_{ow}$  (Figure 1, red dots). This feature was observed again, during an *in situ* out-diffusion experiment of natural dissolved gas released by Opalinus claystone during 8 years (green dots)<sup>[5]</sup>. Similar work is on-going in the context of graphite wastes management and potential degradation into Polycyclic Aromatic Hydrocarbons (PAHs) on tégulines clayrocks.

### Further studies

A considerable work has been achieved on the environmental fate of AOM. “ $P_{ow}$ ” correlations seem useful to estimate adsorption and retardation of both hydrophilic and hydrophobic compounds. These results are not only useful for wastes containment, but provide a roadmap for various investigations on other sedimentary claystones as well as SOM characterization and fossil fuels extraction. Work is still on-going on behaviour of heterogeneous cocktails and competition during co-adsorption. Still, bricks are missing to get a bigger picture on organic molecules behaviour, for example the reactivity controlled by oxydoreduction processes or the behaviour of organic cations and surfactants.

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