



Extent and characterisation of natural groundwater organic matter sorption onto minerals

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Rivers and aquifers have been proven to be physiochemically connected. Despite their interaction, organic matter (OM) concentration in groundwater is much lower than rivers. One might ask where it goes. For example, is sorption responsible for this missing fraction? If so, what components of OM are utilised by groundwater sorption to the minerals? This research aims to quantify the sorption of natural groundwater DOC over a range of groundwater and surface water environments in South East Australia. Batch experiments were set up by adding 40 ml of filtered (0.22 μm) sample to a range of masses of three types of sterilised minerals: iron coated sand, quartz sand and calcium carbonate. The systems were rotated for 1 hour under controlled conditions before analysis by Liquid Chromatography-Organic Carbon Detection (LC-OCD) for the aqueous phase and X-ray Photoelectron Spectroscopy (XPS) for the solid phase.

Size-exclusion chromatography using LC-OCD is used to determine the remaining chemical fractions in solution. LC-OCD separates DOC into biopolymers ($\gg 20,000$ g/mol), humic substances (1000 g/mol), building blocks (300-500 g/mol), low molecular weight neutrals (< 350 g/mol) and low molecular weight acids (350 g/mol). The technique also provides measures of humic substances aromaticity and relative molecular weight. XPS is used to characterise the surface chemistry of the adsorbed organic layer in terms of the relative carbon, nitrogen, and oxygen content, and the types of chemical bonding. The results of solid-phase XPS is compared with the remaining chemical fractions in solution characterised by LC-OCD.

LC-OCD results showed that humic substances were highest in concentration in the groundwater DOC compared to other fractions (13-65%) and was the significant sorbing fraction for all mineral types and water samples. The sorption extent ranges between 4-61%. This sorption was highest for iron coated sand (8-61%) followed by calcium carbonate (10-35%) and then quartz sand (4-22%). XPS showed that more sorbed organics (O, C and N) were found on iron coated sand and calcium carbonate compared to quartz sand. The extent of humic substance sorption was found proportional to its aromaticity and molecular weight for all mineral types and water samples. In conclusion, even though sediment types influence groundwater DOC sorption, the result suggests that groundwater DOM sorption plays an important role in the missing fraction of groundwater DOC (31-9/4%).