



## Relating fluorescent dissolved organic matter to bacterial biomass in English aquifer systems

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Dissolved organic matter (DOM) serves as crucial nutrient for microorganisms in oligotrophic groundwater environment. This study investigated regional-scale variations in fluorescent DOMs (fDOM) across three major English aquifers: Jurassic limestone, Permo-triassic sandstone, and Cretaceous chalk, which display different dominant groundwater flow regimes ranging from karstic, intergranular and fractured respectively. Untreated groundwater samples from 134 public supply pumps were analysed using Fluorescence spectroscopy to characterize fDOM in these aquifers with distinct properties. Our aim was to find the baseline fDOM concentrations in uncontaminated groundwater and explore the associations between fDOM, DOC, and bacterial biomass. PARAFAC modelling of the Excitation Emission Matrices (EEMs) revealed two humic-like components (HLF): component-1 peak-C, and component-2 or peak-M; and two protein-like components: component-3 or peak-T (tryptophan like or TLF) and component 4 or peak-B (Tyrosine like). Humic-like components were predominant in groundwater, with median total HLF of 0.19 raman unit (RU). Bacterial cells were enumerated using flow cytometry. Absence of *E. Coli* in the samples suggested no surface microbial contamination. DOC concentration ranged from 0.76 to 1.11 mg/L, lower than the UK groundwater mean of 3.1 mg/L, implying a carbon-poor environment. Significant difference of fDOM and DOC across three aquifers were observed. Median DOC and HLF were significantly higher in limestone and chalk aquifers than in sandstone aquifers. Higher humification index in limestone (HIX=0.8) and chalk (HIX=0.74) aquifer suggested less complex and high H/C ratio fDOM was present in sandstone aquifer (HIX=0.68). Sandstone also exhibited higher  $\beta/\alpha$  ratio (0.97) and fluorescence index (FI=1.53) than chalk ( $\beta/\alpha$ =0.85, FI=1.4) and limestone aquifer ( $\beta/\alpha$ =0.75, FI=1.4) suggesting fresher and more microbially derived autochthonous fDOM in sandstone aquifer in contrast with more mature and allochthonous fDOM in limestone and chalk aquifers. Positive correlations between HLF, TLF, and total bacterial cell concentration (TCC) were observed across all aquifers. However, DOC was only correlated with TCC in sandstone aquifers. This emphasised that the type of DOM, rather than its quantity, closely associates with bacterial biomass. Median TCC in karstic limestone aquifer ( $2 \times 10^4$ /ml) was nearly double that of intergranular sandstone ( $1 \times 10^4$ /ml), and fractured chalk aquifer ( $8 \times 10^3$ /ml). Despite relatively high fDOMs in chalk aquifers, TCC was significantly lower due to size exclusion of

suspended bacteria through smaller pore-throats of the chalk. This also suggested that the correlation of TCC and fDOMs might not be due to more DOM promoting more bacterial productivity, but possibly due to their similar source. This study highlighted the carbon-poor nature of uncontaminated groundwater environments, with spatially distinct baseline values of fDOM, DOC, and TCC. Limestone and chalk aquifers have high permeability and surface connectivity and are therefore more vulnerable to quality degradation.