

Exploring the potential of DOC fluorescence as proxy for groundwater contamination by pesticides

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Of the different water quality surrogates the fluorescence of dissolved organic content (FDOC) appears particularly promising due to its sensitivity and specificity. A complete spectrum of FDOC can be obtained using bench top instruments scanning a spectral space going from short wavelength UV to visible blue, yielding a so-called an excitation-emission matrix (EEM). The raw EEM can be either used directly for correlation analysis with the variable of interest, or first decomposed into underlying elements corresponding to different groups of organic compounds displaying similar properties using multiway techniques such as Parallel factor analysis (PARAFAC). Fluorescence spectroscopy has up to now only rarely been applied specifically to groundwater environments. The objective of the project was to explore systematically the possibilities offered by FDOC and PARAFAC for the assessment of groundwater contamination by pesticides, taking into account the transit time from the pesticide source to the groundwater outlet.

Three sites corresponding to different transit times were sampled:

- one spring regularly contaminated by surface water from a nearby stream (sub-daily to daily response to fast-flow generating storm events)
- one spring displaying a weekly to monthly response to interflow
- sampling along a flowline consisting of a series of springs and an observation well situated upgradient with mean transit times difference of several years

Preliminary results show that a three component PARAFAC model is sufficient to decompose the raw EEMs, which is less than the seven or eight component models often encountered in surface water studies. For the first site, one component in the protein-like region 275(excitation)/310 (emission) nm measured in the stream samples was filtered completely by the aquifer and did not appear in the spring samples. The other two components followed roughly the trend of the DOC and pesticide breakthrough.

For the second site, soil sampling of the agricultural plots and DOC extraction also allowed to characterise the spectral signature of the pollution source. A humic-like component (250/450 nm) was correlated with the breakthrough of recent soil water and pesticide concentration.

Lastly, the fluorescence intensity of the different components for the third sampling site showed a decrease proportional to the decrease in DOC concentration between the observation well and the springs caused either by dilution, degradation or both. This lack of change in the spectral pattern along a flow line seems to indicate that labile soil DOC fractions have already been degraded by the time water reaches the observation well.