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Sorption or biodegradation? - Evidence from carbon isotope analysis of a transient toluene pulse passing through a pristine aquifer

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Stable isotope fractionation is widely recognized as a robust indicator of organic pollutant transformation in contaminated aquifers. Nonetheless, it has been argued that significant changes in isotope values may alternatively arise from sorption when a contaminant plume is expanding and its front is at non-steady state. Potentially, this may lead to misinterpretations at the field sites using compound specific isotope analysis. In order to investigate the relevance of such a scenario, a 30-hour toluene pulse (water saturated with toluene) was injected along with a conservative tracer (90 % deuterium labeled water) into a pristine indoor aquifer ($0.8 \times 0.7 \times 5$ m), filled with natural sediment and flushed with natural groundwater at a rate of 9L/hr. Water samples were collected 4.2 m away from the injection source. At the front part of the pulse, isotope values were enriched in 13C indicating a fractionation effect ($\Delta\delta 13C = -1.99 \pm 0.18$ % due to sorption. Surprisingly, isotope values were also enriched in 13C at the tail of the pulse leading to an inverse trend ($\Delta\delta 13C = -1.26 \pm 0.21$ %. In addition, all $\delta 13C$ values were more positive than the original input. This is contrary to what would be expected for sorption alone indicating that also biodegradation must be occurring. The comparison between the toluene and D2O breakthrough curves further demonstrated that a portion of toluene was removed by degradation at a pseudo 1st order rate of 0.017/hr. Our study confirms that sorption may lead to significant carbon isotopic fractionation in the case of aquifers contaminated with non-stationary organic plumes. More importantly, it gives evidence that microbes could immediately (within 50 hours) respond to a toluene contamination in a pristine aquifer. In our case, the effect of sorption would therefore not have led to severe misinterpretations since microbial degradation was indeed occurring in the transient pulse.