

Dissolved gaseous hydrocarbons in shallow groundwater of Lower Saxony, Germany – Revisited 2016

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Many concerns arise within the public and government/political institutions over potential groundwater contamination from deep drilling operations. For this reason we initiated a baseline study in 2014 on the distribution of dissolved methane, ethane and propane in shallow groundwater (~1000 groundwater wells, Schloemer et al., 2016) of Lower Saxony, which includes the major petroleum and natural gas provinces in Germany. We observed a variation of dissolved methane concentration over 7 orders of magnitude (20 nI/l to 60 ml/l [v/v]). Methane $\delta^{13}\text{C}$ compositions ranged from -110‰ to +25‰ vs VPDB, narrowly clustering around -70‰ at high concentrations but being increasingly more variable at lower concentrations (-40‰ to -80‰). Most of the data are clearly indicative for methanogenic processes, samples unusually enriched in $\delta^{13}\text{C}$ can best be explained by secondary methane oxidation. Although some general regional trend can be observed, results are highly variable within short lateral distances or within different aquifers/filter depths. Frequently ethane (27% of samples, median 50nI/l) and occasionally propane (8%, median 23nI/l) has been detected. Lacking the carbon isotope composition of these homologues and thus solely based on the extremely low concentrations and atypical ethane/propane ratios, these have been tentatively interpreted as ubiquitous microbial background.

From the original 2014 sample set around 100 wells have been selected for consecutive testing through 2015. In spring 2016 a total number of 1100 wells have been sampled, 700 of which had already been part of the initial study, providing us with the unique opportunity to assess long term variations.

The overall comparison of these 700 samples revealed only small relative variations in methane concentrations (mostly $< \pm 25\%$), although higher variations are common at concentrations less than 1 $\mu\text{l/l}$. Correspondingly the carbon isotopic composition of paired samples is quite stable ($\pm 2\%$) for most of the samples (~60%) but large discrepancies can be observed at low absolute concentrations ($> \pm 5\%$ in 25% of samples). Minor variations could be related to uncertainties in laboratory analysis ($\pm 10\%$ in concentration, $\pm 0.5\%$ $\delta^{13}\text{C}$). To which extent the small number of sampled groundwater with unusually high variations are indeed a result of a naturally occurring process (rapidly changing conditions or anthropogenic influence) is currently under investigation. However, applying different sampling conditions/procedures (i.e. different pumps, flow rates) had to be accepted during the course of the project and might be a reason as well. In any case our preliminary results point toward the necessity of repeated sampling (particularly in shallow unconfined aquifers) to account for possible natural variations and of strictly consistent sampling protocols when analyzing “non-conservative” dissolved gases.

Reference

Schloemer, S., Elbracht, J., Blumenberg, M. and Illing, C.J., 2016. Distribution and origin of dissolved methane, ethane and propane in shallow groundwater of Lower Saxony, Germany. *Applied Geochemistry*, 67: 118-132.