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Distribution and origin of dissolved methane, ethane and propane in shallow groundwater of Lower Saxony, Germany

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ABSTRACT

More than 90% of Germany's domestic natural gas production and reserves are located in Lower Saxony, North Germany. Recently, research has been intensified with respect to unconventional shale gas, revealing a large additional resource potential in northern Germany. However, many concerns arise within the general public and government/political institutions over potential groundwater contamination from additional gas wells through hydraulic fracturing operations.

In order to determine the naturally occurring background methane concentrations, ~1000 groundwater wells, covering ~48 000 km^2, have been sampled and subsequently analyzed for dissolved methane, ethane and propane and the isotopic composition of methane ($\delta^{13}C$).

Dissolved methane concentrations cover a range of ~7 orders of magnitude between the limit of quantification at ~20 nl/l and 60 ml/l. The majority of groundwater wells exhibit low concentrations (<1 µl/l), a small number of samples (65) reveal concentration in the range >10 ml/l. In 27% of all samples ethane and in 8% ethane and propane was detected. The median concentration of both components is generally very low (ethane 50 nl/l, propane 23 nl/l).

Concentrations reveal a bimodal distribution of the dissolved gas, which might mirror a regional trend due to different hydrogeological settings. The isotopic composition of methane is normally distributed (mean ~ −70‰ vs PDB), but shows a large variation between −110‰ and +20‰. Samples with $\delta^{13}C$ values lower than −55‰ vs PDB (66%) are indicative for methanogenic biogenic processes. 5% of the samples are unusually enriched in ^{13}C (≥25‰ vs PDB) and can best be explained by microbial methane oxidation.

According to a standard diagnostic diagram based on methane $\delta^{13}C$ values and the ratio of methane over the sum over ethane plus propane ("Bernard"-diagram) less than 4% of the samples plot into the diagnostic field of typical thermogenic natural gases. However, in most cases only ethane has been detected and the remaining less than 15 samples demonstrate an uncommon ratio of ethane to propane compared to typical thermogenic hydrocarbons. These data do not suggest a migration of deeper sourced gases, but a thermogenic source cannot be excluded entirely for some samples. However, ethane and propane can also be generated by microbial processes and might therefore represent ubiquitous background groundwater abundances of these gases. Nevertheless, our data suggest that due to the exceedingly low concentration of ethane and propane, respective concentration changes might prove to be a more sensitive parameter than methane to detect possible migration of deeper sourced (thermally generated) hydrocarbons into a groundwater aquifer.

1. Introduction

More than 90% of Germany's domestic natural gas production and reserves are located in Lower Saxony, North Germany. Most of these gases are generated from Carboniferous source rocks, while the also prominent and still produced petroleum accumulations in Lower Saxony derive from Jurassic Posidonia or Cretaceous Wealden source rocks (Binot et al., 1993; Kockel et al., 1994). Recently, research has been intensified with respect to unconventional shale gas, revealing a large additional resource potential in northern Germany (Pierau et al., 2013). Simultaneously, concerns arose within the general public and government/political institutions

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over potential environmental impacts from increased exploration and production activities. Many concerns have been raised regarding the potential for contamination of shallow groundwater, i.e. potable or otherwise useable water with a total dissolved solids (TDS) content of less than 1000 mg/L (Jackson et al., 2013a), associated with hydraulic fracturing operations.

Potential risks for groundwater, surface water and/or soil by hydraulic fracturing and/or production of shale gas include contamination by fugitive natural gas (i.e. stray gas contamination), hydraulic fracturing fluids and/or formation (brines) and waste waters from the deep formations (Vengosh et al., 2014).

However, groundwater gas contamination is not necessarily associated with shale gas production and increased hydraulic fracturing operations. Methane can be generated biologically under methanogenic aquifer conditions. Any hydrocarbon accumulation in the subsurface (oil/gas reservoirs, coal bed methane) might lose methane and higher homologues through natural and induced fractures (Myers, 2012; Nakata et al., 2012) or producing and abandoned wells (Kang et al., 2014; Vengosh et al., 2014). Likewise hydrocarbon gases leaking from underground gas storage sites (Laier, 2012; Révész et al., 2010) and pipeline leaks (Jackson et al., 2014) have been observed.

Numerous studies with respect to potential groundwater contamination by stray or fugitive gases related to shale gas production have been published in recent years. Some of them disclaim a relationship of observed dissolved hydrocarbon gases with hydraulic fracturing or drilling activities (Cheung et al., 2010; Davies, 2011; Li and Carlson, 2014; McMahon et al., 2015; Molofsky et al., 2011, 2013), whereas others provide objective evidence for shale gas production-induced stray gas contamination (Darrah et al., 2014; Dyck and Dunn, 1986; Jackson et al., 2011, 2013b; Osborn et al., 2011a; Révész et al., 2010; Warner et al., 2012).

Whether there is enough evidence that the intensive fracturing operations in the main shale gas plays in the US is affecting the groundwater quality is still under debate (e.g. Jackson et al., 2011; Osborn et al., 2011b; Schon, 2011; Saba and Orzechowski, 2011). Modeling and monitoring of vertical fracture heights induced by hydraulic fracturing shows that these do not exceed several hundred meters (Davies et al., 2012; Fisher and Warpinski, 2012; Flewelling et al., 2013), hence suggesting they will usually not extend to the typically shallow (<200 m) groundwater bodies (Vengosh et al., 2014) and the highest risk is gas release due to a loss of well integrity.

Background measurements of hydrocarbon concentrations in groundwater wells are mandatory in many states of the US (Jackson et al., 2013a) and in Canada (e.g. baseline water well testing program for coal-bed methane development according to ERCB, 2006). Several national (e.g. UBA, 2014) and international recommendations (EU, 2014; IEA, 2012) call for intensive pre- and post-production groundwater monitoring programs particularly mentioning dissolved hydrocarbon gases in groundwater. Additionally, the analysis of the isotopic composition (carbon and hydrogen) of methane is mandatory at high concentrations, e.g. >2 mg/l (~2.8 ml/l) according to the Colorado Oil and Gas Conservation Commission (COGCC orders 112–156 and 112–157), >5 mg/l (~7.1 ml/l) according to the Wyoming OGCC or in Pennsylvania above 7 mg/l (~9.9 ml/l) (PA Code, Oil and Gas Act Regulations Chapter 78) to pinpoint the source of the dissolved gas.

So far only sparse data sets are available for German groundwater concerning the composition and isotopic signatures of dissolved hydrocarbons. Scherer (2000) published the methane concentration of 68 groundwater extraction wells in northern Germany ranging from 0.15 to 52 ml/l (0.1–37 mg/l). Melchers (2008) published data from the Cretaceous Münsterland basin (bordering southeast to Lower Saxony) where elevated methane concentrations up to 67 ml/l have been observed. Intensive mining operations (coal, strontianite) induced mine subsidence thus potentially creating effective migration pathways for deeper sourced methane from underlying coal seams. Gruendger et al. (2015) published a small data set (10 wells) of deep aquifers close to an open pit coal mine in North Rhine-Westphalia. Dissolved methane concentrations in this data set range from 0.3 to 2.2 ml/l.

The aim of this study is to gain a first comprehensive data set on present day background hydrocarbon concentrations in groundwater of Lower Saxony, Germany as well as the methane stable carbon isotope ratios. Due to the limited number of hydraulic fracturing operations (327 Frac stages in Lower Saxony, depth generally >1100 m; LBEG, 2014) results of this study represent a virtual "pre-fracking" baseline.

For our study approximately 1000 groundwater wells covering ~48 000 km^2 have been sampled and subsequently analyzed for dissolved methane (CH_4), ethane (C_2H_6) and propane (C_3H_8). The isotopic composition of methane ($\delta^{13}C$) as diagnostic tool to characterize the origin of methane and as sensitive parameter to any additional methane input to the groundwater, in particular at initially low CH_4 concentrations, was also analyzed. Hence, special emphasis has been devoted to develop a sample preparation line for routine GC-irMS (Gas Chromatographic System coupled to isotope-ratio Mass Spectrometry) analysis at low dissolved gas concentrations (lower limit for $\delta^{13}C$ measurements of methane is ~0.7 μl/l), which is considerably lower than for other baseline studies e.g. > 0.5 ml/l (Darrah et al., 2014).

2. Regional geological and hydrogeological conditions

The two main structural geological units of the area under investigation comprise the Lower Saxony Sedimentary Basin (LSB) in the north and the Mesozoic/Paleozoic mountainous region in the south (Weser, Osnabrück and Leine hills, Harz mountains). The most common rocks in the Harz Mountains in the southeast are Devonian to early Carboniferous argillaceous shales and greywackes, the Weser, Osnabrück and Leine highlands are dominated by Mesozoic rocks. In the northwestern part of the LSB the principal source rocks for natural gas are Upper Carboniferous coals, while the marine Jurassic Posidonia and Cretaceous Wealden shale represent the primary source rock for oil. The Posidonia Shale is present throughout the LSB while the Wealden Shale exists primarily in the western portion of the basin. In the northeastern part of the LSB Upper Permian (Zechstein) marine shales, Kupferschiefer and Stinkschiefer, are the primary sources of oil.

Above Mesozoic rocks of the LSB thick Cenozoic sediments have been deposited. The early Paleogene sediments have been deposited under marine conditions that changed during time into a continental accumulation environment. These common unconsolidated Paleogene sediments can reach thicknesses of several hundred meters in synclines around the widespread salt structures of Lower Saxony. Quaternary glaciation cycles resulted in sedimentation of thick glacial sands and debris in large areas in the northern part of the LSB. In addition major areas are dominated by fluvial deposits and the northeastern coastal area by shore sediments.

The groundwater bodies of Lower Saxony are composed of 11 major terranes (Fig. 1) which can be further divided into 81 subunits (Elbracht et al., 2010). Briefly, the southern/southeastern part of Lower Saxony is dominated by aquifers in fractured consolidated sediments and the majority of the potable groundwater is related to porous aquifers in unconsolidated sands and gravels of Quaternary age.

The northwest of Lower Saxony, bordering the North Sea, is dominated by intertidal flats, near-shore estuarine flat und bog lands of the rivers Elbe and Weser. Marine saltwater intrusion is