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Spatial distribution and temporal variation of methane, ethane and propane background levels in shallow aquifers – A case study from Lower Saxony (Germany)

S. Schloemer[a,*], J. Oest[b], C.J. Illing[a], J. Elbracht[b], M. Blumenberg[a]

[a] Federal Institute for Geosciences and Natural Resources (BGR), Stilleweg 2, D-30655 Hannover, Germany
[b] State Authority of Mining, Energy & Geology (LBEG), Stilleweg 2, 30655 Hannover, Germany

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ABSTRACT

Study region: This survey was conducted in Lower Saxony/Northern Germany, the major German hydrocarbon province.

Study focus: The study aimed at improving our understanding of background concentrations for dissolved hydrocarbon gases in shallow groundwater. More than 1700 groundwater wells were sampled, determining the concentrations of dissolved methane, ethane and propane.

New hydrological insights for the region: Methane was detected in all wells with 34% < 0.001 ml/l and 14% > 1 ml/l (with 80% < 0.1 ml/l). A decreasing regional trend of methane concentrations from the North West towards South East was observed. Highest concentrations are encountered in marshes and lowlands although numerous exceptions are noted. Methane is prevalently of biogenic origin, as demonstrated by its isotopic composition. Generally, high methane concentrations are linked to high DOC, low sulfate and oxygen concentrations. Methane oxidation appears to be locally important. Ethane was detected in 30% of all wells, propane in 12.5%. The occurrence is interpreted as microbial/geogenic background related to methanogenesis or organic matter degradation during diagenesis. Low present day ethane and propane concentrations make them the preferred monitoring parameter with respect to possible anthropogenic induced input of thermogenic gas. Sampling of identical wells between 2014 and 2017 demonstrate that methane concentrations and carbon isotopic composition remain stable in general, although if it comes down to individual wells, significant fluctuations were noticed.

Conversion Factors.

	EPA, NIST (NTP)	IUPAC (STP)
Temperature [K]	293.15	273.15
Pressure [Pa]	101,325	101,325
1 ml/l CH_4	0.667 mg/l	0.716 mg/l
	41.5 µmol/l	44.6 µmol/l

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* Corresponding author.
E-mail address: s.schloemer@bgr.de (S. Schloemer).

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	EPA, NIST (NTP)	IUPAC (STP)
1 ml/l C_2H_6	1.25 mg/l 41.5 µmol/l	1.34 mg/l 44.6 µmol/l
1 ml/l C_3H_8	1.83 mg/l 41.5 µmol/l	1.97 mg/l 44.6 µmol/l

Nomenclature

AOV	Analysis of variance
BGR	Federal Institute for Geosciences and Natural Resources
C_1	Methane
$C_1/(C_2+C_3)$	Gas dryness expressed as molar ratio of methane over the sum of ethane & propane
C_2	Ethane
C_3	Propane
cv	Coefficient of variation
DIN	Deutsches Institut für Normung (German Standards Committee)
DOC	Dissolved organic carbon
DVWK	Deutscher Verband für Wasserwirtschaft und Kulturbau (rules and standards)
EPA	Environmental Protection Agency
GC	Gas chromatograph
IUPAC	International Union of Pure and Applied Chemistry
K	Temperature in Kelvin
LBEG	State Authority of Mining, Energy & Geology
LSP	Lower Saxony Plain
NIST	National Institute of Standards and Technology
nl/l, µl/l, ml/l	Concentration of dissolved gas in water given as volumetric ratio (1 nl/l = 10^{-9}l/l, µl/l = 10^{-6}l/l, ml/l = 10^{-3}l/l) at 293K and 101,325 Pa
NLWKN	Lower Saxony Water Management, Coastal Defense and Nature Conservation Agency
NTP	Normal Temperature and Pressure Conditions
p	p-value, probability value in statistical analysis
Pa	Pressure (101,325 Pa = 1 bar)
PDB	Pee Dee Belemnite, carbon isotope reference material
rho	Spearman´s rank correlation coefficient
sd	Standard deviation
SMOW	Standard Mean Ocean Water, reference material for hydrogen and oxygen isotopes
STP	Standard Pressure and Temperature Conditions
$\delta^{13}C$	carbon isotope ratio
δD	deuterium isotope ratio
δ-notation	The ratio of two stable isotopes normalized to the ratio in the standard material reported in parts per thousand (per mil, ‰)

1. Introduction

It is long known that methane, ethane and propane are common constituents in shallow groundwater (Barker and Fritz, 1981a; Swain, 1986; Coleman et al., 1988; Grossman et al., 1989; Aravena and Wassenaar, 1993) and seawater (e.g. Jones et al., 2015). However, only after initial studies in the US the occurrence of methane and thus the potential impact on the environment became a public concern. Since then numerous studies in different parts of the world have been focusing on this issue. Research is mainly directed on US unconventional shale gas plays, like the Marcellus/Utica (e.g. Osborn et al., 2011; Molofsky et al., 2013; Jackson et al., 2013; Darrah et al., 2014, 2015; Siegel et al., 2015, 2016; Warner et al., 2012), Bakken (McMahon et al., 2015), Barnett (Darrah et al., 2014; Nicot et al., 2017c), Denver-Julesburg Basin (Sherwood et al., 2016), Fayetteville (Warner et al., 2013), Haynesville (Nicot et al., 2017a) or Eagle Ford Shale (Nicot et al., 2017b). Additional studies have been conducted in Canada (Rivard et al., 2017; Humez et al., 2016a, 2016b; Lavoie et al., 2014, 2016), Great Britain (Bell et al., 2016; Darling and Gooddy, 2006), Romania (Ionescu et al., 2017), China (Huang et al., 2017) and Australia (Currell et al., 2017; Atkins et al., 2015).

Within the context of these studies a discussion on stray gas contaminations of potable groundwater resources induced by anthropogenic activities arose (e.g. Osborn et al., 2011; Vengosh et al., 2014, 2015; Vidic et al., 2013). While some studies were able to correlate high methane concentrations with hydrocarbon exploitation, i.e. fracking or leaking gas wells (e.g. Sherwood et al., 2016; Darrah et al., 2014; Reese et al., 2014;) others encountered similar high concentrations but attributed these to natural occurring background concentrations (e.g. McMahon et al., 2015; Molofsky et al., 2016a) and to migration through existing geological faults and fractures (“natural stray gas”), like in the area of the Haynesville Shale in east Texas (Nicot et al., 2017a). Only a few studies included data on repeated sampling. Most data revealed coefficients of variance up to ~60% (Harkness et al., 2017; Sherwood et al., 2016; Smith et al., 2016; Vigneron et al., 2017; Humez et al., 2015). Rivard et al. (2017) reported variations of methane concentrations over a period of 2.5 years of 2.5–6 times relative to the lowest recorded concentration of the respective well.

This study aims at a better understanding of the genetic history of dissolved hydrocarbon gases (baseline) in the largest hydrocarbon province in Germany and as a possible future tool for baseline monitoring. Hydrocarbon gases are predominantly formed by the decomposition of organic precursors, either due to thermal cracking related to increased pressure and/or temperature conditions during subsidence (thermogenic gas; e.g. Tissot and Welte, 1984; Hunt, 1996), or due to microbial methanogenesis (biogenic gas; e.g. Milkov, 2011; Thauer, 1998; Oremland, 1981; Hinrichs et al., 2006; Fukuda et al., 1984).