

Coalbed methane in the Ruhr Basin, Germany: a renewable energy resource?

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Abstract

Around the globe underground hard coal mining leads to a release of methane into the atmosphere. About 7% of the global annual methane emissions originate from coal mining. In the year 2002, 16 countries used coal gas to generate heat and electricity. In many cases, the exact size of coalbed methane reservoirs is not identified. The possibility of a long-term gas production and its profitability at single sites are unknown. To clarify these points, the processes of gas generation as well as the gas-in-place volume have to be determined. Both issues are tackled here for the Ruhr basin. Within this basin, coal gas samples were taken at 13 gas production sites, spread over three samplings within 14 months. There were virtually no changes in the concentrations of gas components at single sites within this period. The isotope composition of methane ($\delta^{13}\text{C}$ -methane: -40.0 to -57.3% vs. PDB) revealed that the produced methane is a mixture of gases of thermogenic and microbial origin. The microbial contribution of methane seems to be more pronounced at sites of active and especially abandoned coal mining than at unmined places. Ethane and propane are of thermogenic origin, with ethane's isotopic composition tending to heavier values (richer in ^{13}C) with time. This time-dependent phenomenon is interpreted as being caused by desorption. In addition, living methanogenic archaea were detected in mine water samples from depths down to 1200 m.

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1. Introduction

Total methane emissions from hard coal mines range between 25 and 45 Mt (Boyer et al., 1990; Beck et al., 1993; Clayton et al., 1993; Khalil et al., 1993) on a global scale. Within the last 5 years, more and more countries utilized a part of the coal gases for energy production. The reasons for this trend are an increasing utilization of abandoned mining areas, and a more effective and sustainable utilization in active mining. This utilization comprises all different kinds of coal gases. Coal gases are subdivided into coalbed methane (CBM), coalseam

methane (CSM), and coalmine methane (CMM). CBM is coal gas produced from boreholes in unworked coal-bearing rocks. CSM is coal gas released in active collieries, whereas CMM escapes or is produced from abandoned mines. The coal gases produced in the Ruhr Basin are CSM and CMM.

In the Ruhr Basin, 77 power stations with a total of 70 MW converted CSM and CMM into 650 GWh energy in 2002. About 85 million Euros have been invested in these plants, which consumed $280 \times 10^6 \text{ m}^3$ of coal gas in 2002. The annual production and the production characteristics differ considerably between the sites. There are sites with generally rising, falling as well as stable production rates.

The geology, structural evolution, and basin subsidence of the area have been described in detail by Bükler

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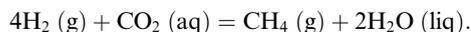
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et al. (1995), Drozdowski (1993), Littke (1987), Littke et al. (1994, 2000) and Wrede (1987, 1992). The Ruhr Basin is part of the European Subvariscan Foredeep and consists of about 3.5 km of clastic, Late Carboniferous sediments. More than 100 coal seams are intercalated in this sequence. The caprocks vary in age (Permian to Tertiary), in thickness (overall 0–1500 m), in facies (marine to eolian) and in other parameters like permeability (10^{-13} – 10^{-19} m² and 10^{-6} – 10^{-12} m/s). The rock permeabilities in the Ruhr Basin are either still natural or enhanced by underground mining and surface subsidence. They control the gas loss via migration through the caprocks which diminishes the coal gas reservoir (Thielemann et al., 2000, 2001). Maximum subsidence of the coal-bearing strata was reached in Late Carboniferous/Early Permian (Büker et al., 1995; Karg, 1998). At the same time (about 312–288 Ma ago) all of the thermogenic methane in the Ruhr Basin was formed. This was proven by mathematical combination of the basin subsidence history with reaction kinetics of methane generation (Thielemann, 2000). There was no later formation of thermogenic methane. In this entire basin, between 50,000 and 100,000 km³ (10^9 m³) of thermogenic methane were generated. Only around 1% of this volume is remaining in the coal today (Juch et al., 2004).

Coal gas can be generated by different reaction pathways. Each pathway leads to a certain isotopic signature (hydrogen and carbon isotopes) of the components. Schoell (1980, 1983, 1988) and Whiticar (1990, 1996) used isotopic differences to establish a generic classification scheme, which is used here for interpretation as well.

First reports about microbial coal conversion have been published by Potter (1908) and Fischer (1932). Research has been intensified in the 1980s (Fakoussa, 1981; Cohen and Gabriele, 1982), and recently the work in this field has been reviewed (Hofrichter and Fakoussa, 2001). Most of the research was concentrated on brown coal and lignite rather than on hard coal, and it was focussed on aerobic conditions. Fakoussa (1981, 1988, 1990) showed that some aerobic bacteria and fungi can use hard coal as the sole carbon source.

A variety of coenzymes and cofactors of enzymes typical of methanogens catalyze methane generation by carbon dioxide reduction in five steps with eight enzymes, favourably at pH 6.8–7.2 (Mudrack and Kunst, 1994, Ottow and Bidlingmaier, 1997, Schwörer and Thauer, 1991, Thauer et al., 1993). The simplified reaction is



The energy balance of this reaction (Gibbs energy, G) may reach a maximum of $\Delta G = -139.2$ kJ/mol, calculated according to Thauer et al. (1977) for pressures of hydrogen and methane of 1 bar each and for concentrations of CO₂ (aq) and H₂O (liq) of 1 mol/l. In natural systems the partial pressure of hydrogen is much lower,

reaching between 10^{-4} and 10^{-6} bar. This reduces the energy win for methanogens down to between 0 and –20 kJ/mol (Scherer, 2001).

However, the anaerobic microbial conversion of a substantial proportion of native hard coal into methane was questionable (Crawford et al., 1990). Hard coal contains only a few hydrolytic bonds. Anaerobic microorganisms can only cleave recalcitrant ether- and carbon-carbon bonds in coal to a small extent into molecules that are sufficiently small (molecular weight less than 500 Da) to be taken up into microbial cells (Hofrichter and Fakoussa, 2001). So far, an in vitro system with consortia of anaerobic hydrocarbon converting microorganisms has been demonstrated by Zengler et al. (1999). Scott et al. (1994) and Kaufmann and Scott (1994) developed a chemical cocktail of different enzymes (hydrogenases stabilized by derivation in organic solvents) plus hydrogen and cofactors to convert coal independently of living cells and of expensive nutrient media. They achieved dissolution rates of 19–40 mass% of coal.

The objectives of the work presented here are to unravel the generation processes and history of the coal gases by means of isotope geochemistry and microbiology. This contributes to the understanding of the formation of coal gas reservoirs in general and provides information to estimate the future gas production characteristics in the Ruhr Basin.

2. Materials and methods

2.1. Sampling

Gas samples were taken in the Ruhr Basin, in areas of abandoned, active and no hard coal mining for comparison. Coalbed gas was sampled at 13 sites (Fig. 1) over a period of 14 months in February and November 2002 as well as in March 2003. The ranges of concentrations are given in Table 1, some hydrocarbon concentration ratios in Table 2 and the isotopic composition in Table 3. The periods of mining activity for sites 1–11 are given in Table 2. Localities 1 and 2 are within the city of Dortmund, localities 3 and 4 in the city of Herne, site 5 is situated in Gelsenkirchen, locality 6 in Bottrop, sites 7, 8, and 9 are placed in Lünen, locality 10 is in the town of Werne, site 11 in Ahlen. Coal has never been mined below localities 12 and 13, in the outskirts of Hamm. At site 12 a coal exploration well was drilled in 1906. At all 13 sites gas escaped into the atmosphere with an overpressure of a few hPa so that the gases could easily be bottled in 150 ml gas flasks and in evacuated 100 ml gas containers. Localities 1, 2, 3, 6, 7, 8, 9, and 10 were sampled three times. At the remaining localities (4, 5, 11, 12, and 13) samples were taken one to two times (Fig. 1).

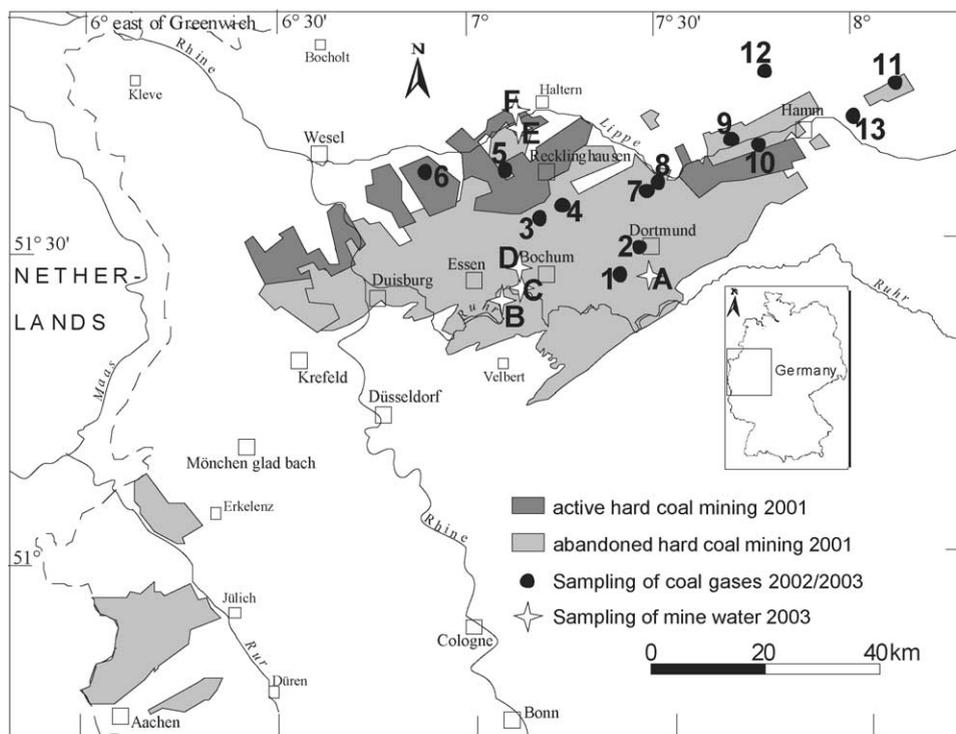


Fig. 1. Map of the Ruhr Basin with the position of all sampling locations (6 for mine waters and 13 for coal gases).

Water samples were taken at six sites (A–F, see Fig. 1) in April 2003. Site A is a more or less natural water spring in the city of Dortmund which produces water from abandoned mine works since coal mining

and water drainage measures ceased (Table 4). Locality B in the city of Essen as well as C and D in Bochum are pumping stations within abandoned mining areas which transport mine waters from depths of several hundred

Table 1
Range of concentrations of gas components in the samples taken during 14 months at 13 localities within the Ruhr Basin

Site no.	N ₂ (vol%)	O ₂ (vol%)	CO ₂ (vol%)	CH ₄ (vol%)	C ₂ H ₆ (vol%)	C ₃ H ₈ (ppm)	<i>i</i> -C ₄ (ppm)	<i>n</i> -C ₄ (ppm)	<i>i</i> -C ₅ (ppm)	<i>n</i> -C ₅ (ppm)
1	31.5–42.7	1.28–1.54	4.91–5.29	50.5–62.0	0.06–0.08	11–16	0–4	0–1	0–1	0
2	14.7–29.9	0.59–0.86	8.88–10.6	60.2–73.9	0.03–0.07	0–15.2	0–4	0–2	0–1	0–1
3	19.0–22.3	0.46–0.66	13.6–14.5	62.3–66.3	0.36–0.40	315–348	56–64	30–36	8–11	4–6
4	39.2–46.6	0.72–1.17	19.2–19.5	32.9–40.4	0.16–0.19	117–151	24–33	13–17	4–6	2–3
5	36.5–36.52	1.59–1.63	6.78–6.82	51.7–51.8	0.49–0.50	424	67	30–31	10	3
6	29.1–35.3	6.88–8.63	0.66–1.27	54.3–63.2	0.11–0.45	13–43	0–4	0–4	0–1	0–1
7	14.2–26.3	0.37–0.69	9.03–10.8	64.0–74.4	0.03–0.07	0–18	0–4	0–2	0–2	0–1
8	15.3–20.7	1.63–3.53	10.7–11.7	65.1–71.4	0.06–0.07	0–15.3	0–3	0–2	0–1	0–1
9	13.3–15.4	0.37–0.87	9.27–10.8	73.7–75.2	0.20–0.22	130–269	29–103	13–155	5–88	2–82
10	24.3–45.7	0.58–1.08	10.0–12.0	41.2–64.6	0.09–0.30	92–142	28–39	9–11	6–12	1–2
11	16.7–17.1	0.42–0.58	17.0–17.6	64.3–64.4	0.81–0.83	764–806	105–112	54–61	15–19	6–9
12	3.20–15.7	0.23–3.72	0.40–0.52	79.5–95.3	0.68–0.76	41–285	34–38	20–21	4	2
13	90.7–91.1	7.36–7.82	0.24–0.25	1.28–1.33	0	0	0	0	0	0

These data are not air-corrected because at most localities oxygen is an original proportion of the gas and not contamination during sampling.

Table 2

Time period of mining activity and some hydrocarbon concentration ratios in the samples taken at 13 localities within the Ruhr Basin

Site no.	Mining activity	$C_1/\sum C_1-C_3$	$C_1/(C_2 + C_3)$	C_2/C_1	i/n butane	i/n pentane
1	1842–1971	0.9986–0.9989	729–878	0.0011–0.0013	–3.81	–
2	1840–1988	0.9995–0.9996	2073–2343	0.0004–0.0005	–3.19	–
3	1858–1963	0.9933–0.9936	152–159	0.0058–0.0061	1.76–1.89	1.79–2.07
4	1858–1929	0.9947–0.9949	192–201	0.0046–0.0048	1.76–1.99	2.10–2.25
5	1870–2000	0.9894–0.9895	96	0.0096	2.17–2.23	3.44–3.65
6	1861–today	0.9918–0.9981	121–538	0.0018–0.0082	–1.12	–1.36
7	1875–1992	0.9990–0.9991	1014–1106	0.0009–0.0010	1.86–2.18	1.49–2.60
8	1875–1992	0.9990–0.9991	965–1074	0.0009–0.001	–2.09	–2.04
9	1870–1964	0.9961–0.9971	296–350	0.0027–0.0030	0.67–2.37	1.06–2.91
10	1898–1979	0.9950–0.9977	204–455	0.0020–0.0047	2.72–4.70	–11.67
11	1900–2000	0.9858–0.9862	71–73	0.0126–0.0129	1.82–1.95	2.16–2.39
12	No mining	0.9914–0.9919	117–124	0.0080–0.0085	1.69–1.76	1.73–2.00
13	No mining	0.9989	885–913	0.0011	–	–

Table 3

Carbon isotopic composition of methane, ethane, propane, carbon dioxide, and hydrogen isotopic values of methane in the samples taken during 14 months at 13 localities within the Ruhr Basin

Site no.	$\delta^{13}\text{C}-\text{CH}_4$ (PDB)	$\delta^{13}\text{C}-\text{C}_2\text{H}_6$ (PDB)	$\delta^{13}\text{C}-\text{C}_3\text{H}_8$ (PDB)	$\delta^{13}\text{C}-\text{CO}_2$ (PDB)	$\delta\text{D}-\text{CH}_4$ (SMOW)	Methane origin
1	–56.2 to –57.3	–20.3 to –22.4	–15	–29.4 to –33.7	–181 to –187	Mixture
2	–55.3 to –57.3	–19.8 to –21.8	–	–24.7 to –27.7	–186 to –191	Mixture
3	–48.7 to –50.4	–21.1 to –23.0	–18.0 to –21.8	–9.7 to –11.7	–196 to –200	Mixture
4	–50.9 to –51.5	–22.0 to –24.0	–19.0 to –19.7	–10.8 to –11.6	–196 to –201	Mixture
5	–45.3 to –45.9	–23.1 to –24.1	–18 to –20	–13.0	–196 to –200	Mixture
6	–47.1 to –52.4	–22.6 to –24.8	–16	–5 to +3	–190 to –201	Mixture
7	–55.9 to –56.5	–19.5 to –20.8	–19	–17.3 to –19.3	–197 to –200	Mixture
8	–51.1 to –54.9	–19.0 to –21.8	–18 to –20	–15.3 to –17.7	–192 to –199	Mixture
9	–48 to –49	–21.6 to –23.4	–21.0 to –23.2	–14.1 to –17.7	–186 to –191	Mixture
10	–48.2 to –52.1	–22.7 to –26.0	–23.0 to –24.5	–14.0 to –15.9	–185 to –191	Mixture
11	–40.0 to –40.1	–22.8 to –23.5	–21.3 to –23.0	–7.5 to –8.1	–175 to –187	Mixture
12	–42.7 to –42.8	–19 to –21.3	–11 to –13	–2 to +0.8	–181 to –196	Mixture
13	–85.1 to –85.9	–	–	–21.9 to –23.6	–257 to –260	Microbial

metres to the surface, with hardly any contact to oxygen (air). Samples E and F were received from an active mine near the town of Haltern.

2.2. Organic geochemistry

Ninety-five samples of coal gases were analyzed with geochemical methods. Concentrations of gas compounds were measured with a GC (Varian CP-3800). 0.2 ml of every gas sample was injected into the TCD-side of the GC, which contained three packed columns (Hayesep T 0.5 Mx 1/8" nickel, Hayesep Q 0.5 Mx 1/8" nickel, and a Molsieve-13X 1.5 Mx 1/8" SS). Here, the concentrations of hydrogen, nitrogen, oxygen, and carbon dioxide were quantified. Into the FID-side of the GC 0.5 ml of every gas sample were injected, passing three capillary columns (CP-Siel 5CB 30 Mx 0.32 mm, Sili-

caplot 30 Mx 0.32 mm, and again a CP-Siel 5CB 30 Mx 0.32 mm). The FID was used for analyzing the concentrations of methane to pentane. All six columns were placed in one oven, heated to 50 °C at the start of the analysis. After 10 min, temperature was increased at 10 °C/min up to 180 °C, which was kept for another 10 min. Finally, the oven temperature was returned to 50 °C at 50 °C min. The detection limit for hydrogen is 500 ppm, the one for oxygen, nitrogen and carbon dioxide 100 ppm, and the detection limit for hydrocarbons (methane to pentane) is as low as 100 ppb.

Stable carbon and hydrogen isotope measurements of methane, ethane, propane and carbon dioxide (Table 3) were conducted with a FinniganTM-mass spectrometer (IRMS). The different gases were separated cryogenically and burnt in a combustion furnace at 1000 °C, converting the hydrocarbon gases into carbon dioxide.

Table 4
Main characteristics of the six samples of mine waters taken from the Ruhr Basin, April 2003

No.	Sampling depth a.s.l. (m)	Temperature (°C)	pH	EH (mV)	Salinity (g/l)	Conductivity (μ S/cm)	Sulphate (mg/l)	DOC (mg/l)	TOC (mg/l)	TIC (mg/l)	free CO ₂ (mg/l)	Living methanogenic archaea detected?
A	70	12.9	6.5	160	1.630	1920	677	3.4	2.0	133	199	Yes
B	-514.7	21.3	6.6	160	1.692	2490	239	2.8	1.4	140	170	Yes
C	-165	19.8	6.9	130	2.012	2490	358	1.8	1.7	201	159	Yes
D	-950	26.0	6.7	120	13.264	22,200	190	1.9	2.2	215	286	Yes
E	-1178	27.0	5.5	260	60.369	>25,000	–	2.4	3.0	26	–	No
F	-1175	27.0	5.5	260	59.225	>25,000	–	1.9	2.3	36.5	–	No

(a.s.l., above sea level).

They were subsequently cryofocussed and measured in the IRMS. Isotope values are given in the δ notation relative to the internationally adopted PDB and SMOW standards. The precision of the $\delta^{13}\text{C}$ -measurements for methane is $\pm 0.2\%$, for carbon dioxide, ethane and propane $\pm 0.5\%$. The variability of δD values for methane is $\pm 2\%$.

2.3. Microbiology

For microbiological analysis six samples of mine water have been taken from natural springs as well as from depths down to 1200 m (Table 4). The water was sampled in glass bottles with a gas-tight lid. The bottles were completely filled with water samples to minimize a contamination with air to prevent inactivation of anaerobic microorganisms by oxygen. The bottles were closed, kept cool at 6 °C, brought to the microbiology lab and treated immediately.

Total prokaryotic cell numbers were determined using acridine orange as a fluorochrome dye with epifluorescence microscopy (Fry, 1988). Of each water sample 5 ml were mixed with 0.5 ml of an acridine orange solution, which has previously been filtered through a bacteria tight 0.2 μm membrane. After 5 min incubation time the stained water sample was filtered through a bacteria tight 0.2 μm black polycarbonate membrane. Excess dye was flushed from the membrane by rinsing with filtered sterilized water. Afterwards, the membrane was immediately mounted for microscopic analysis in a minimum of paraffin oil under a coverslip. Mounted membranes were viewed under incident illumination with an Olympus BX60 POL-microscope fitted with a 100-W mercury vapour lamp, a wide-band interference filter set for blue excitation, a 60 \times UPlanFl 40 \times /0.75P dry-objective lens, and 10 \times oculars. Prokaryote-shaped fluorescing objects were enumerated, and the cell concentration per ml sample was calculated.

To check for the occurrence of methanogenic archaea, 1 ml of each sample was used to inoculate a specific medium for enrichment of methanogenic archaea. The medium with H₂ and a mixture of fatty acids as substrates for growth was anaerobically prepared under a gas atmosphere of CO₂/N₂ (10/90, v/v) as described by Widdel and Bak (1992). The composition of the medium is shown in Table 5.

About 30 ml portions of the medium were filled under a stream of CO₂/N₂ (10/90, v/v) into 50 ml glass serum flasks. The flasks were closed with air-tight butyl rubber seals and evacuated, and gassed with a mixture of CO₂/N₂ (10/90, v/v). With sterile syringes 5 ml H₂ were added to each flask through the butyl rubber seal. After inoculation with the water samples (1 ml each) using sterile 1 ml syringes, the assays were incubated at 30 °C in the dark for 1 month. Liquid samples were taken using sterile syringes flushed with CO₂/N₂ (10/90, v/v)

Table 5
Composition of the medium used to enrich methanogenic archaea

Component	Quantity
<i>Medium to enrich methanogenic archaea</i>	
KH ₂ PO ₄	0.5 g
MgSO ₄ × 7H ₂ O	0.4 g
NaCl	0.4 g
NH ₄ Cl	0.4 g
CaCl ₂ × 2H ₂ O	0.05 g
FeSO ₄ × 7H ₂ O	0.002 g
Yeast extract	1.0 g
Na-acetate	1.0 g
Na-formate	2.0 g
NaHCO ₃	4.0 g
Resazurin	0.001 g
Cysteine–HCl × H ₂ O	0.5 g
Na ₂ S × 9H ₂ O	0.5 g
Fatty acid mixture (see below)	20.0 ml
Trace element solution (see below)	1.0 ml
Deionized water	ad. 1000.0 ml
The pH was adjusted to 6.7–7.0	
<i>Fatty acid mixture</i>	
Valeric acid	0.5 g
Isovaleric acid	0.5 g
α-Methylbutyric acid	0.5 g
Isobutyric acid	0.5 g
Distilled water	20.0 ml
The pH was adjusted to 7.5 with concentrated NaOH	
<i>Trace element solution</i>	
HCl (25%; 7.7 M)	10.0 ml
FeCl ₂ × 4H ₂ O	1.5 g
ZnCl ₂	70 mg
MnCl ₂ × 4H ₂ O	100 mg
H ₃ BO ₃	6.0 mg
CoCl ₂ × 6H ₂ O	190 mg
CuCl ₂ × 2H ₂ O	2.0 mg
NiCl ₂ × 6H ₂ O	24.0 mg
Na ₂ MoO ₄ × 2H ₂ O	36.0 mg
Distilled water	990.0 ml

and analyzed for microorganisms by microscopy. An enrichment was counted as positive, if cells (more than 10⁶ cells/ml) were visible, and if methane could be detected in the headspace of the flask.

3. Results

Coalbed gas samples from the German Ruhr Basin have been analyzed for their geochemical and isotopic compositions. Results (GC and IRMS) are presented in Tables 1–3. Concentrations of methane to pentane as well as of carbon dioxide, oxygen and nitrogen remain rather constant with time at single sites. The same applies for the isotopic compositions of methane, ethane,

propane and carbon dioxide. Therefore, data in Tables 1–3 are summarized results of all samplings at the 13 sites. Concentration data are given exactly as measured in vol% and not air-corrected. Overall, methane concentrations range between around 33 and 95 vol% (Table 1), with generally higher concentrations at mines closed decades ago (only exception is site 13: 1.3 vol% of methane). Ethane and propane are present in minor concentrations. Ethane ranges between 0.03 and 0.83 vol% (site 13: not detected), propane between 0 and 806 ppm. Carbon dioxide shows a rough trend of most pronounced enrichments in collieries which have been abandoned for more than 40 years. Carbon dioxide concentrations range from 0.4 to 19.5 vol% (site 13: 0.2–0.3 vol%). Nitrogen makes between 3 and 47 vol% (site 13: 91 vol%), oxygen between 0.2 and 8.6 vol%. Butane and pentane (*i*- and *n*-isomers) occur in concentrations of a few ppm. Hydrogen was not detected.

The concentration ratio of methane to the sum of methane to pentane ranges between about 0.9858 and 0.9996 (Table 2). The ratio of methane to the sum of ethane plus propane varies between 71 and 2343, whereas the ethane-to-methane-ratio reaches from 0.0004 to 0.0129. The *i*-isomers of butane and pentane (with one exception) are more frequent than the corresponding *n*-isomers. For butane the *i/n*-ratio ranges from 0.67 to 4.70. For pentane this *i/n*-ratio varies from 1.06 up to 11.67.

The stable isotopic composition of methane varies between –40.0‰ and –57.3‰ δ¹³C (the exception is site 13: –85.1‰ to –85.9‰) as well as between –175‰ and –201‰ δD (site 13: –257‰ to –260‰). Ethane data range between –19.0‰ and –26.0‰ δ¹³C. Propane values are distinguished by δ¹³C values between –11 and –24.5‰. Both, ethane and propane, show a trend towards heavier (¹³C-richer) isotope data with time (14 months) at those sites which showed ethane and propane concentrations sufficiently high for isotopic analysis all three sampling times. For ethane, these are sites 1, 2, 3, 6, 7, 8, 9, and 10. For propane, these are localities 3, 7, 9, and 10. Carbon dioxide is characterized by highly differing δ¹³C-values from site to site. They vary between +3‰ at one active colliery (site 6) and down to –33.7‰ δ¹³C at abandoned mines. Radiocarbon (¹⁴C) analysis of carbon dioxide in coalbed gas resulted in an (apparent) age of 12,270 a ± 1620 a and 13,520 a ± 1290 a, respectively (Dr. E. Kunz, Deutsche Montan Technologie (DMT), unpublished data).

The stable isotopic compositions (C, H) of methane, ethane, propane and carbon dioxide reveal that no gas sample consists of purely thermal components (Table 3). All samples contain either a mixture of thermal with microbial methane or (in one case) purely microbial methane (site 13).

The microbial origin of methane gave rise to the question whether living methanogenic archaea can be

found in the coal mines today. To test this idea, mining waters from the surface down to depths of 1178 m b.s.l. were sampled at six localities in April 2003 (Table 4). The salinities in these waters ranged from 1.6 to 60.4 g/l. All samples are brines or saline waters. Concentrations are rising with increasing sampling depth, as described earlier by Wedewardt (1995). Temperatures varied from 13 to 27 °C, pH values from 5.5 to 6.9. The redox potentials, measured as Eh values, ranged from 120 to 260 mV (Table 4). Conductivities reached 1920–25,000 S/cm (25 °C). Carbon was present in these waters in different forms. DOC values varied from 1.8 to 3.4 mg/l, TOC data from 1.4 to 3.0 mg/l. TIC made between 26 and 215 mg/l and free carbon dioxide between 159 and 286 mg/l. Sulphate concentrations ranged between 190 and 677 mg/l.

The microbiological investigations of the mine waters revealed that the total cell numbers (bacteria plus archaea) were in the range of 10^4 – 10^6 cells per ml (Table 4). Very likely, only a small portion of these microbes were methanogenic archaea. In four of six water samples methanogenic archaea were detected by enriching them in a specific medium with H_2 and with a mixture of fatty acids as substrates for growth. The colour of the medium turned from colourless and transparent to translucent and cloudy. Formation of methane in the headspace of the culture flasks was confirmed by gas analysis. The generated methane in one sample had an isotopic composition of -64‰ $\delta^{13}C$ and -439‰ δD .

4. Discussion

4.1. Thermogenic methane

As shown by Thielemann (2000) and based on basin modelling results by Bükér et al. (1995), Bükér (1996), Littke et al. (1994, 2000) and Karg (1998), thermogenic coalbed gases were generated within the Ruhr Basin during coalification of the Carboniferous organic matter, about 312–288 Ma ago. Between 50,000 and 100,000 km^3 ($=10^9 m^3$) of methane were generated in that period. Only about 1% of this gas volume is left today (Juch et al., 2004). Around 99% of the thermogenic methane escaped during geological history. The gas migrated along cleavage planes where during the Variscan orogeny traces of methane were trapped and fixed in fluid inclusions of ore minerals of Variscan age (Jochum, 1999). Since Carboniferous times three major emission events in the Ruhr Basin occurred. The first took place during coalification about 300 Ma ago. Two basin inversions, one in late Permian (250 Ma) and the second in mid Cretaceous times (95 Ma), were periods of massive gas emission as well (Thielemann, 2000). Between these three periods (300, 250, and 95 Ma) the Ruhr Basin was subject to permanent degassing at a low

rate, as Thielemann et al. (2001) showed for the recent situation.

The isotopic composition of methane revealed a bi-partite generation. On one hand, the original isotopic composition of coalbed methane is mainly thermal. This is obvious at sites where coal never has been mined like locality 12 with $\delta^{13}C$ -values of methane around $-42.7 \delta^{13}C$. Also, site 11 – where coal was mined spatially separated from other collieries (Fig. 1) – presents $\delta^{13}C$ -values of methane around $-40.0 \delta^{13}C$. These data show a comparably limited microbial influence. On the other hand, the microbial imprint at sites 1–10 is more pronounced than or is in contrast to what was described in older literature (Colombo et al., 1968, 1970, Lommerzheim, 1994; Teichmüller et al., 1970, Wingerning, 1975). If we assume a bulk isotopic composition of thermal methane from Ruhr hard coal of $-25 \delta^{13}C$ (Gaschnitz, 2001) and a pure microbial methane of $-64 \delta^{13}C$ (see laboratory data at the end of chapter results), the microbial proportion in the recent methane varies between 38% (site 11) and around 90% (sites 1, 2, and 7).

The gas reserves of the Ruhr Basin may be subdivided into compartments of different microbial influence. The biggest compartment is the central Ruhr Basin (with sites 1–10, Fig. 1) with coal mining lasting for more than 800 years and intensive coal production since about 1850. Groundwater with methanogenic microbes could infiltrate this reservoir for centuries via shafts and cleavages. Gas in this compartment is characterized by high contributions of microbial methane.

Compartment no. 2 is represented by site 11. Here, coal mining (since 1900) was probably not intense enough to give the recently produced methane a pronounced microbial signature. Site 12 proves that there is a compartment no. 3, the Carboniferous rocks unaffected by mining. At site 12, the microbial impact in the natural, non-mined coal-bearing rocks was and is below 40% of the volume of coalbed methane.

4.2. Microbial methane

According to the isotopic data, methane in the coalbed gases of the Ruhr Basin is a mixture of thermogenic and microbial methane, the latter produced by CO_2 -reduction (Fig. 2). At site 13 the methane trapped was pure microbial gas. This is not investigated in detail here, as it is a local phenomenon of microbial methane generation close to the surface. Fig. 2 shows that a proportion of the methane in the coalbed gas of the Ruhr Basin is of microbial origin. Our incubation experiments demonstrated that at least a portion of this microbial methane might be generated today.

Other coal basins show similar data. The isotopic composition ($\delta^{13}C$, δD) of methane in Belgium (Dusar, unpublished data), Poland (Kotarba, 2001), Turkey (Hosgörmez et al., 2002) and Australia (Smith and

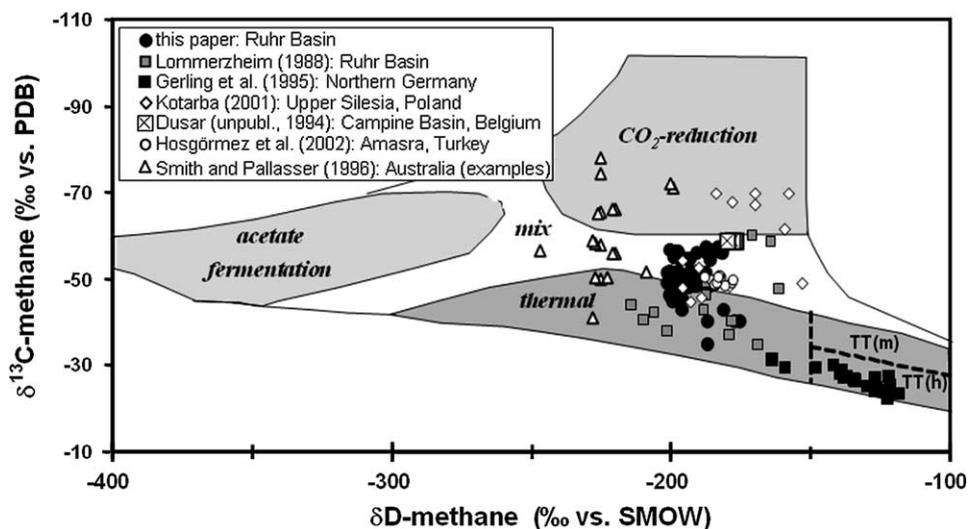


Fig. 2. Isotopic composition ($\delta^{13}\text{C}$ and δD) of methane in coalbed gases of the Ruhr basin, of hard coal mining districts in Belgium, Poland, Turkey and Australia as well as of coal-derived natural gases in Northern Germany (Gerling et al., 1995).

Pallasser, 1996) also reveals the influence of methane generation by microbial CO_2 -reduction (Fig. 2). It seems to be a global pattern, typical of coalbed gases worldwide at depths shallower than about 1500 m. These data do not give information about the timing of microbial methane generation.

4.3. Thermogenic ethane and propane

The stable isotopic composition of thermogenic hydrocarbons like methane, ethane and propane generated during coalification correlates with the vitrinite reflectance of the gas source, the organic matter (Berner and Faber, 1988, 1997; Berner et al., 1992, 1995). The iso-

topic composition of ethane and propane in all samples proves a purely thermogenic generation of these two alkanes (Fig. 3). They are typical of alkanes generated from hard coal of maturities between 0.7% and 2.2% vitrinite reflectance. These maturities are typical of coals in Carboniferous rocks of the Ruhr Basin.

Primary isotope effects (during gas generation) and secondary isotope effects (after gas generation) modify the isotopic composition of hydrocarbons. These effects are different generation pathways, mixtures of gases of different origin and physicochemical processes like adsorption and desorption. The effect of desorption from coal is a prograding isotopic shift of the methane, ethane or propane released to less negative (i.e. ^{13}C -richer)

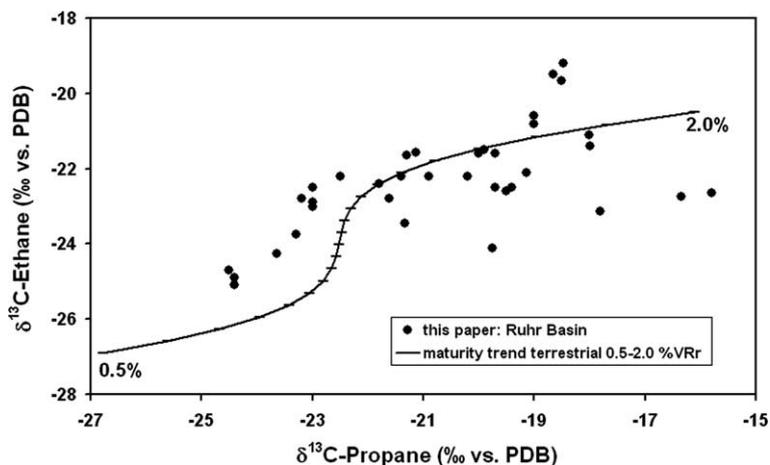


Fig. 3. Isotopic composition ($\delta^{13}\text{C}$) of ethane and propane in coalbed gases of the Ruhr basin. Maturity trend according to Faber, 1987, Berner and Faber, 1988, and Berner et al., 1992, 1995.

values (Wingerning, 1975; Gaschnitz et al., 2000). Such a trend could be observed here. Eight of 13 localities have been sampled three times and, hence, allow the observation of an isotopic trend with time. Seven of them show a distinct shift to ^{13}C -richer values with time (14 months). This drift ranges between +1.3‰ (site 7) and +2.8‰ (site 8) for ethane, as shown for two sites (8 and 9) in Fig. 4. The shift varies from +0.5‰ (site 7) to +3.8‰ (site 3) for propane. This strongly argues for the interpretation that the gas reservoir in the Ruhr Basin is slowly desorbing from coal and vanishing.

4.4. Carbon dioxide

Carbon dioxide is a gas of manifold generation pathways – thermogenic or biogenic (fermentation, respiration). During coalification – within a maturity interval of 0.65–2.7% VR_r – up to about 81 m³ of thermogenic carbon dioxide per ton organic matter were produced from Westphalian coal (Gaschnitz, 2001). During geological history most of the carbon dioxide was dissolved in water and removed with the water flow. This reduced the concentration of thermogenic carbon dioxide to today's few percent (e.g. below 1.3% at site 6). In contrast, aerobic microbial carbon dioxide generation took and takes place as soon as coal mining introduces oxygen-rich ventilation air and water into the coal beds. This microbial carbon dioxide only accumulates in the mining claims if a colliery is closed, if the ventilation is stopped, and if the carbon dioxide loss via gas escape through caprocks or by dissolution in the water flow is smaller than its generation rate. Carbon dioxide then

rises up to 19.5% like at site 4, where it probably accumulated during seven decades. Site 4 was the earliest colliery of the examined mines to be closed, back in 1929 (Table 2; Huske, 1998).

The radiocarbon (apparent) age of carbon dioxide ranges around 13,000 a. That could mean a variety of carbon sources for microbial carbon dioxide. Carbon dioxide was not likely generated from organic matter of an age of 13,000 a exclusively. This (apparent) age could be interpreted as a mixture of carbon from coal (dead carbon) with carbon from recent organic matter. It could also be a mixture of carbon sources without any coal impact, but with carbon contribution from mine timber and from DOC. This remains open at this stage.

The isotopic composition of carbon dioxide ($\delta^{13}\text{C}$) is diverse. It varies from +3‰ to –33.7‰ vs. PDB. The carbon dioxide in active mines does not only show concentrations below 1.3%, but with –5‰ to +3‰ it is also much heavier than carbon dioxide in high concentrations from abandoned mines. The isotopic composition of methane is also variable (Fig. 5). One possible explanation might be that the carbon dioxide in active mines is dominated by atmospheric input, whereas the carbon dioxide in abandoned mines mainly was microbially generated from local organic matter (hard coal or mine timber or carbon dissolved in mine waters). Isotopic compositions of carbon dioxide of below –30‰ (like at site 1, see Table 3 and Fig. 5) may point to the process of microbial methane oxidation. This metabolic reaction might take place locally in the Ruhr Basin. If so, it is of minor importance as most of the carbon dioxide is heavier than –30‰ (Table 3).

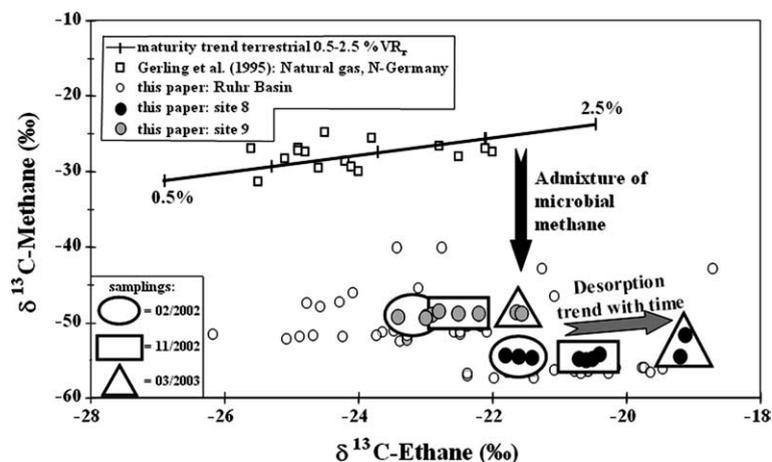


Fig. 4. Isotopic composition ($\delta^{13}\text{C}$) of methane and ethane in coalbed gases of the Ruhr Basin, and in coal-derived gases of Northern Germany. Maturity trend according to Faber, 1987, Berner and Faber, 1988, and Berner et al., 1992, 1995. Obvious is the shift of the Ruhr Basin methane data towards more negative values due to microbial imprint. With time (14 months) a couple of localities show an isotopic drift. Ethane moves to more positive values (e.g. sites 8 and 9). This might indicate a prograding desorption and, hence, depletion of the reservoir. Methane is characterized by a similar trend which might indicate recent microbial generation rates being smaller than the daily gas production.

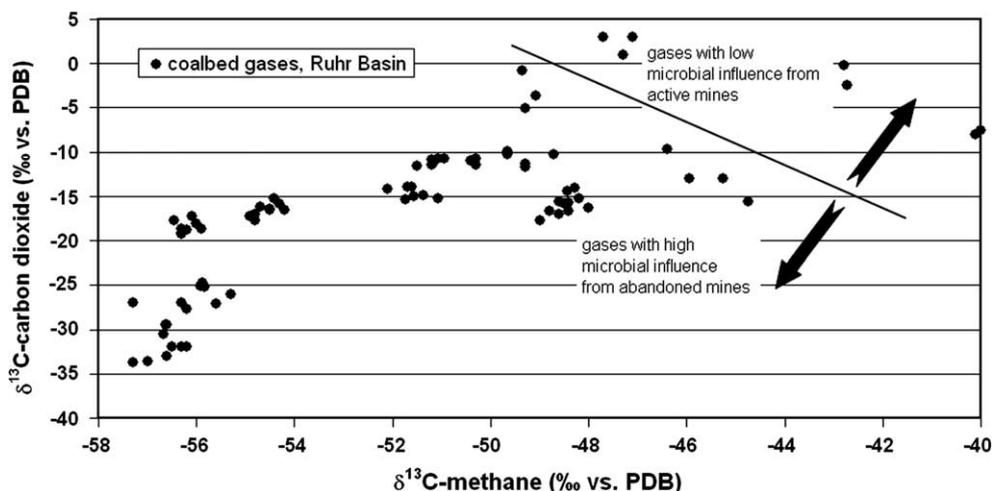


Fig. 5. Carbon isotopic composition of methane versus carbon dioxide in coalbed gases of the Ruhr basin. Samples from active collieries and areas of no mining show heavier (atmosphere-dominated) carbon dioxide than abandoned mines due to microbial carbon dioxide production in the abandoned mines.

4.5. Mine waters

Four out of six mine water samples contained living methanogenic microorganisms with an isotopic composition of the produced methane of -64‰ $\delta^{13}\text{C}$ and -439‰ δD in one sample. These four samples were from closed mines, sampled at the surface and down to 1000 m. The other two samples from an active mine had a pH of 5.5 and high salinities of around 60 g/l. These values show that the conditions at these sites are not very suitable for the growth of methanogenic archaea. However, the lack of methanogens in the waters from active mining does not necessarily prove their absence in active mines. The microbes could well exist in active mines but might have been inactivated during and after sampling. It took about 24 h after sampling before these two samples were stored under oxygen-free conditions.

To our knowledge this study is the first report that living methanogens were proven to exist in abandoned hard coal mines. This means that coalbed gas could be recently formed. As far as no information exists about the rates of recent microbial methane generation in abandoned mines it is not worthwhile to argue about the ability to naturally refill such a gas resource. Nevertheless, assuming a significant recent methane generation at least a part of the gas from these mines could be classified as renewable like methane from waste deposits or sewage sludge.

4.6. Reaction pathways to microbial methane

The production of microbial methane from polymeric organic substances is a complex process and requires the interaction of bacteria and archaea. In

general, the process comprises two main steps, the oxidation of organic substances (here: coal or mine timber or organic compounds transported in water) to carbon dioxide by bacteria and the reduction of the latter to methane by archaea. The degradation of polymeric organic molecules into soluble products (oligomers) is catalyzed by exoenzymes which are excreted by bacteria. These or other bacteria take up the oligomers and oxidize them to carbon dioxide, hydrogen, acetate and/or fatty acids. Finally, archaea produce methane by carbon dioxide reduction and hydrogen oxidation. Another reaction, methane formation via acetate fermentation, can be excluded here according to the isotopic composition of the methane measured (Fig. 2). Zengler et al. (1999) could show that methane can be microbially generated from hexadecane and pentadecane, but they needed more than two years for their incubation experiment. Hence, even in the case that this process might occur in coal seams, it would be rather uncertain if considerable amounts of methane can be produced. However, irrespective of the reaction pathways, a partly anaerobic microbial degradation of hard coal to methane seems to occur in nature.

5. Conclusions and outlook

The long-term (14 months) observations showed that the coalbed methane is of bipartite generation, thermal and microbial. The carbon source for thermal methane is purely coal (a limited fossil fuel), whereas the carbon source for microbial methane might be coal, but could also well be other fossil or recent biomass. This study shows that between 38% and 90% of the recently

sampled methane is of microbial origin. The proof of living methanogenic microbes in mine water makes it possible that at least a portion of this microbial methane seems to be generated today. They produce the gas by CO₂ reduction. Acetate fermentation is of no importance.

However, microbial methane production rates are not known so far. Their determination would require permanent in situ sampling during days or weeks in a completely flooded and anaerobic environment within the mines. Additionally, fossil production and emission rates are not known. This complicates the development of future gas production models. Nevertheless, isotopic data of ethane show a more or less distinct depletion in ¹²C with time. Prograding desorption of ethane and propane from coal may indicate the emptying of this coal gas reservoir.

A direct detection of significant recent microbial generation of coalbed gas in the Ruhr Basin could give bright perspectives to the gas producing companies.

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