Discovery of a natural CO$_2$ seep in the German North Sea: Implications for shallow dissolved gas and seep detection

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Abstract

A natural carbon dioxide (CO$_2$) seep was discovered during an expedition to the southern German North Sea (October 2008). Elevated CO$_2$ levels of ~10–20 times above background were detected in seawater above a natural salt dome ~30 km north of the East-Frisian Island Juist. A single elevated value 53 times higher than background was measured, indicating a possible CO$_2$ point source from the seafloor. Measured pH values of around 6.8 support modeled pH values for the observed high CO$_2$ concentration. These results are presented in the context of CO$_2$ seepage detection, in light of proposed subsurface CO$_2$ sequestering and growing concern of ocean acidification. We explore the boundary conditions of CO$_2$ bubble and plume seepage and potential flux paths to the atmosphere. Shallow bubble release experiments conducted in a lake combined with discrete-bubble modeling suggest that shallow CO$_2$ outgassing will be difficult to detect as bubbles dissolve very rapidly (within meters). Bubble-plume modeling further shows that a CO$_2$ plume will lose buoyancy quickly because of rapid bubble dissolution while the newly CO$_2$ [...]

Reference


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Discovery of a natural CO₂ seep in the German North Sea: Implications for shallow dissolved gas and seep detection

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[1] A natural carbon dioxide (CO₂) seep was discovered during an expedition to the southern German North Sea (October 2008). Elevated CO₂ levels of ~10–20 times above background were detected in seawater above a natural salt dome ~30 km north of the East–Frison Island Juist. A single elevated value 53 times higher than background was measured, indicating a possible CO₂ point source from the seafloor. Measured pH values of around 6.8 support modeled pH values for the observed high CO₂ concentration. These results are presented in the context of CO₂ seepage detection, in light of proposed subsurface CO₂ sequestering and growing concern of ocean acidification.

We explore the boundary conditions of CO₂ bubble and plume seepage and potential flux paths to the atmosphere. Shallow bubble release experiments conducted in a lake combined with discrete-bubble modeling suggest that shallow CO₂ outgassing will be difficult to detect as bubbles dissolve very rapidly (within meters). Bubble-plume modeling further shows that a CO₂ plume will lose buoyancy quickly because of rapid bubble dissolution while the newly CO₂-enriched water tends to sink toward the seabed. Results suggest that released CO₂ will tend to stay near the bottom in shallow systems (<200 m) and will vent to the atmosphere only during deep water convection (water column turnover). While isotope signatures point to a biogenic source, the exact origin is inconclusive because of dilution. This site could serve as a natural laboratory to further study the effects of carbon sequestration below the seafloor.


1. Introduction

1.1. General Background

[2] The most significant carbon dioxide (CO₂) emission to the atmosphere is from burning fossil fuels and deforestation [Intergovernmental Panel on Climate Change (IPCC), 2007]. The importance of the oceans, particularly the coastal shelf seas, as sources and sinks for atmospheric CO₂ is subsequently an area of increasing focus [Siegenthaler and Sarmiento, 1993; Kennett et al., 2003; Sabine et al., 2004; Friedrich and Oschlies, 2009]. The oceans are a principal sink for anthropogenic atmospheric CO₂; however, rising CO₂ concentrations are estimated to have caused a 30% increase in the concentration of H⁺ in ocean surface waters since the early 1900s and may lead to a drop in seawater pH of up to 0.5 units by 2100 [Siegenthaler and Sarmiento, 1993; Caldeira and Wickett, 2005; IPCC, 2007].

[3] To mitigate the effects on ocean acidification and climate forcing, CCS (carbon capture and storage), in which point source CO₂ emissions are captured and sequestered within the geosphere, has been extensively proposed [e.g., Lenton and Canney, 2002; Haugan and Joos, 2004; Hazeldine, 2009; Orr, 2009; Schrag, 2009]. Some proponents argue that CCS below the seafloor has the advantage of the overlying water acting as a buffer in case of accidental or unexpected leakage. However, there is concern and little known about the impact of leakage on local ecosystems, the potential of CO₂ interaction liberating toxic substances (e.g., heavy metals), or the potential for seepage to vent to the atmosphere (bubbles, plumes, etc.) [Leifer and Patro, 2002; Dimitrov, 2003; Holloway et al., 2007; Kharaka et al., 2006].

[4] While many studies have been devoted to investigating methane (CH₄) seabed release [e.g., Reeburgh, 2003, 2007; Keir et al., 2005, 2008; Judd and Howland, 2007; and references therein], very little is known about natural CO₂ seepage, especially from sedimentary settings on continental shelves. In fact, with the exception of the natural CO₂ gas venting at Panarea (Aeolian Islands, Italy) [Esposito et al.,
2.06], there are few studies at natural shallow CO\textsubscript{2} bubbling sites in the ocean. Natural CO\textsubscript{2} seepage is commonly found in CO\textsubscript{2}-prone geological provinces, for example, in sedimentary basins at carbonated springs and mofettes or in volcanic and hydrothermal areas [Dando et al., 2000; Holloway et al., 2007; Lewicki et al., 2007]. While natural CO\textsubscript{2} fluxes from volcanic vents and high-flow areas amount to less than 0.5\% of anthropogenic emissions, these releases can alter local ocean geochemistry [Hall-Spencer et al., 2008]. While most naturally occurring CO\textsubscript{2} originates from degassing magma, it can also be produced by metamorphism or dissolution of carbonate rocks, and thermal alteration or biodegradation of organic matter [e.g., Berner, 1980; Ague, 2000; Fischer et al., 2006].

The subsurface-produced CO\textsubscript{2} is typically emitted through the seabed as bubbles or enriched fluid [e.g., Lupton et al., 2006; Hall-Spencer et al., 2008]. In general, seepage from the seafloor is intermittent in response to hydrostatic pressure changes [Tivey et al., 2002; Linke et al., 2010; Schneider von Deimling et al., 2010] and commonly produces pockmarks or other seabed expressions [e.g., Judd and Hovland, 2007; Cathles et al., 2010]. If there are sufficient bubbles, then the induced buoyancy can create an upwelling of water together with the gas (bubble plume) [Italino and Nuccio, 1991; Linke et al., 2010]. Besides the obvious concern of CO\textsubscript{2} as a greenhouse gas, leaked CO\textsubscript{2} will decrease the pH of the water in the vicinity of the gas plume and increase its density, resulting in the tendency of CO\textsubscript{2}-rich water to remain at or sink to the seafloor [Ohsumi et al., 1992; Haugan et al., 1995; Alendal and Oranje, 2001]. Such conditions could potentially bleach corals and alter local flora or fauna [Orr et al., 2005; Hall-Spencer et al., 2008; Veron et al., 2009]. Determining emissions and flux pathways from natural CO\textsubscript{2} seeps can provide estimates of the local risks and impacts, as well as the potential to reach the atmosphere. This knowledge can then be extrapolated to proposed or active anthropogenic CO\textsubscript{2} (CCS) storage sites [Lewicki et al., 2007].

1.2. The North Sea as a “Continental Shelf Pump”

As a net sink, the North Sea has been proposed to act as a “continental shelf pump” for atmospheric CO\textsubscript{2}. It is suggested that ~93\% of the atmospheric CO\textsubscript{2} absorbed by the surface waters is then transported to the North Atlantic Ocean where it is potentially sequestered within the interior [Thomas et al., 2004; Bozec et al., 2005]. Thomas et al. [2007], however, found that the CO\textsubscript{2} buffering capacity of the North Sea is diminishing as the surface water pCO\textsubscript{2} has increased (2 \micro atm increase from 2001 to 2005) twice as fast as the atmospheric pCO\textsubscript{2} (11 \micro atm) in the same period.

While the water column experiences seasonal stratification in the north and central sections of the North Sea, the southern North Sea is vertically well mixed year round because of the shallow depth and strong currents [Thomas et al., 2004; Bozec et al., 2005; Prowse et al., 2009]. With respect to CO\textsubscript{2} fluxes, the central and north (and largest) portions of the North Sea (north of the 54° parallel) act as a strong sink. However, the southern North Sea and English Channel are generally sources of CO\textsubscript{2}. Prowse et al. [2009] estimate that 0.78 mol C m\textsuperscript{−2} yr\textsuperscript{−1} of CO\textsubscript{2} is released on an annual basis from the southern North Sea, while Bozec et al. [2005] report values from 0.8–1.7 mmol m\textsuperscript{−2} d\textsuperscript{−1}. Prowse et al. [2009] suggest that CO\textsubscript{2} fluxes increase in September up to 20 to 50 mmol m\textsuperscript{−2} d\textsuperscript{−1} with ΔpCO\textsubscript{2} values approaching 100 ppm. Bozec et al. [2005] also reported that the highest pCO\textsubscript{2} concentrations (400–450 \micro atm), compared to atmospheric values of 365 \micro atm, were found in the German Bight and English Channel water columns. They explain such high concentrations as being due to the mixing regime; however, the sources of CO\textsubscript{2} in the southern North Sea remain unknown.

1.3. Study Approach

During a recent cruise to the southern German North Sea (Figure 1), we discovered elevated CO\textsubscript{2} values at the shallow (~30 m) study site, Salt Dome Juist, with values ranging from ~10–20 times above background, and a peak of >53 times above background (7000 \micro atm or ~300 \micro mol L\textsuperscript{−1}). We attribute these elevated concentrations to a natural CO\textsubscript{2} seep from a suspected biogenic source.

In the context of CO\textsubscript{2} seep detection related to CCS, we present these findings of CO\textsubscript{2} emission in conjunction with modeling results demonstrating the expected seepage boundary conditions and projected flux paths to the atmosphere. Along with bubble release experiments conducted in Lake Lucerne (Switzerland), we show that CO\textsubscript{2} bubbles dissolve very rapidly in the sediment and the water column (within meters from the bottom) and compare CO\textsubscript{2} versus CH\textsubscript{4} bubble plume behavior. We anticipate that Salt Dome Juist and similar sites will serve as natural analogs to study ocean acidification and CO\textsubscript{2} seep detection at the ecosystem and geoengineering level in view of planned CCS sites in the North Sea [Blackford et al., 2008].

2. Study Site and Methods

Within the framework of the industry-founded project “Fluid and gas seepage in the southern German North Sea” (SDNS), an expedition onboard R/V Alkor (8–29 October 2008) was carried out to detect and map sediment gas and fluid migration pathways and to quantify gas fluxes and analyze their chemical composition. Bubble release experiments were conducted at Lake Lucerne (Switzerland) to compare the acoustic detection signal and rise behavior of CH\textsubscript{4} and CO\textsubscript{2} bubbles.

2.1. Study Site Geology

Salt Dome Juist is located in the southern North Sea about 30 km offshore the East Frisian Island Juist, Germany (Figure 1). The Pleistocene and Holocene shelf architecture of this area is mainly affected by three extensive glaciations [Ehlers, 1990]. Consequently, repeated changes from glacial, periglacial, terrestrial and marine periods have formed a system of deep, Quaternary valleys and depressions [House and Lykke-Andersen, 2000]. These structures have been filled with Pleistocene-aged organic rich deposits (e.g., peats and lignites) during a period of rising sea level. Decomposition of the organic matter subsequently led to the accumulation of shallow gas [Streff, 2002]. Deep seismic exploration in this area has revealed a complex structure of salt diapirism and tectonic faults in the deeper sediment strata [Schroot and Schüttenhelm, 2003]. These structures were created during the late Paleozoic and reach the seafloor.
in certain areas. Surface sediments in the region of Salt Dome Juist show a homogenous distribution of predominantly fine to medium coarse sands with shell fragments.

2.2. Onboard Equipment

[12] A 600 kHz acoustic Doppler current profiler (ADCP; Workhorse Monitor; Teledyne RDI Instruments, Poway, USA) was mounted downward looking in R/V Alkor’s moon pool ~1.5 m below the sea surface in standard profiling mode (Mode 5) with bottom tracking. The vertical bin size was set to 0.5 m for a total of 60 bins with a blanking distance of 1.12 m (range was therefore ~33 m). The ADCP tracks were simultaneously logged from the NMEA ship data. In addition to measuring current speed and direction, the ADCP measures individual beam backscatter which shows areas of increased turbidity and potentially indicates the presence of bubbles.

[13] Water column measurements were performed and water samples collected simultaneously with a SBE911plus conductivity-temperature-depth (CTD) profiler equipped with a 12 bottle rosette carousel (Sea-Bird Electronics, Inc., Washington, USA). The CTD sampled at 24 Hz and was also equipped with an O2 sensor (dissolved oxygen), altimeter, and ship NMEA coordinate integration. As the water column was well mixed during our expedition, the CTD was towed several meters above the seafloor to search for constituent anomalies associated with seepage. Towed CTD casts were conducted with the ship drifting and the data were read online. The Niskin bottles were triggered when CTD anomalies were observed (e.g., spikes in temperature or conductivity). Bottle sample intervals typically ranged from about 10–100 m horizontally along the drift track. A total of 164 gas samples were obtained from 15 CTD/water sampling tracks in the Salt Dome Juist area.

[14] Dissolved gases were extracted from the sampled seawater by transferring 1.8 L of seawater from the Niskin bottle into a preevacuated gas-tight 2 L glass bottle directly after recovery [Keir et al., 2008]. After temperature equilibration at laboratory conditions the gas phase was compressed into 20 mL headspace vials at atmospheric pressure. The gas tight headspace vials were stored for further quantification and stable isotope measurements. This method has a proven >90% efficiency in extracting physically dissolved gases from seawater [Keir et al., 2009]. Although the method used for degassing water samples is not an established method for determining pCO2 and δ13C-CO2, we will present the data here as qualitative results. Degassing of water samples at comparable temperatures was performed at about 18 ± 1°C and salinities of 34 ± 0.5‰.

[15] The program CO2SYS was used to calculate equilibrium CO2aq concentrations of between 6 to 13 μmol L⁻¹ (T = 15°C, pH = 8.2–8.4, Alk = 2.4 meq L⁻¹) [Pierrot et al., 2006].

2.3. Lake Lucerne Bubble Experiment

[16] A bubble measurement lander system was deployed at 12.5 m depth in a small boat harbor in Lake Lucerne (Switzerland). The system produced CO2 bubbles (5000 ppm, CO2 3.0 of Linde AG) of various sizes and was equipped with an online video recorder. We attached the CO2 tank and pressure-compensated regulator, gas tight tubing, and a straight tube
filing (Swagelok) directly to the lander frame. The bubble orifice was placed in the view of the underwater SuperSeaCam video camera (D6000, Deepsea Power and Light, San Diego, CA, USA) recording at 30 frames per second. The camera was connected via an underwater cable to the SuperSeaCam rack mount controller (S/N 104, Deepsea Power and Light, San Diego, CA, USA), which was used to zoom and focus from the surface. The video was recorded using Dazzle Video Creator Platinum (DVC107, Pinnacle Systems, Avid Technology) and images were analyzed in ImageJ (National Institutes of Health, USA). CO$_2$ bubbles released from the lander were recorded by a Simrad splitbeam echosounder (EK60, 7° beam angle) with a 120 kHz transducer operating at a rate of 5 pings s$^{-1}$. The transducer was mounted to a small boat dock ~30 cm below the water surface and ~12 m directly above the lander. The echosounder was calibrated with a 23 mm diameter standard copper target [Foote et al., 1987] and all data were recorded using Simrad ER60 software.

3. Bubble and Plume Modeling

3.1. Discrete Bubble Model

[17] The fate of CO$_2$ bubbles within and released from the sediment was modeled using a discrete bubble model (DBM) [McGinnis and Little, 2002; McGinnis et al., 2006]. The behavior was then compared to that of CH$_4$ bubbles [Ostrovsky et al., 2008]. The discrete bubble model predicts gas transfer (both dissolution and stripping) of five gaseous and dissolved species simultaneously (Ar, CO$_2$, CH$_4$, N$_2$, O$_2$). For a simple, stationary bubble (i.e., a bubble within the sediment), the equation is given as

$$\frac{dM_i}{dt} = -K_{Li}(H_iP_i - C_i)A_S,$$

which describes the rate of mass transfer in both directions across the bubble surface, where $K_{Li}$ (m s$^{-1}$) is the liquid-side mass transfer coefficient of species $i$, $A_S$ is the bubble surface area (m$^2$), and $C_i$ is the dissolved concentration (mol m$^{-3}$). The local saturation concentration is given by the product of Henry’s law constant $H_i$ (mol m$^{-3}$ Pa$^{-1}$) and partial pressure of gas within the bubble $P_i$ (Pa), which largely controls the rate of dissolution or stripping.

[18] For a rising bubble, the change in location with time is a function of the bubble rise velocity, $v_b$ (m s$^{-1}$), and any associated vertical water velocity, $v$, and is expressed as

$$\frac{dz}{dt} = v_b + v.$$

[19] Substituting for $dt$, equation (3) gives the change in moles of gas within the bubble per unit depth (m) as

$$\frac{dM_i}{dz} = -K_{Li}(H_iP_i - C_i) \frac{A_S}{v_b + v}.$$

[20] Bubble size–dependent parameterizations for bubble rise velocity and mass transfer coefficient, as well as a temperature–dependent solubility constant, are listed in Table 1. The above equation is the gas transfer component of the plume model described in section 3.2. The model has been independently validated in discrete-bubble oxygen transfer tests using air bubbles in shallow water (13 m) [McGinnis and Little, 2002].

3.2. Bubble-Plume Model

[21] When gas bubbles are released rapidly enough, the resulting local buoyancy increase leads to the upwelling and entrainment of water, thus creating a two-phase plume of water and gas. As the plume rises, the gas bubbles dissolve into the entrained and surrounding water, decreasing the bubble-driven buoyancy. The plume water will lose momentum as the driving force (i.e., bubbles) decreases and as the plume encounters density gradients. When momentum reaches zero, the water will detrain and “fall back” to its equilibrium depth. The density of the plume water is, however, slightly altered because of the increased concentrations of dissolved CO$_2$ (increases density) or CH$_4$ (decreases density), and is accounted for in the state equations. Modifying a well-established bubble plume model [Wüest et al., 1992; McGinnis et al., 2004], we investigate the behavior of both CO$_2$ and CH$_4$ driven bubble plumes.

[22] The plume model theory and assumptions are detailed by Wüest et al. [1992], with the key variables and the associated six simultaneous differential equations given in Table 2 and the range of input values listed in Table 3. The following overview of the model is summarized from McGinnis et al. [2004] and Wüest et al. [1992]. The model is based on horizontally integrated equations for conservation of mass, momentum, heat, salinity and gases [McDougall, 1978]. As the plume rises, water is entrained from the background into the plume proportional to the plume velocity and circumference at depth [Morton, 1959]. This entrainment incorporates the boundary effects on the plume due to density and dissolved gas gradients. A key contribution of the Wüest et al. [1992] plume model was the variable buoyancy flux resulting from the changing bubble size (section 3.1). Wüest et al. [1992] accounted for changing bubble volume due to not only decompression and thermal expansion but also gas dissolution and stripping. Most prior studies neglected gas exchange; however it is particularly important in deep systems or, as in this study, with highly soluble gases (i.e., CO$_2$) where dissolution is very rapid.

[23] One of the unknowns is the initial water velocity. Wüest et al. [1992] suggested using an initial Froude number of 1.6 and solving for the initial velocity where

$$v = Fr[2\lambda \beta g (\rho_a - \rho_p) / \rho_p]^{-1/2}.$$
Table 1. Gas, Bubble and Water Parameterizations

<table>
<thead>
<tr>
<th>Equation</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>H° = 2.125 - 5.021 × 10^−2 T + 5.77 × 10^−4 T^2 (mol/m^3 bar)</td>
<td>(T in Celsius)</td>
</tr>
<tr>
<td>H°N = 1.042 - 2.450 × 10^−2 T + 3.171 × 10^−7 T^2</td>
<td>(T in Celsius)</td>
</tr>
<tr>
<td>HCH4 = exp[127.173804 - 155.575631 T + 100 × 65.255291 × LN(T/100) + 0.16975729 × T/100] (Pa)</td>
<td>(T in Kelvin)</td>
</tr>
<tr>
<td>HCO2 = exp[−58.0931 + 0.027766 × (T/100) + 0.0050578 × (T/100)^2]</td>
<td>(T in Kelvin)</td>
</tr>
</tbody>
</table>

K_L = 0.6r (m/s) r < 6.67 × 10^−3 m
K_L = 4 × 10^−4 (m/s) r ≥ 6.67 × 10^−3 m
v_b = 4474r^0.357 (m/s) r < 7 × 10^−4 m
v_b = 0.23 (m/s) 7 × 10^−4 ≤ r < 5.1 × 10^−3 m
v_b = 4.202r^0.427 (m/s) r ≥ 5.1 × 10^−3 m

SC = exp[S × (0.027766 + 90.5069 × (100/T) + 22.294 × LN(T/100)) / (100/T) + 1.01325 (mol/L bar)]

SC = exp[S × (0.027766 + 90.5069 × (100/T) + 22.294 × LN(T/100)) / (100/T) + 1.01325 (mol/L bar)]

ρ(T, S, CO_2, CH_4) = ρ(T, S) × (1 + β_{CO_2} × CO_2 + β_{CH_4} × CH_4) (5)

where β_{CO_2} = 2.84 × 10^−4 and β_{CH_4} = −1.25 × 10^−3 kg g^−1 [see Schmid et al., 2002, and references therein].

4. Observations: North Sea Elevated CO_2 Concentrations

[35] High values of CO_2 were measured in the water column at Salt Dome Juist during the October 2008 campaign aboard R/V Alkor. During the time of the study the water column was well mixed, with temperatures around 13°C–15°C and salinities at ~34 PSU (Table 4). Average concentrations (and standard deviation) are listed in Table 4. Background gas concentrations were determined from a CTD/water cast at Borkum Reef (CTD 1; Figure 1 and Table 4).

[36] Dissolved oxygen levels were close to saturation around 320 μmol L^−1. Methane concentrations were near background values and ranged from 1.9 to 3.2 nmol L^−1 (about 70%–120%) [Wiesenburg and Guinasso, 1979]. Water velocity was measured with the ADCP and was fairly high with ~0.5 m s^−1 flowing to the WSW around the time of CTD 13. This towed CTD cast delivered the highest measured CO_2 value (discussed below; Figure 2).

[37] The CO_{2(extr)} concentrations were surprisingly high with ~90 (±30, n = 70) μmol L^−1 measured in bottom waters.

Table 2. The Dynamic Variables and the Nonlinear Differential Flux Equations of the Bubble-Plume Model

<table>
<thead>
<tr>
<th>Variable</th>
<th>Definition</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water volume flux</td>
<td>Q = πb^2v</td>
<td>m^3/s</td>
</tr>
<tr>
<td>Momentum flux</td>
<td>M = πb^2v^2</td>
<td>m^3/s</td>
</tr>
<tr>
<td>Temperature flux</td>
<td>F_T = QT_a</td>
<td>deg C m^3/s</td>
</tr>
<tr>
<td>Dissolved solids flux</td>
<td>F_D = QG_b</td>
<td>g/s</td>
</tr>
<tr>
<td>Dissolved gas fluxes</td>
<td>F_G = QG_i</td>
<td>mol/s</td>
</tr>
<tr>
<td>Undissolved gas fluxes</td>
<td>F_Gi = πb^2λ^2(v + v_b)b_i</td>
<td>mol/s</td>
</tr>
<tr>
<td>Water volume flux</td>
<td>dQ/dt = 2πrbv</td>
<td>m^3/s</td>
</tr>
<tr>
<td>Momentum flux</td>
<td>dM/dt = πb^2g rb^2 λ^2 + πb^2v^2 g rb^2(1 − λ^2)</td>
<td>m^3/s</td>
</tr>
<tr>
<td>Temperature flux</td>
<td>dF_T/dt = 2πrbvT_a</td>
<td>deg C m^3/s</td>
</tr>
<tr>
<td>Salinity flux</td>
<td>dS/dt = 2πrbvρ_sS_a</td>
<td>g/s</td>
</tr>
<tr>
<td>Dissolved gas flux</td>
<td>dG_i/dt = 2πrbvC_i + 4πnN_i K_L (H_P_i - C_i)</td>
<td>mol/s</td>
</tr>
<tr>
<td>Undissolved gas flux</td>
<td>dGi/dt = 4πnN_i K_L (H_P_i - C_i)</td>
<td>mol/s</td>
</tr>
</tbody>
</table>

*Modified after Wüest et al. [1992] and McGinnis et al. [2004].

Table 3. Plume Variables and Initial Conditions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Variable</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Depth (m)</td>
<td>z</td>
<td>25, 70</td>
</tr>
<tr>
<td>Source area (m^2)</td>
<td>π</td>
<td>0.2</td>
</tr>
<tr>
<td>Entainment factor</td>
<td>α</td>
<td>0.11</td>
</tr>
<tr>
<td>Plume diameter ratio</td>
<td>λ</td>
<td>0.8</td>
</tr>
<tr>
<td>Initial Froude number</td>
<td>Fr</td>
<td>1.6</td>
</tr>
<tr>
<td>Source rate (Nm/s)</td>
<td>Q_G</td>
<td>1E–6–1</td>
</tr>
<tr>
<td>Gas flux (mol/s)</td>
<td>F_G</td>
<td>4.1E–5–4</td>
</tr>
<tr>
<td>Initial bubble radius (mm)</td>
<td>r</td>
<td>6</td>
</tr>
</tbody>
</table>
of the Salt Dome Juist area (Figure 2 and Table 4). These values are already substantially elevated by a factor of ~15 over the background concentration of 6 µmol L⁻¹. An exceptionally high value of 318 µmol L⁻¹ (~53 times higher than background) was measured in a water sample from 11 m water depth during CTD profile 13 (Figure 2 and Table 4). The δ¹³C-\text{CO}_2(\text{extr.}) values determined from selected gas samples range between −10.2 and −24 ‰ (Table 4 and Figure 2), whereas the mean value of all δ¹³C values is about −14.5 ‰ (SD = 2.2, n = 33), suggesting biogenic origin (discussed below).

5. \text{CO}_2 and CH₄ Bubble Dynamics

[38] The source and type of \text{CO}_2 seepage at Salt Dome Juist are unknown. In the following analyses, we combine simple measurements and modeling of \text{CO}_2 bubbles to determine under which conditions bubble release could occur and the potential for acoustic detection. The rate of bubble dissolution in a fluid is largely defined by the local saturation concentration \(H/P_i\) and the concentration of dissolved gas in the surrounding environment \(C_i\), known as the concentration driving force \((H/P_i - C_i)\) (see equation (3)). A review of Henry’s coefficients suggest the rapid dissolution of gaseous \text{CO}_2 as it is ~25–30 times more soluble in seawater than \text{CH}_4 and \text{O}_2, and almost 60 times more soluble than \text{N}_2 [Steinmann et al., 2008; R. Sander, Compilation of Henry’s law constants for inorganic and organic species of potential importance in environmental chemistry (version 3), 1999, available at http://www.henrys-law.org].

5.1. Acoustic Bubble Detection

[39] Methane bubble seepage is relatively simple to detect via hydroacoustics as \text{CH}_4 bubbles tend to rise relatively high in the water column because of its low solubility in seawater [Greinert et al., 2006]. In contrast, \text{CO}_2 bubbles released in shallow marine environments dissolve much more rapidly. We investigated this experimentally by using an in situ bubble measurement lander in Lake Lucerne. Images of bubbles immediately after being emitted from the bubble orifice were captured from the video. In order to calculate an average diameter of a bubble an elliptical shape is assumed in the first step, and then an equivalent radius is calculated knowing that the actual shape of a rising bubble can change dramatically [Ostrovsky et al., 2008].

[40] Figure 3a shows the tracks produced from \text{CO}_2 bubbles with initial measured diameters of 9.7 mm (A), 3.1 mm (B) and 7.8 mm (C). For comparison, Figure 3b shows \text{CH}_4 bubbles with initial diameter of 3.0 mm (D) rising compared with the 3.1 mm \text{CO}_2 bubble (B). Figure 3b clearly shows that the rise velocity from the \text{CO}_2 bubble is much slower than the \text{CH}_4 bubble (Figure 3c). As rise velocity is a function of bubble size [Haberman and Morton, 1954], we can deduce that the \text{CO}_2 bubble (B) dissolved much more rapidly, and must be quite small by the time it is “seen” by the sonar. Bubbles with diameters of 2–10 mm rise at around 22–25 cm s⁻¹. Below 2 mm, the bubble rise velocity drastically drops so that the bubble with a rise velocity of 7 cm s⁻¹ must be around 0.6 mm in diameter (see bubble velocity equation in Table 1). This was also visually confirmed when the bubble lander was brought toward the surface and bubbles were released about 1.5 m below the water surface.

[41] These observations agree very well with the model results using the solubility constant reported for \text{CO}_2 by Weiss [1974]. Both the rapid and preferential dissolution

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**Table 4.** Results From a Reference Station (CTD 1) and CTDs Collected Over Salt Dome Juist

<table>
<thead>
<tr>
<th>CTD Profile</th>
<th>Average Depth (m)</th>
<th>Alkalinity (meq/L)</th>
<th>T (deg C)</th>
<th>S (PSU)</th>
<th>(\text{CO}_2(\text{extr.})) (µmol/L)</th>
<th>Standard Deviation (µmol/L)</th>
<th>(\delta ^{13} \text{CO}_2(\text{extr.})) (% PDB)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12.0</td>
<td>2.31</td>
<td>15.1</td>
<td>34.5</td>
<td>6.1</td>
<td></td>
<td>−10.2</td>
</tr>
<tr>
<td>11</td>
<td>23.7</td>
<td>2.32</td>
<td>13.4</td>
<td>33.3</td>
<td>65.7</td>
<td>15.7</td>
<td>−14.5</td>
</tr>
<tr>
<td>12</td>
<td>25.7</td>
<td>2.35</td>
<td>13.2</td>
<td>33.3</td>
<td>82.1</td>
<td>14.2</td>
<td>−13.6</td>
</tr>
<tr>
<td>13</td>
<td>11.7</td>
<td>2.35</td>
<td>13.3</td>
<td>33.9</td>
<td>105.8</td>
<td>71.9</td>
<td>−17.0</td>
</tr>
<tr>
<td>14</td>
<td>24.4</td>
<td>2.34</td>
<td>13.3</td>
<td>34.0</td>
<td>89.3</td>
<td>8.8</td>
<td>−14.9</td>
</tr>
<tr>
<td>15</td>
<td>25.5</td>
<td>2.29</td>
<td>12.9</td>
<td>33.4</td>
<td>85.3</td>
<td>16.2</td>
<td>−14.4</td>
</tr>
<tr>
<td>16</td>
<td>23.3</td>
<td>2.33</td>
<td>13.3</td>
<td>34.1</td>
<td>117.2</td>
<td>28.2</td>
<td>−14.1</td>
</tr>
</tbody>
</table>

*Results are only for casts where \text{CO}_2 was measured. Data were averaged over the sample bottles for each CTD cast (up to 12).
of CO₂ (compared to N₂) was also reported by White et al. [2006]. We did attempt to calibrate the model using these measurements; however, this was proven to be difficult as the gas composition of CO₂ bubbles forming on the nozzle changed too rapidly, and results are highly sensitive to the initial mole fraction of CO₂ (discussed below). Therefore a more sophisticated modeling approach is needed that includes gas transport during the time of bubble growth and formation at the nozzle, or a method of producing CO₂ bubbles that do not remain on the nozzle during formation for any length of time.

5.2. Implications

[42] The fact that CO₂ bubbles released in shallow waters dissolve very rapidly presents complications with respect to their detection. For example, Figure 4a is the ADCP backscatter at the time CTD 13 measured the highest CO₂ concentrations, in which the backscatter shows persistent high signals at the bottom starting at ~25 m. Figure 4b also shows the results from the bubble model for CO₂ bubbles (solid lines) with 4, 6, and 8 mm initial diameters demonstrating that the bubbles mostly dissolved within the first 1–3 m upon release. The backscatter signal drastically decreases between 21 and 23 m depth, and almost entirely disappears at 17 m, a range that corresponds with the modeled dissolution of CO₂ bubbles. Therefore, it is not possible to determine if the high backscatter at the seafloor indicates CO₂ bubble release or is due to entrained sediment as a result of rough weather during sampling or a combination of both. Further modeling results presented below suggest that the bubble release scenario is unlikely and that the backscatter is likely attributed to resuspended sediment.

[43] The rapid dissolution rate of the CO₂ bubble becomes more obvious when compared with that of CH₄ (Figure 4b). The methane bubbles reach the surface with ease and remain the same or even increase in volume as they rise. These bubbles are therefore much more easily detectable with hydroacoustic technology. As shown in Figure 4b, as the diameter of the CO₂ bubbles decrease to ~1 mm (depending on initial size), the rate of dissolution becomes much slower. As the CO₂ is being dissolved, other dissolved gasses are stripped from the water column into the bubble (Figure 4c). When nearly all the CO₂ in a bubble is dissolved, the gasses that were previously stripped (N₂ and O₂) begin to redissolve. Note that after CO₂ is dissolved from the bubble, the O₂ and N₂ mole fractions approach atmospheric levels (Figure 4c), while the CH₄ bubble is still around 80%–90% methane at 10 m depth.

5.3. CO₂ Bubbles in Sediment

[44] We evaluated the dissolution rate of a hypothetical stationary bubble as if it would have instantly appeared, e.g., in the sediment pore water (Figure 5). For this basic modeling exercise we assumed that there is no dissolved gas accumulation in the pore water (assumed saturated levels of O₂ and N₂), and that any gas that is transferred from the bubble to the dissolved phase is instantly carried away. This model simulation was performed at 20°C and 35 PSU.

[45] Figures 5a and 5b illustrate the change in the mole fraction over time. As seen in the case of our 3 mm bubble, the mole fraction approaches 0.5 for CO₂ in less than 3 s. This does not include the time when the bubble is growing, e.g., on the nozzle, as in the case of our bubble release experiment. The CO₂ is almost completely gone within 4 s for the 3 mm bubble and about 6 s for the 6 mm bubble.

[46] The 6 mm CO₂ bubble “lifetime” in our hypothetical gas-depleted pore water would only last for about 10 s. The lifetime of the CH₄ bubble would be about 300 s (30 times longer) and the N₂ bubble would be 700 s (70 times longer), which scales to the Henry’s coefficients. These results suggest that unless there is a strong and persistent source of CO₂, it is very unlikely that there would be small-scale CO₂ bubble seepage as is commonly observed at CH₄ bubble seeps. As discussed later, the pore water concentrations of CO₂ would have to approach 100 mmol L⁻¹ for small-scale seepage to occur.
5.4. Comparing CO$_2$ and CH$_4$ Plumes

The difference between the dissolution rates of CO$_2$ bubbles versus CH$_4$ bubbles obviously will have a large impact on the buoyancy of the plume. We performed plume model simulations for both CO$_2$ and CH$_4$ bubbles released from A) a deep stratified, and B) shallow well-mixed water columns (Table 3). For the shallow runs we assume the initial conditions present at Salt Dome Juist during the October 2008 cruise (CTD 1; Table 4), and for the deep summer stratified case we used conditions from a profile at Tommeliten (Figure 6a), a 70 m deep site in the central North Sea.

Plume model runs were conducted with mass flux rates (gas input) shown in Table 3. Results are shown in Figure 6. The initial velocities are solved for using an initial Froude number of 1.6 in equation (4). For a given depth, the initial velocity is independent of the gas used as long as the gas density is approximately the same (Figure 6b).

Figure 6c shows the final plume concentrations when it falls back to the density equilibrium depth. As expected, the CO$_2$ plumes include generally higher CO$_2$ concentrations due to the much more rapidly dissolving bubbles. The plume typically stops and the water “peels” away even though bubbles are still present. These bubbles could go on to create secondary plumes.

Figure 6d shows the depth of maximum plume rise (solid symbols), and the fall back (detrained water equilibrium) depth (open symbols). In the shallow case, the CO$_2$ plume does not rise very high with the lower gas inputs. This is because the CO$_2$ completely dissolves and the plume does not receive as much buoyancy as does the CH$_4$ plume. The CH$_4$ plume, however, reaches the surface every time. Not shown here are the fall back depths. In every case, the CH$_4$ plume remains at the surface because of the slightly decreased density imparted by the dissolved CH$_4$ concentrations. Conversely, the
CO₂ plume water will fall completely back to the seafloor (this assumes no mixing for the downwelling plume water).

For the deeper, stratified conditions shown in Figure 6a, the CO₂ plume barely rises for the lower flow rates (closed squares) and then falls back to the seafloor (open squares). The rise height is even less due to the slight bottom stratification and the decreased volume flux as a result of the release depth increase. The CH₄ plume, however, makes it to the bottom of the thermocline even at lower fluxes (or inputs). Eventually with the high flux of 41 mol s⁻¹ (58 t d⁻¹), the plume finally渗透 through the thermocline and reaches the surface.

Our highest measured CO₂ value was 300 m mol L⁻¹. If we assume that this is a plume-generated source, it would correspond to a CO₂ input of 1 mol s⁻¹ (nearly 4 t d⁻¹) and a final plume diameter of 14 m (area = 150 m²), which is substantial. If this was indeed a plume, then this would be a conservative estimate of source strength as it likely would have been considerably diluted when we obtained the measurement.

6. CO₂ in the North Sea

6.1. Thermodynamic Calculations

CO₂ₐq equilibrium concentrations were estimated to be between 6 and 13 μmol L⁻¹ (T = 15°C, pH = 8.2–8.4, Alk = 2.4 meq L⁻¹) [Pierrot et al., 2006]. This is in the range of gaseous CO₂ extracted from water samples from station CTD 1 (Background station; Table 4). A calculated value of about 200–300 ppm (CO₂ in dry atmosphere) would reflect a CO₂ sink compared to, for example, 370 ppm CO₂ in the atmosphere.

The high CO₂ concentration of 318 μmol L⁻¹ measured from CTD 13–7 (Figure 2) had a pH of 6.8 ± 0.2. A pH value of 6.8 corresponds to calculated values of about 9000 ppm CO₂ in dry air and a CO₂ₐq value of about 320 m mol L⁻¹. Slight reduction of pH in North Sea waters has been seen where respiration takes place, and annual cycles of pH vary between 7.8 and 8.4 depending on the distance to the coast [Blackford and Gilbert, 2007]. On the basis of measured data and box modeling, Blackford and Gilbert [2007] determined riverine inflow, respiration, and benthic or pelagic processes as the main reasons for reduced pH values in the North Sea. Obviously our measured pH value of 6.8 would require a much stronger CO₂ input.

6.2. Origin of the CO₂

CH₄ oxidation in the water column is not the source for high CO₂ concentrations as only background methane concentrations reflecting equilibrium with atmospheric methane were observed (data not shown). Moreover, methane concentrations are orders of magnitude (∼2–3 μmol L⁻¹) lower than CO₂ₐq and they did not vary significantly with CO₂ concentrations.
[56] The negative $\delta^{13}$C-$\text{CO}_2$ values indicate a dominant biogenic source in the working area. The most negative $\delta^{13}$C value (~$-24\%$, Figure 2) is related to the highest $\text{CO}_2$ concentration. Consequently, it is assumed that the carbon of the seeping $\text{CO}_2$ mainly originates from degradation of organic matter or methane oxidation within the sediment [Whiticar and Faber, 1986; Mook and Tan, 1991]. Considering the isotope fractionation at laboratory temperatures between $\text{CO}_2(g)$-$\text{CO}_2(aq)$ of ~$1\%$ and $\text{CO}_2(aq)$-$\text{HCO}_3^-$ of about ~$10\%$ [Chacko et al., 2001], sample CTD 1 reflects normal North Sea water conditions [Mook and Tan, 1991] and sample CTD 13 a mixed fluid. Therefore, it is difficult to determine the exact fluid origin (i.e., the benthic layer, Holocene peat deposits, or even deeper strata) that serves as a $\text{CO}_2$ source [e.g., del Giorgio and Williams, 2005; Fischer et al., 2006; Steinmann et al., 2008].

6.3. Pathways, Fate, and Potential Detection of $\text{CO}_2$ Seepage

[57] We have found evidence of $\text{CO}_2$ seepage, although the source and mechanism are still unclear. Using a simple modeling approach we suggest that bubbles were unlikely to be present under the prevailing conditions at Salt Dome Juist during the R/V Alkor cruise. Bubble formation would only occur when the solubility of gases (i.e., $\text{CO}_2$) in seawater is exceeded. For the actual seafloor conditions at Salt Dome Juist (T~290 K, S~35%, 20 m depth) about 100 mmol L$^{-1}$ $\text{CO}_2$ is calculated as $\text{CO}_2$ solubility after Duan and Sun [2003] and Duan et al. [2006], which would imply a pH value of ~4.3 in the fluid and sediment. Such a significantly acidic pH is far lower than the pH range measured for high respiratory shelf sediment [Zhu et al., 2006] and would therefore open the discussion for additional, perhaps deep-seated $\text{CO}_2$ sources.

[58] The bubble plume modeling did not rule out such a plume source; however, it would likely be a single phase plume (i.e., only liquid) with no bubbles (free gas). A buoyant enough point source with inputs ranging from roughly 1–10 t d$^{-1}$ is needed to explain the observed strong $\text{CO}_2$ signal. Such a buoyancy source driving the plume could be a (1) slightly elevated seepage temperature, (2) fresher groundwater input, or (3) strong hydrostatic head (perhaps driven from onshore rain events). We would like to note that during a return cruise aboard R/V Celtic Explorer in August 2009 the seep could not be relocated. This would suggest (not surprisingly) that it is an intermittent, and perhaps seasonal, source.

[59] Even without bubbles, $\text{CO}_2$ entering the water column from the sediment at Salt Dome Juist will reach the atmosphere. This is due to the well-mixed, shallow water column and surface mass transfer. However, for the stratified summer deep (70 m) situation, any potential $\text{CO}_2$ bubbles and plume would stop at the thermocline, thus trapping the $\text{CO}_2$ in the bottom water. This $\text{CO}_2$ could reach the atmosphere during the fall turnover, which may help explain the $\text{CO}_2$ flux increases reported by Bozec et al. [2005], or be transported and sequestered within the North Atlantic Ocean deep waters as suggested by Thomas et al. [2004].

[60] The results of this study have implications and present challenges for the detection of $\text{CO}_2$ seepage at shallow CCS sites:

[61] 1. Significant seepage of $\text{CO}_2$ is necessary for $\text{CO}_2$ bubbles to be present.

[62] 2. Even if $\text{CO}_2$ bubbles are present, they are hard to detect because of rapid dissolution.

[63] 3. $\text{CO}_2$ bubble-driven plumes would not rise as high in the water column as would $\text{CH}_4$ bubble-driven plumes and tend to fall back farther.

[64] 4. $\text{CO}_2$ adds density, and thus monitoring and sampling should be concentrated at the seafloor.

[65] 5. $\text{CH}_4$ bubbles could be sought out as precursors or indicators of potential $\text{CO}_2$ seepage.

Notation

- A area, m$^2$
- b plume radius, m.
- C dissolved concentration, mol m$^{-3}$
- d bubble diameter, mm.
- $F_B$ dissolved species flux, mol s$^{-1}$
- $F_G$ gaseous species flux, mol s$^{-1}$
- $F_r$ Froude number, dimensionless.
- $F_S$ salinity flux, g s$^{-1}$
- $F_T$ temperature flux, °C m$^3$ s$^{-1}$
- g gravitational acceleration, m s$^{-2}$.
- $K_T$ mass transfer coefficient, m s$^{-1}$
- M plume momentum, m$^4$ s$^{-2}$.
- N number flux of bubbles, s$^{-1}$.
- P pressure, bar.
- Q plume flow rate, m$^3$ s$^{-1}$.
- r bubble radius, m.
- S salinity, g kg$^{-1}$
- SC salinity correction, PSU.
- t time, s.
- $T$ temperature, °C.
- v velocity, m s$^{-1}$.
- y gaseous concentration, mol m$^{-3}$.
- z depth, m.

Greek letters

- $\alpha$ entrainment coefficient, dimensionless.
- $\beta$ density contraction coefficients, kg g$^{-1}$.
- $\lambda$ ratio of bubble-containing region of plume.
- $\rho$ density, kg m$^{-3}$.
- $\sigma$ surface.

Subscripts

- a ambient water.
- b bubble.
- I gas species.
- p plume water.
- w plume water.

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