Carbon Dioxide in Lake Nyos, Cameroon, Estimated Quantitatively From Sound Speed Measurements

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Gases dissolved in the deep water of lakes can pose a hazard when extreme concentrations are reached. A sudden release of large amounts of gas can cost the lives of humans living in the neighbourhood, as happened at Lake Nyos in 1986. Since 2001, the gas risk at Lake Nyos has been mitigated by induced degassing, but the lake continues to be supplied by CO2, and a regular survey needs to be implemented to guarantee safe conditions. Frequent sampling of this remote lake requires an enormous effort, and many analytical techniques are very difficult to run at the lake site. In this contribution, we combined a commercially available sound speed sensor with a CTD (electrical conductivity, temperature, depth) probe to obtain an indirect but quantitative estimate of carbon dioxide concentrations with fine depth resolution (decimetre scale). Dissolved carbon dioxide increases sound speed but does not contribute to electrical conductivity. Hence the difference between measured and calculated (on the base of electrical conductivity, temperature and pressure) sound speed gives a quantitative indication of dissolved carbon dioxide. We infer the vertical distribution of dissolved CO2 and hence continue the survey of the progress of the intended degassing. In conclusion, we present an easy to implement method for very high CO2 concentrations in deep lakes, and we highly recommend the implementation of the sound speed-CTD probe combination at Lake Nyos and at other gas-laden volcanic lakes, as such an approach could safeguard the people living in the area with acceptable cost and effort for the operators. In this manner, alarming CO2 concentrations in deep parts of lakes can be detected in a timely fashion.

Keywords: gas, gas pressure, lake Nyos, limnic eruption, remediation, sound speed

INTRODUCTION

Extreme concentrations of dissolved gases in deep waters of lakes can pose a threat to the local population. Sudden limnic overturns can liberate large volumes of gas, which can asphyxiate humans and livestock, as happened at Lake Monoun in 1984 and at Lake Nyos in 1986 (Kling et al., 1987; Sigurdsson et al., 1987). More than 1700 humans perished in these natural disasters. Also at other places, extreme gas pressures have been detected and assessed for their danger to the local population (Lake Kivu: Lorke et al., 2004; Schmid et al., 2005; Guadiana Pit Lake: Sánchez España et al., 2014;
Boehrer et al., 2016; Lake Vollert-Sued: Horn et al., 2017; Lago Monticchio Piccolo: Caracausi et al., 2009; Cabassi et al., 2013. All these lakes are meromictic, and accumulation of solutes in the deep water can occur over long periods (e.g., Boehrer et al., 2013; Boehrer et al., 2021). In some cases, artificial degassing is considered necessary to reduce risk around the lakes (Nyos, Monoun, Guadiana Pit Lake; Sánchez España et al., 2020).

Even after removal of the gas, some of the lakes still maintain their connection to the gas source, allowing for gas recharge, as seen in Lake Monoun (Kusakabe, 2017). Other lakes, such as Lago Albano, can be recharged with gas in a sudden manner by seismic activity (Chiodini et al., 2012; Rouwet et al., 2019; Rouwet et al., 2021; Rouwet, 2021). To avoid dangerous levels of gas accumulation, gas concentrations need to be surveyed regularly. Reliable measurements of high gas concentrations are difficult, as intensive efforts on Lake Kivu have shown (Boehrer et al., 2019; Bärenbold et al., 2020, and references therein). Especially in remote localities such as Lake Nyos, measurements with sophisticated equipment and complex procedures require an enormous logistical effort. Simple, portable equipment would be most practicable for such surveys. Sanemasa et al. (2017) provided measurements of sound speed which were affected by high concentrations of carbon dioxide; they indicated that sound speed measurements could be used to quantify carbon dioxide in Lake Nyos. Saiki et al. (2017) presented measurements of sound speed with a Minos X (AML Oceanographic) used for calibrating a multibeam sonar.

They correlated measured CO2 concentrations with measured sound speeds, and demonstrated that such measurements are feasible and provide a good quantitative estimate of the carbon dioxide dissolved in the lake water.

In March 2016, 30 years after the disaster of the Nyos limnic eruption, a conference was held in Yaounde (Cameroon) to reflect upon the work so far that dealt with managing the danger of limnic eruptions at Lake Nyos and Lake Monoun. The goal was to understand the underlying volcanic connections and to examine lessons learnt from the Nyos and Monoun remediation efforts (Tanyileke et al., 2019). Artificial degassing had been induced beginning in 2001 when the first degassing tube went into operation. Degassing was enhanced in 2011 with two additional degassing tubes. The scientific meeting, the 9th Workshop of the International Association of Volcanology and Chemistry of the Earth’s Interior (IAVCEI) Commission on Volcanic Lakes, was complemented by a short field campaign to document the situation in 2016, i.e., at a time when the forced degassing had removed most of the gas from the deep layer of Lake Nyos (Kusakabe, 2017; Kusakabe et al., 2019; Tanyileke et al., 2019; Halbwachs et al., 2020).

The aim of this study was the field deployment of commercially available equipment (i.e., a conductivity-density-depth probe with a sound speed sensor) to yield a profile of dissolved inorganic carbon (DIC hereafter) concentrations based on the excess sound speed in comparison to calculated sound speed. The well studied Lake Nyos itself was arguably the best suited natural laboratory to develop and verify our approach. However, in addition to the studies by Saiki et al. (2017) and Sanemasa et al. (2017), we included conductivity in the calculations and considerations of sound speed to correlate actual CO2 (instead of DIC) with sound speed. We present a pH and site independent (background salinity) approach; hence this method has the potential to be applied to other highly CO2-laden lakes.

**MEASUREMENTS**

Lake Nyos is located in the Cameroon Volcanic Line in the western part of Cameroon (06°26' N, 10°17' E) at an altitude of 1,091 m asl. Its maximum depth reaches 210 m with a surface area of 1.58 km² compared to the catchment area of about 8 km² and a lake volume of 1.6 × 10⁸ m³ (Tanyileke et al., 2019). The lake has been meromictic and is known for its high carbon dioxide concentrations in the deep water, which caused a limnic eruption in 1986 costing the lives of 1,746 people.

We took part in the Nyos field campaign in 2016. We lowered our custom-built oceanographic multiparameter probe by hand from the surface to the maximum depth on a rope to document the stratification of temperature and electrical conductivity (EC hereafter) at the time. The probe was also equipped with an oxygen sensor and a pH sensor. In addition, it carried a sound speed sensor for direct measurements. Both the probe (“i152”, Ocean Seven 316, Idronaut, Italy) and the sound speed sensor (VALEPORT, United Kingdom) were commercially available, and the probe manufacturer customized the sound speed sensor.
in the probe (see Figure 1). The sound speed sensor provided a direct time of flight measurement over 10 cm from a transducer to a reflector table and back. As a backup, we also mounted a CTD probe “CTM102” (Sea and Sun Technology, Trappenkamp Germany; data were for backup but not used in this publication). The full instrument weighted 9.9 kg; it was easy to handle and could be carried in a case on an airplane.

Measurements of EC showed the removal of the deep water from the monimolimnion (120–209 m depth) by syphoning water from close to the lake bed to the surface. As a consequence, the upper water body of constant salinity grew in thickness from ca. 100 m in 2014 to 120 m in 2016 (Figure 2). The rates of the gradient lowering agreed well with the expected value from the discharge through the degassing pipes (see Ohba et al., 2020). The higher salinity water at the surface induced mixing and created the water body of constant EC.

The temperature profile showed a shallow epilimnion of about 10 m thickness, below which we found an isothermal hypolimnion (Figure 2, see also Boehrer and Schultzze 2008; Boehrer et al., 2013). Below 120 m depth, i.e., in the monimolimnion, temperature increased along with EC. The difference from 2014 could be explained by the continued drawdown by siphoning deeper water (Ohba et al., 2020). The higher salinity water at the surface induced mixing and created the water body of constant EC.

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The profiles of temperature, EC, and pressure (depth) facilitated the calculation of sound speed \( \nu_{\text{UNESCO}} \) by implementation of the UNESCO formula. We followed the Saiki et al. (2017) convention and called the difference to measured sound speed \( \nu_{\text{meas}} \) the “excess sound speed”:

\[
\Delta \nu = \nu_{\text{meas}} - \nu_{\text{UNESCO}}
\]

Carbon dioxide is the only dissolved substance present at high concentrations that does not contribute to EC. However, as dissolved carbon dioxide affects both density and adiabatic compressibility of water, it increases the sound speed as shown by Sanemasa et al. (2017). Hence we assumed that it is a measure for carbon dioxide. We first used the conversion factor \( k_1 = 0.0323 + 0.000523 \cdot T \) (with T in °C) from Sanemasa et al. (2017) to calculate:

\[
\epsilon_{\text{CO2}} = \frac{\Delta \nu}{k_1}
\]

In a second step, the pH information was used to calculate bicarbonate concentration from
\[ c_{\text{HCO}_3^-} = K_c \frac{c_{\text{CO}_2}}{c_{\text{H}^+}} = 10^{pH-pKs} \cdot c_{\text{CO}_2} \]  

(3)

where \( pKs = 6.36 \) (Worch, 2015), pH was taken from the multiparameter profile and \( c_{\text{CO}_2} \) from the calculation above (Eq. 2). The sum represented dissolved inorganic carbon (DIC):

\[ c_{\text{DIC}} = c_{\text{HCO}_3^-} + c_{\text{CO}_2} = \left( 1 + 10^{pH-pKs} \right) \cdot c_{\text{CO}_2} \]  

(4)

\[
\rho(T, C_{25}) = \rho_W(T) + C_{25} \cdot (\lambda_0 + \lambda_1 \cdot (T - 25^\circ C)) + \gamma \cdot G \cdot c_{\text{CO}_2}
\]

(5)

with fractional density contribution \( \gamma = 0.212 \) of CO\(_2\) from Dietz et al. (2012), and molar mass \( G = 44.01 \text{ g/mol of CO}_2\). The coefficients \( \lambda_0 = 0.77 \text{ kg/m}^3/\text{mS/cm} \) (±0.014) and \( \lambda_1 = -0.0015 \text{ kg/m}^3/\text{K/eq/mS/cm} \) (±0.0005) were obtained from the Moreira et al. (2016) density calculator, by inserting the salt composition measured in 2016 at 160 m depth (Table 1).

To check the variability with composition, we also inserted the salt composition measured by Kusakabe et al. (2008) at a depth of 195 m as reported by Sanemasa et al. (2017) and Anazawa et al. (2019), where we closed the charge balance with bicarbonate. The results for \( \lambda_0 \) and \( \lambda_1 \) agreed for all three solute compositions within the given narrow bounds. As a consequence, the density formula for Lake Nyos can be considered quite robust and valid for the time period covered by observations. The value for \( \lambda_0 \) is large, i.e., formulae based on ocean water conditions would greatly underestimate the density effect of solutes affecting EC. Inserting the measured and calculated values into Eq. 5 yielded the (potential) density profile (Figure 4), where we also showed the contribution of CO\(_2\) separately.

Gas pressure profiles are essential to judge the proximity to spontaneous gas exsolution (Kusakabe, 2017). Hence we calculated the gas pressure induced by carbon dioxide using

### RESULTS

A comparison of the resulting DIC profile with the DIC profile published by Saiki et al. (2017) for 2014 showed the vertical shift due to the drawdown, but also the considerably higher concentrations (Figure 3B “2014 Saiki”).

Stability is controlled by density. Similar to sound speed, we capture the contribution of ionically dissolved substances by their contribution to EC. For quantification, we use the lambda-approach by Moreira et al. (2016) and Boehrer et al. (2010), who added the density contributions of solutes to the (potential) density of pure water. As in Schmid et al. (2003), we added the contribution of CO\(_2\) in a separate term:
Henry’s law and the temperature-dependent Henry coefficient. The values lie between 2 and 3 bars through the monimolimnion and rise approaching 4 bars close to the lake bed (Figure 4). In addition, we converted oxygen saturation into oxygen gas pressure, which started at about 0.2 bar at the surface (low atmospheric pressure at the altitude of 1,100 m a.s.l.), about 0.1 bar (50% saturation of atmospheric pressure at 1,100 m a.s.l.) throughout the hypolimnion and zero in the monimolimnion. Gas pressure for nitrogen was assumed to be in equilibrium with atmospheric N₂ partial pressure at the altitude of Lake Nyos, i.e., 0.68 bar. A similar procedure was implemented for argon (Ar) to yield 0.0087 bar. The contribution of vapour pressure reached less than 0.025 bar at temperatures measured in Lake Nyos (22–24°C, Figure 2).

**DISCUSSION**

Our goal was to test whether commercially available equipment was suited for estimating dissolved carbon dioxide on the basis of the sound speed. We used the complete UNESCO equation (Fofonoff, 1986, including the temperature scale change in 1990) for sound speed from temperature, salinity (i.e., EC), and pressure. This formula connects physical quantities, such as density and sound speed, to accurately measurable quantities of electrical conductivity, temperature and pressure. The conversion is valid for the salt composition of ocean water and applicable to limnic waters with some loss of accuracy. Most oceanographic CTD probes supply this UNESCO sound speed as a derived quantity. We compared the calculated sound speed with the sound speed from directly measured time-of-flight to find the excess sound speed for estimating carbon dioxide concentration (Eqs 1, 2).

The inclusion of the salinity term in the UNESCO equation resulted in very good agreement between measured and calculated sound speeds at depths, where we did not expect high concentrations of CO₂, i.e., in the hypolimnion between 10 and 120 m depth. In the temperature-stratified top layer, larger deviations in the range of a few m/s were visible, which could be identified as artefacts and attributed to the different measuring volumes of sound speed (10 cm), temperature (as well as EC; more in the range of 2 cm; see Figure 1) and the high vertical temperature gradients that pronounced this feature. Below 120 m depth, the differences between calculated and measured sound speed were indicative of increasing carbon dioxide concentrations up to about 150 mmol/l at the lake bed, in good agreement with expectations from earlier measurements.

In comparison with the 2014 data, the drawdown effect became clearly visible. The steep gradient of carbon dioxide was moved downward by about 20 m due to the degassing facility removing deep water from close to the lake bed. At depths between 140 and 180 m, DIC concentrations in 2016 were marginally higher than in 2014; at depths below 180 m, the difference was larger. This indicated additional DIC, which should be the case very close to the lake bed, but probably not in the depth range from 140 to 200 m. It is more likely that this difference arose from the different approaches and different types of equipment that were implemented by the various research groups. We used the original coefficient \( k_1 \) form the laboratory measurement by Sanemasa et al. (2017), as the data from 2014 indicated a reasonably good agreement. In contrast, Saiki et al. (2017) saw evidence from samples that the correlation between...
DIC and sound speed excess required corrections, which they mainly attributed to the presence of bicarbonate. The measurements by Sanemasa et al. (2017) were done at smaller outside (hydrostatic) pressures, hence may not exactly reflect the situation at great depth in Lake Nyos. We did not have the capabilities to resolve this disagreement. A closer investigation of the correlation between dissolved carbon dioxide (as well as other dissolved substances) and sound speed would be desirable. This may be possible by additional laboratory experiments or application of this method to other gas-charged lakes.

We calculated dissolved bicarbonate from the dissociation product of carbonic acid. At a pH about 1 unit smaller than the pKs of 6.36, bicarbonate contributed about 10% to DIC; hence even a considerable error in the pH measurement would not heavily bias the DIC. In comparison to the calculated values from Saiki et al. (2017) approach, very small but visible differences appeared between 10 and 120 m depth (hypolimnion). The commercial probe showed good agreement between calculated and measured values (i.e., no CO2 in Figure 3B), most likely due to the inclusion of salinity in the calculation.

We implemented Eq. 5 to calculate a density profile. We used the formula by Tanaka et al. (2001) for density of pure water. We evaluated the density contribution of dissolved ions on the basis of the measured EC profile, and finally added the density contribution of the dissolved CO2. The increasing temperatures in the monimolimnion resulted in a density contribution which counteracted the stability, providing the potential for double diffusive convection (Schmid et al., 2004; Hirsldun 2019). This was outbalanced by the dissolved solids, which contributed a density difference of about 0.5 kg/m^3, tantamount to the density effect of a 2°C temperature difference that the mixolimnion would need to be colder than the monimolimnion to overcome the density of the monimolimnion. The density contribution of the dissolved CO2 was considerably larger, i.e. about 0.7 kg/m^3. In conclusion, the major contribution that maintained the stable stratification came from the dissolved CO2. Together, all terms indicated a density difference of 1 kg/m^3 between waters above and below the major chemocline at 120 m depth. However as this mainly relied on the contribution of the volatile CO2, this could not be considered safe, and the degassing of the lake had to be completed until the remaining CO2 would not pose a danger.

From our results, gas pressures could be calculated by solving Henry’s law. The contributions of CO2 (from sound speed), oxygen from sensor measurements, and vapour pressure from temperature could be calculated in a straightforward manner. For nitrogen and argon, we assumed equilibrium with the atmospheric pressure at the altitude of the surface of Lake Nyos. These calculations yielded a total gas pressure profile as the sum of these single terms. As shown in the paper by Bärenbold et al. (2019) for the extreme case of Lake Kivu, non-linearities were expected to be small (in the range of few percent). The total gas pressure is considerably smaller than the absolute (local) pressure. Hence spontaneous exsolution of CO2 would require that water be lifted from a depth of 140 m to about 15 m depth. This could only happen if the entire water column lost its stability, as described in the paragraph above on density.

**CONCLUSION**

The CTD and sound speed measurements in March 2016 at Lake Nyos, Cameroon, provided a data set that correlated very well with the CO2 concentrations observed along a vertical depth profile from earlier measurements. A commercial sound speed sensor attached to a high accuracy CTD probe was successfully tested for its suitability to survey carbon dioxide in Lake Nyos. The instrumentation can be easily transported to remote areas, such as Lake Nyos, to acquire vertical profiles at regular time intervals. Although this approach was not a direct measurement, the accumulation of carbon dioxide is manifested in detectable, increasing sound speed values, i.e., sound speed excess with respect to calculated sound speed based on EC, temperature and depth following the UNESCO formula. As a mitigation strategy, once sound speed measurements indicate carbon dioxide concentrations of concern, direct gas measurements and dissolved gas sampling campaigns could be implemented rapidly in order to confirm the elevated gas concentrations.

Finally, the measurements of CTD and sound speed relied only on physical quantities that could be measured at high accuracy, frequency and reproducibility. Although possibly more difficult to assess in terms of absolute accuracy, this method is particularly well-suited for documenting temporal evolution and quantifying changes much more rapidly and frequently compared to direct CO2 measurements. Profiles at high vertical resolution (decimetres) could be accomplished which guarantee that no layers remain undetected. In addition, vertical displacement, such as drawdown through siphoning, might be detectable on the base of the profile shape. Our measurements extend the documentation of the degassing progress by a further two years. We recommend frequent surveys using this approach for the timely detection of dangerous dissolved CO2 concentrations at Lake Nyos, as well as at other similarly hazardous lakes.

Extending the work of Saiki et al. (2017), we separated the effect of CO2 on sound speed from the bicarbonate contribution. This made the correlation factors independent of pH and background salinity. This was a step towards using the approach at other lakes with high CO2 (e.g., the episodically recharged Lago Albano, Italy). A further investigation of the quantitative connection between solutes and sound speed remains desirable.

**DATA AVAILABILITY STATEMENT**

The original contributions presented in the study are included in the article, further inquiries can be directed to the corresponding author.

**AUTHOR CONTRIBUTIONS**

BB was responsible for the measurements 2016, and he was the lead author of this contribution. KS and TO provided the 2014 data and the detailed numerical approach of 2014. GT, DR, and MK provided information on the geological setting, comparison with other volcanic lakes and the information about the degassing history. All authors were present at the 2016 meeting and/or field measurements in 2016. All were involved in writing this paper.
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