

Decreasing removal rate of the dissolved CO₂ in Lake Nyos, Cameroon, after the installation of additional degassing pipes

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Abstract: The amount of dissolved CO₂ (CO_{2aq}) in Lake Nyos, Cameroon, has been measured annually since January 2011. First, HCO₃⁻ concentration was estimated by a chemical analysis with the assumption of equilibria between CO_{2aq}, HCO₃⁻ and CO₃²⁻. The estimated [HCO₃⁻] was correlated with the observed electrical conductivity of lake water. The profile of [CO_{2aq}] was generated from the electrical conductivity, pH and temperature profiles. The [CO_{2aq}] profile was integrated over the water column to obtain the total amount of CO_{2aq}. The amounts were 8.4, 6.8, 5.5, 4.4 and 3.9 Gmol (=10⁹ mol) in 2011, 2012, 2013, 2014 and 2015, respectively. The fast reduction between 2011 and 2013 was attributed to the installation of two additional degassing pipes in April 2011. However, the rate of reduction decreased between 2014 and 2015 due to the reduced [CO_{2aq}] at the inlet of the degassing pipes.

Limnic eruption is a term to indicate an explosive discharge of dissolved CO₂ gas from lake water. J.C. Sabroux coined the term at the UNESCO conference on the disaster at Lake Nyos in 1986 (Halbwachs *et al.* 2004). Only two limnic eruptions have been recorded so far in the world. The first eruption happened at Lake Monoun in 1984 (Sigurdsson *et al.* 1987), resulting in 37 victims. The second eruption happened at Lake Nyos (Fig. 1) in 1986, killing about 1700 people (Sigvaldason 1989). Both of the lakes are located in the Cameroon Volcanic Line (CVL), traversing the northwestern part of Cameroon. The $\delta^{13}\text{C}_{\text{PDB}}$

(= -3.5‰) of CO₂ and the ³He/⁴He value (= 8 × 10⁻⁶) measured in the lake water suggested that CO₂ and He gas originate from the mantle (Sano *et al.* 1990; Nagao *et al.* 2010). Considering the magmatic nature of the gases, the lake CO₂ supply is expected to continue over a long period, and dissolved CO₂ gas in the lakes should be monitored for the mitigation of possible disasters.

The driving force of a limnic eruption is the quantity of dissolved CO₂ in lake water (Kling *et al.* 1989; Kusakabe *et al.* 1989). In the Lake Nyos limnic eruption in 1986, it was estimated that 5.6 Gmol of CO₂ was explosively discharged

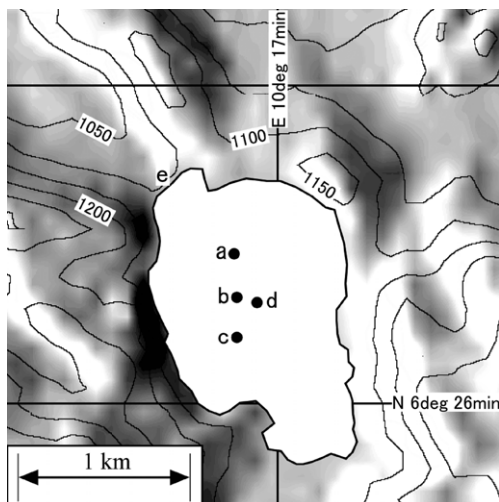


Fig. 1. Point of observation (d) and location of the degassing pipes (a, b and c) on Lake Nyos.

(Giggenbach 1990), whilst 13 Gmol were left in the deeper part of the lake (Kusakabe *et al.* 2008). After the limnic eruption, the amount of dissolved CO_2 started to increase at a rate of 0.12 Gmol a^{-1} , finally reaching 14.8 Gmol in 2001 (Kusakabe *et al.* 2008).

In 2001, a degassing pipe was installed at the centre of Lake Nyos (point b in Fig. 1) to remove the dissolved CO_2 gas from the deeper water layers of the lake (Halbwachs *et al.* 2004). After the installation, the amount of CO_2 steadily decreased (Kusakabe *et al.* 2008) at a rate of 0.63 Gmol a^{-1} . In 2006, the amount of CO_2 was reduced to 11.7 Gmol (Kusakabe *et al.* 2008). In April 2011, two additional degassing pipes were installed at points 'a' and 'c' in Figure 1 to enhance the removal rate of dissolved CO_2 . In this study, we report the amount of CO_2 in Lake Nyos to estimate the effect of the two additional degassing pipes.

Lake Nyos

Lake Nyos is a maar lake, although the shape is not circular (Fig. 1). The lake is located along the CVL and the catchment area around the lake collects the surface water through small streams. The lake water overflows through point 'e' in Figure 1 during the rainy season (April to November) and, in the dry season, the lake level lowers by about 1 m relative to point 'e'. Monitoring of the lake water for chemical and physical parameters was carried out at point 'd' in Figure 1 where the depth is 210 m. Annual monitoring was carried out in January 2011 and March of 2012, 2013, 2014 and 2015.

Observations and sampling of lake water

For the physical properties, a CTD probe (Ocean Seven Model 316, IDRONAUT) was used to record parameters such as water pressure, temperature, electrical conductivity and pH. The lake water was sampled to determine the concentration of carbonate species. Owing to the high concentration of dissolved CO_2 , deep water effervesces when brought to the surface and most of the dissolved CO_2 gas is lost by degassing. To fix the dissolved CO_2 in the lake water *in situ*, a plastic syringe containing 10 ml of 5M KOH solution was used. The syringe was attached to a device and sent to the desired depth (Kusakabe *et al.* 2000; Tassi & Rouwet 2014). About 30 ml of lake water was introduced into the syringe. The accurate amount of the sampled lake water was determined by the difference in the weight of the syringe before and after the sampling. The sample was analysed in the laboratory for the total carbonate content ($\text{CO}_{2\text{aq}} + \text{HCO}_3^- + \text{CO}_3^{2-}$) using the microdiffusion titration method (Conway 1950). We call the above summation 'total CO_2 ', hereafter denoted C_t in this study. The fundamental advantage of the above method is the high accuracy of the determination of C_t . The analytical error of the method was about $\pm 2.5 \text{ mmol l}^{-1}$, which corresponds to a relative precision as small as 1% if C_t is 250 mmol l^{-1} .

Results

The depth profiles of temperature, electrical conductivity and pH from 2011 to 2015 are shown in Figure 2a, b and c, respectively. Since the electrical conductivity of a solution depends on temperature, the raw conductivity was normalized to the electrical conductivity at 25°C assuming a temperature dependence of +2% per $^\circ\text{C}$, as expressed by the following equation,

$$C_{25} = \frac{C}{1 + 0.02(t_c - 25)} \quad (1)$$

where C and C_{25} are the raw conductivity at t_c in $^\circ\text{C}$ (i.e. measured lake water temperature) and the normalized conductivity at 25°C , respectively. As shown in Figure 2a, the depth of the lake water thermocline was about 70 m in 2011. The depth dropped annually, reaching 110 m in 2015, which is an effect of the degassing pipe. The inlets of the degassing pipes are located at 207 m depth. The hot bottom water was transported to the surface of the lake, which results in the subsidence of the thermocline. This effect can be seen in Figure 2b and c. The analytical results for C_t are listed in Table 1 and are plotted as a function of

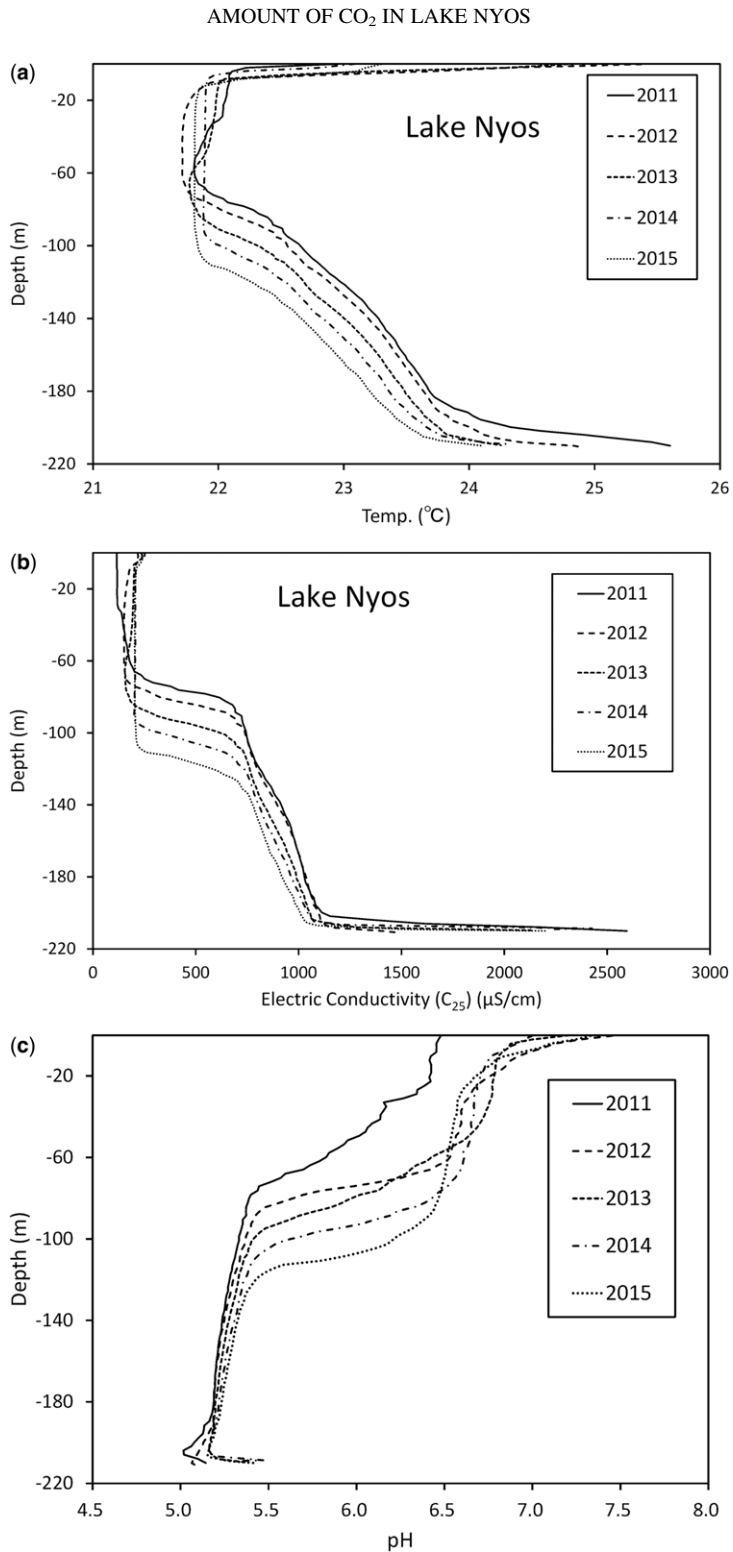


Fig. 2. (a) Temperature profile, (b) electrical conductivity profile and (c) pH profile observed by CTD logger.

Table 1. Properties of Lake Nyos water in January 2011

Depth (m)	total CO ₂ (mmol l ⁻¹)	Temp. (°C)	pH	C ₂₅ (μS cm ⁻¹)	HCO ₃ ⁻ (mmol l ⁻¹)
70.0	23.3	21.9	5.57	252	3.4
80.3	60.0	22.3	5.39	615	6.2
90.5	78.5	22.5	5.35	723	7.6
109.2	90.3	22.8	5.31	767	8.1
119.4	101.6	23.0	5.28	808	8.6
129.8	117.8	23.1	5.26	866	9.5
140.0	123.6	23.3	5.24	916	9.6
150.4	138.6	23.4	5.22	957	10.4
170.9	144.0	23.6	5.20	1010	10.4
179.2	153.3	23.7	5.19	1027	10.9
185.3	155.9	23.8	5.18	1045	10.9
189.5	159.8	23.9	5.16	1058	10.8
193.6	180.6	24.0	5.13	1078	11.4
195.6	181.9	24.1	5.13	1082	11.4
197.7	187.9	24.2	5.10	1100	11.1
199.7	206.2	24.3	5.08	1112	11.7
201.8	211.3	24.6	5.06	1153	11.5
205.9	300.8	25.2	5.02	1612	15.3
207.9	333.9	25.5	5.10	2175	20.5
210.0	372.1	25.6	5.14	2596	25.6

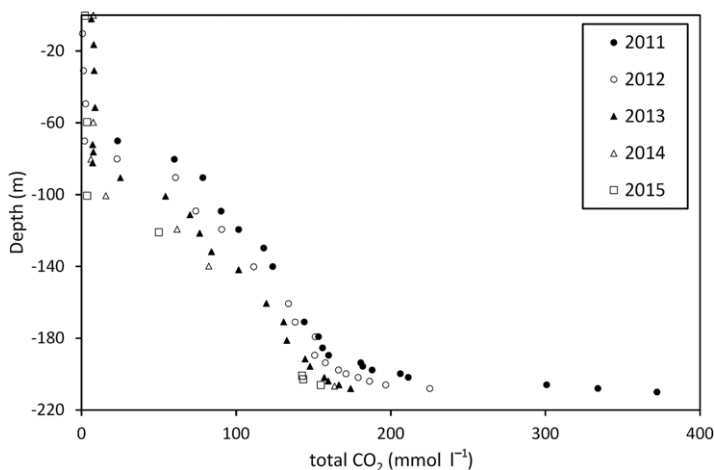
depth in Figure 3. The data points for C_t are discrete in terms of depth, because the sampling of the lake water with the KOH syringe requires time. We smoothed the profiles using the following procedure.

Combining the electrical conductivity profile with the C_t, a smooth profile can be obtained. The essential principle of the combination is the linear relationship between the electrical conductivity and the ion concentration in the water. The electrical conductivity of Lake Nyos water is dominated

mainly by HCO₃⁻ and cations (e.g. Mg²⁺, Fe²⁺, Ca²⁺, NH⁴⁺, Na⁺, K⁺).

In this study, the concentration of any chemical species is expressed with the parentheses [] in mmol l⁻¹. The [HCO₃⁻] can be estimated by the following equation (Butler 1991; Stumm & Morgan 1996), assuming equilibria among CO_{2aq}, HCO₃⁻ and CO₃²⁻:

$$[\text{HCO}_3^-] = C_t \left(\frac{a_{\text{H}} \gamma_{\text{HCO}_3}}{K_{a1}} + 1 + \frac{K_{a2} \gamma_{\text{HCO}_3}}{a_{\text{H}} \gamma_{\text{CO}_3}} \right)^{-1} \quad (2)$$

**Fig. 3.** Total CO₂ concentration determined by chemical analysis.

where C_t is defined by:

$$C_t = [\text{CO}_{2\text{aq}}] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \quad (3)$$

The activity of the H⁺ ion, a_{H} is given by:

$$a_{\text{H}} = 10^{-\text{pH}} \quad (4)$$

K_{a1} and K_{a2} in equation (2) are, respectively, the first and the second acid dissociation constants of H₂CO₃ as a function of temperature (T in K). They are defined by:

$$\log K_{a1} = 1.019 \times 10^7 T^{-3} - 9.656 \times 10^5 T^{-2} + 5.655 \times 10^3 T^{-1} - 14.84 \quad (5)$$

$$\log K_{a2} = 3.309 \times 10^8 T^{-3} - 3.797 \times 10^6 T^{-2} + 1.473 \times 10^4 T^{-1} - 27.45 \quad (6)$$

The above equations are valid in the range of 273–323 K. $\gamma_{\text{HCO}_3^-}$ and $\gamma_{\text{CO}_3^{2-}}$ in equation (2) are the activity coefficients of the HCO₃⁻ and CO₃²⁻ ions, respectively, calculated by the following Davies equation (Butler 1991):

$$\log \gamma = -0.5z^2 \left(\frac{I^{0.5}}{1 + I^{0.5}} - 0.2I \right) \left(\frac{298}{T} \right)^{2/3} \quad (7)$$

where z and I are the ion charge and ionic strength (mol l⁻¹), respectively. Based on the cationic composition of water in Lake Nyos at 205 m depth in 2006 (Kusakabe *et al.* 2008), I is

estimated by:

$$I = 1.46 \frac{[\text{HCO}_3^-]}{1000} \quad (8)$$

In order to evaluate [HCO₃⁻] based on equation (2), the activity coefficients should be calculated. For the calculation, I is necessary. However, I is given by equation (8) from [HCO₃⁻]. To solve this problem, I was assumed to be zero as the initial value, which means the activity coefficients are one. Then, the first value of [HCO₃⁻] was given by equation (2). The second value of I was given by equation (8), which was used to recalculate the activity coefficients. The coefficients were used to recalculate [HCO₃⁻] based on equation (2). The obtained [HCO₃⁻] in 2011 is listed in Table 1, with the parameters necessary for the above calculation.

The [HCO₃⁻] is correlated to C_{25} in Figure 4. The correlation is linear over the entire range of C_{25} . The slope and y-axis intercept in Figure 4 were used to estimate the smooth [HCO₃⁻] profile based on C_{25} . The smooth C_t profile was given by the [HCO₃⁻] profile using equation (2). The C_t profile and the discrete C_t values given by chemical analysis are compared in Figure 5.

The [CO_{2aq}] profile is estimated by the C_t profile using the following equation:

$$[\text{CO}_{2\text{aq}}] = C_t \left(1 + \frac{K_{a1}}{a_{\text{H}} \gamma_{\text{HCO}_3^-}} + \frac{K_{a1} K_{a2}}{a_{\text{H}}^2 \gamma_{\text{CO}_3^{2-}}} \right)^{-1} \quad (9)$$

The estimated [CO_{2aq}] profiles are also shown in Figure 5. The profile of [CO_{2aq}] was obtained for the period 2012–15 in the same way as for 2011 (Fig. 6).

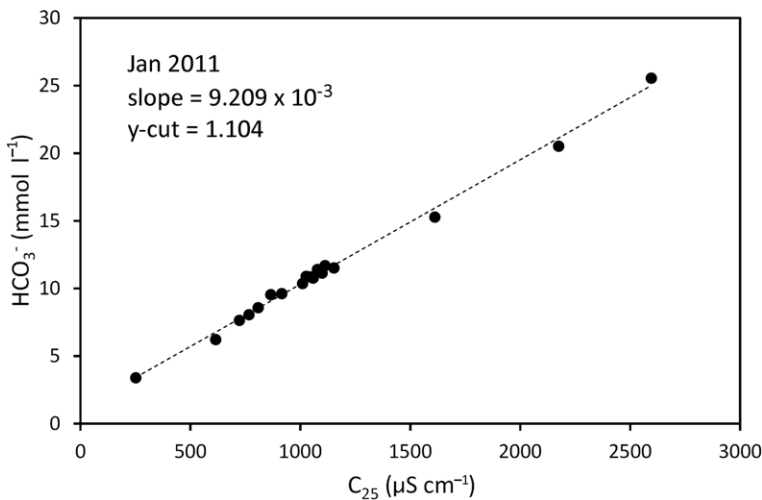


Fig. 4. Correlation between C_{25} and [HCO₃⁻] in 2011.

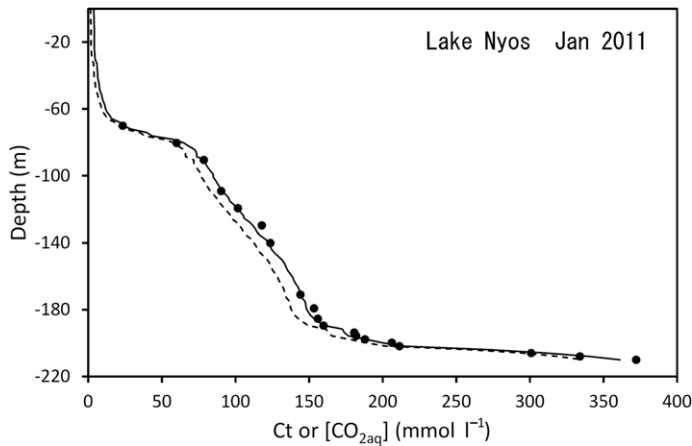


Fig. 5. C_t (solid line) and $[\text{CO}_{2\text{aq}}]$ (dashed line) profiles with the data (solid circles) obtained by chemical analysis in 2011.

To estimate the $\text{CO}_{2\text{aq}}$ amount in the lake water, the volume of the lake water is required as a function of depth (m). Based on the bathymetric map obtained by Halbwachs (2003), the bathymetry was digitized with a resolution of $20 \text{ m} \times 20 \text{ m}$. The volume of lake water was calculated using the digitized map and approximated with the following polynomial equation:

$$V(x) = 5.4910 \times 10^{-6}x^6 + 3.5835 \times 10^{-3}x^5 + 0.95818x^4 + 135.21x^3 + 12465x^2 + 1.5386 \times 10^6x + 1.5467 \times 10^8 \quad (10)$$

where V and x are the volume of lake water (m^3) and the depth of lake water (m) ($-209 < x < 0$),

respectively. Differentiating equation (10), the lake surface area $S(x)$ (m^2) is obtained.

$$S(x) = \frac{dV(x)}{dx} \quad (11)$$

The water in Lake Nyos is well stratified (Kusakabe *et al.* 2008) so the $\text{CO}_{2\text{aq}}$ content is strongly depth-dependent. We calculated the amount of $\text{CO}_{2\text{aq}}$ (M in Gmol) dissolved in the lake water by integrating $[\text{CO}_{2\text{aq}}]$ over the whole lake,

$$M = 10^{-9} \int_{-209}^0 S(x)[\text{CO}_{2\text{aq}}]dx \quad (12)$$

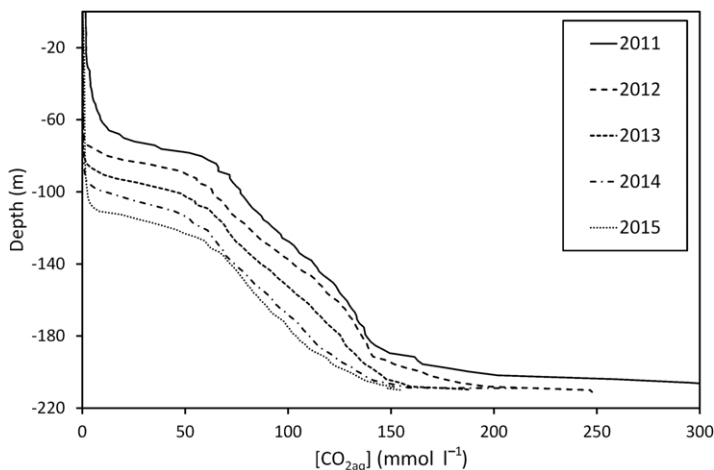


Fig. 6. $[\text{CO}_{2\text{aq}}]$ profiles from 2011 to 2015.

Table 2. Amount and concentration of CO_{2aq}

Date	<i>M</i> (Gmol)	Reduction in <i>M</i> (Gmol)	[CO _{2aq}] at 207 m depth (mmol l ⁻¹)
13 January 2011	8.37	1.56	319
7 March 2012	6.81	1.33	190
11 March 2013	5.48	1.04	157
1 March 2014	4.44	0.50	151
5 March 2015	3.94		145

The calculated *M* is listed in Table 2 and plotted in Figure 7 together with the amount of dissolved CO₂ for a period of time ranging from 1986 to 2006 (Kusakabe *et al.* 2008).

Discussion

The amount of CO_{2aq} dissolved in the lake water decreased quickly at a rate of 1.44 Gmol a⁻¹ from 2011 to 2013, the first two years after the introduction of two additional degassing pipes in the lake (Fig. 7). This rate is about twice the rate of 0.63 Gmol a⁻¹, which was recorded between 2001 and 2010, when a single pipe was working. Between 2014 and 2015 the rate decreased significantly to 0.50 Gmol a⁻¹.

The lake water flux through the degassing pipes depends on [CO_{2aq}], because the buoyancy generated by the degassed CO₂ gas is the driving force of the water flow. As shown in Table 2, [CO_{2aq}] reduced to 145 mmol l⁻¹ in 2015 at 207 m, corresponding to the depth at which the degassing pipe inlets are located. The value is about half of that in 2011 (Fig. 7). Kozono *et al.* (this volume, in press) developed a physical model for the flow in the degassing pipe. In their model, the flux through the pipe is expressed as a function of [CO_{2aq}] at the inlet. Their model also suggested that there is a threshold value under which the flux in the pipes cannot be sustained. For the degassing pipes at Lake Nyos the threshold value was calculated to be 90 mmol l⁻¹ (Kozono *et al.*, this volume, in press). Between 2013 and 2015, [CO_{2aq}] at 207 m

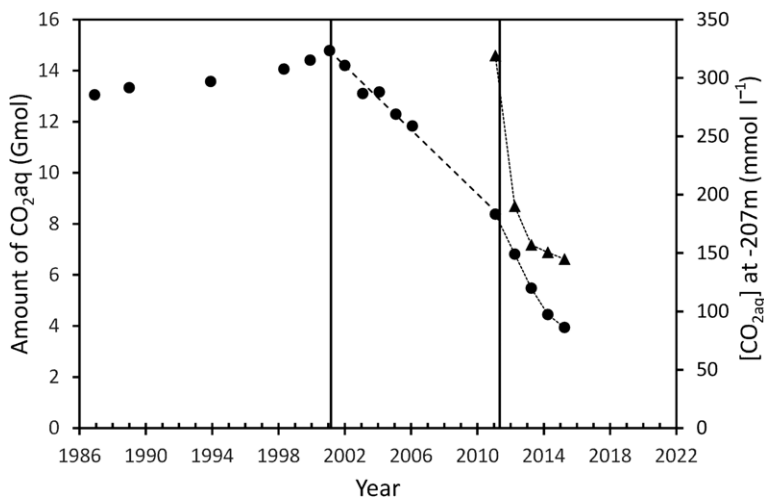


Fig. 7. Variations through time of dissolved CO_{2aq} amount with [CO_{2aq}] at 207 m depth. The vertical lines indicate the date of degassing pipe installation. The circles indicate the amount of CO₂ (left y-axis). The triangles indicate [CO_{2aq}] (right y-axis).

depth decreased with a rate of about $6 \text{ mmol l}^{-1} \text{ a}^{-1}$. Considering this decreasing rate, it will be 9–10 years until $[\text{CO}_{2\text{aq}}]$ arrives at the threshold value and the flux of the degassing pipes will cease. As the threshold value is approached, the reducing rate of $[\text{CO}_{2\text{aq}}]$ will decrease even more because the flux through the pipes is reduced. Therefore, the time until the degassing flux stops could be more than 10 years.

Conclusions

The results of recent monitoring (2011–15) of Lake Nyos were presented. Assuming chemical equilibrium among $\text{CO}_{2\text{aq}}$, HCO_3^- and CO_3^{2-} , $[\text{HCO}_3^-]$ were estimated based on the total CO_2 concentration and pH at various depths. The estimated $[\text{HCO}_3^-]$ was found to be linearly correlated with electrical conductivity. Using the linear relationship between electrical conductivity and $[\text{HCO}_3^-]$ a smooth profile of $[\text{CO}_{2\text{aq}}]$ was obtained. Integrating the $[\text{CO}_{2\text{aq}}]$ for the whole lake, taking its chemical stratification into consideration, the total amount of $\text{CO}_{2\text{aq}}$ in the lake was estimated. After the installation of two additional degassing pipes in 2011, the amount of CO_2 started to decrease quickly at a rate of 1.44 Gmol a^{-1} until 2013, which is twice the rate prior to 2011. Nevertheless, after 2014, the rate dropped to 0.50 Gmol a^{-1} . Considering the temporal change of $[\text{CO}_{2\text{aq}}]$ at the depth at which the degassing pipe inlet is located, the flux will be sustained at least for the next 10 years.

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