

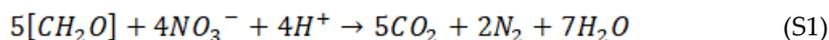
Supporting Information

We include a brief overview of the geochemical involvement of the considered gases.

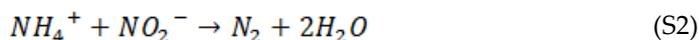
S.1 Nitrogen

Though seldom in the focus of gas investigations, the first gas to list is nitrogen (N₂). It is an elementary gas consisting of 2-atom molecules. At normal pressure of 1013.25 mbar, an atmospheric portion of 78% (of dry atmosphere) and water in the usual limnological range, we find an equilibrium concentration of about 0.5 mmol N₂/l or 1 mmol N/l in surface water (see Henry law). Though solubility is low (Table 1), N₂ concentrations usually lie far above nitrate, ammonium or organic N concentrations in lake waters (N₂ is not included in “inorganic nitrogen”). N₂ is considered chemically relatively inert and consequently N₂ concentrations are largely independent of depth and close to 100% saturation throughout the water column (Miyake 1951[8]; Ramsey 1962 [63]).

There are biogeochemical reactions in the environment that involve N₂ as reagent or product and there is an aquatic, biogeochemical nitrogen cycle: When oxygen is depleted, nitrate can act as oxidizing agent for the decomposition of organic matter (written as [CH₂O] (representing one sequence of carbohydrates) in the following chemical equations):



or nitrite can oxidize ammonia (anammox):

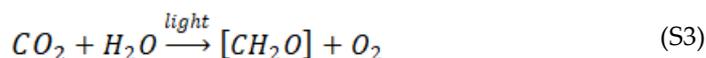


and finally result in the production and release of N₂ into the water (Mulder et al. 1995 [121]; Schink 2006 [127]; Hamersley et al. 2009 [110]). On the contrary, some cyanobacteria species fixate (into organic nitrogen) and hence remove N₂ from the water (Wetzel 2001 [6]; Hamersley et al. 2011 [109]; Higgins et al. 2018 [7]). Although these processes are of high ecological relevance, they act at a slow rate and dominate the N₂ budgets only in special cases when very long time periods are required for atmospheric renewal.

S.2 Oxygen

The second most abundant gas in the atmosphere is oxygen (O₂): Like nitrogen, oxygen forms 2-atom molecules. O₂ makes about 21% of the (dry) atmosphere: It is of highest relevance for nearly all organisms in the water: all higher organisms and many microorganisms need oxygen for respiration. Its presence indicates whether the environment is chemically oxidising or reducing. Almost all biogeochemical cycles involve reactions with oxygen (Wetzel 2001 [6]). Oxygen is only slightly better soluble than N₂ and the equilibrium concentration at 25°C results in 0.264 mmol/l.

Oxygen is produced via photosynthesis when primary production forms organic matter from carbon dioxide and water:



The decomposition, i.e. the oxidation, of organic matter is a redox process and is thereby coupled to the reduction of an electron accepting substance. This substance is organic carbon in fermentative disproportionation reactions and an external electron acceptor in respiration processes. Oxygen as the primary electron acceptor is the external

electron acceptor with the highest energy yield and is thereby used whenever it is available (Stumm and Morgan 1996 [129]). Aerobic decomposition is exemplarily shown at one sequence of a carbohydrate:



The reaction removes oxygen from the water column and produces carbon dioxide, which is soluble in high concentrations in water (see Henry coefficient Table 1).

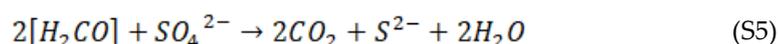
S.3 Argon

Argon (Ar) contributes 1% to the atmosphere. It is a noble gas and it is usually considered fully inert (in limnological time scales), and hence is perfectly suited as a tracer; concentration differences give indications of dilution and changing temperatures (Emerson et al. 1995 [102]; Brennwald et al. 2005 [71]; Bärenbold et al. 2020 [97]).

S.4 Carbon dioxide

Carbon dioxide (CO₂) constitutes only about 0.04 percent of the atmosphere. The solubility of CO₂ is much higher than most common environmental gases: in equilibrium, concentrations in water and adjacent air gas space have the same order of magnitude (Table 1). As a consequence, large volumes of CO₂ can be stored at a relatively low gas pressure (Sander 2015 [19]; Freeth et al. 1990 [15]). Other than most gases, CO₂ contributes positively to density and hence stabilizes a stratified water column, when it is formed at the lake bed (Boehrer and Schultze 2008 [56]; Dietz et al. 2012 [27], Moreira et al. 2016 [120]). CO₂ is the most intensively discussed greenhouse gas. Rivers, lakes and reservoirs release considerable amounts of CO₂ to the atmosphere (2.1 Pg yr⁻¹; Raymond et al. 2013 [124]).

CO₂ is a key compound for many biogeochemical cycles and processes. It connects the organic and the inorganic branches of the global biogeochemical cycle of carbon by being the inorganic raw material of autotrophic organisms for primary production, i.e. the synthesis of organic matter (see 2.3.2 eq. C3). In addition, CO₂ is also the final product of the complete decay of organic matter via respiration (eq. C4), fermentation and biologically mediated oxidation by nitrate (eq. C1) or sulfate (eq. S5) (Wetzel 2001 [6]; Schink 2006 [127]):



In addition, CO₂ is the major agent in chemical weathering of many kinds of rock, e.g. carbonates, such as limestone and dolomite, which are widely distributed and form an important contribution of the Earth crust (Press et al. 2003 [123]). Much CO₂ is produced in the soil and in aquifers and transported by groundwater. As a consequence, groundwater tends to show CO₂ oversaturation of typically 10-100 times towards the atmosphere (Macpherson 2009 [119]). Groundwater seepage hence introduces additional carbon dioxide into lakes. Guadiana pit lake received its high gas load from dissolved carbonates (Sánchez-España et al. 2014 [84]).

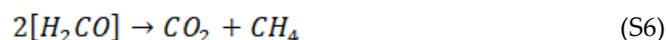
Subduction of organic matter containing sediments and carbonate rock results in production of CO₂ in the deeper underground (Kelemen and Manning 2015 [113]). This CO₂ is released back to the atmosphere in volcanic and tectonic activities in many regions of the globe (Kerrick 2001 [114]; Burton et al. 2013 [100]; Kämpf et al. 2013 [112], Bräuer et al. 2016 [99]; Hunt et al. 2017 [111]; Frondini et al. 2019 [106]). Maar lakes and caldera lakes receive gases from deeper parts of the Earth's crust and the mantle. CO₂ is the main component of the gas, e.g. Laacher See in Germany and Lac Pavin in France (Giggenbach et al. 1991 [107], Aeschbach-Hertig et al. 1996 [96], Aeschbach-Hertig et al. 1999a [59]). Continental rift zones and the margins of geologically young mountains are generally known as regions of elevated geogenic gas release, mainly CO₂ (Kämpf et al. 2013 [112]; Kelemen and Manning 2015 [113]; Bräuer et al. 2016 [99]; Hunt et al. 2017 [111]; Frondini

et al. 2019 [106]), e.g. Lake Sevan (Armenia; Avagyan et al. 2020 [61]) and Lake Kivu (Ross et al. 2015 [125]).

S.5 Methane

Methane (CH₄) can be found in traces in the atmosphere. It is the simplest hydrocarbon and it forms an important element of the organic branch of the global carbon cycle. It plays an important role in the greenhouse effect and is considered one of the most potent gases for global warming (Myhre et al. 2013 [3]; Turner et al. 2017 [4]). Limnic waters have been identified as a major source of methane for the atmosphere, though the role of limnic waters in the carbon cycle has not finally quantitatively been determined (Bastviken et al. 2011 [1]).

Methane is predominantly formed in anoxic compartments of lakes (sediment, oxygen depleted hypolimnion, monimolimnion; Wetzel 2001 [6]; Bastviken 2009 [62]). In the absence of electron acceptors, methanogenesis at the thermodynamic threshold can take place (Schink 1997 [126]; Madigan et al. 2015 [118]):



In lake sediments, organic material is available in practically unlimited amounts and no further oxidizing agent is needed (Bastviken 2009 [62]). Both CO₂ and CH₄ can dissolve in water. Methane however, is producing a much higher contribution to gas pressure due to its low solubility (low Henry coefficient, Table 1). Diffusive effects transport methane into the water column. Methane can be stored in the water over longer time periods, as long as no suitable oxidising agents, such as ferric iron (Fe³⁺), nitrate (NO₃⁻) or sulphate (SO₄²⁻) are present. When gas pressures allow, bubbles can be formed in the sediment (Bastviken 2009 [62]). Exposed to diffusion into the ambient water and stripping of gases from the water column, methane bubbles reach the surface and release the remaining gas mixture into the atmosphere (McGinnis et al. 2006 [11]; Bastviken et al. 2011 [1]).

Methane has also been detected in degassing regions of the lithosphere containing abiotically formed methane (Etiope and Lollar 2013 [104]). Natural leakage of geologic reservoirs of hydrocarbons (natural gas, oil, maturing coal) have been reported to be a wide spread origin of methane for groundwater (Etiope et al. 2019 [105]) and possibly also for lakes (sensu Etiope and Klusman 2010 [103]).

S.6 Comparison solubilities

Comparison of the simple exponential fits of solubilities of gases are checked against more sophisticated formulas supplied in the literature indicate an error for the solubilities in the range of 3% in the temperature range between 10 and 40°C. Towards 0°C deviations are even larger (up to 10%). The transition to a new temperature standard ITS-90 does not affect the coefficients noticeably.

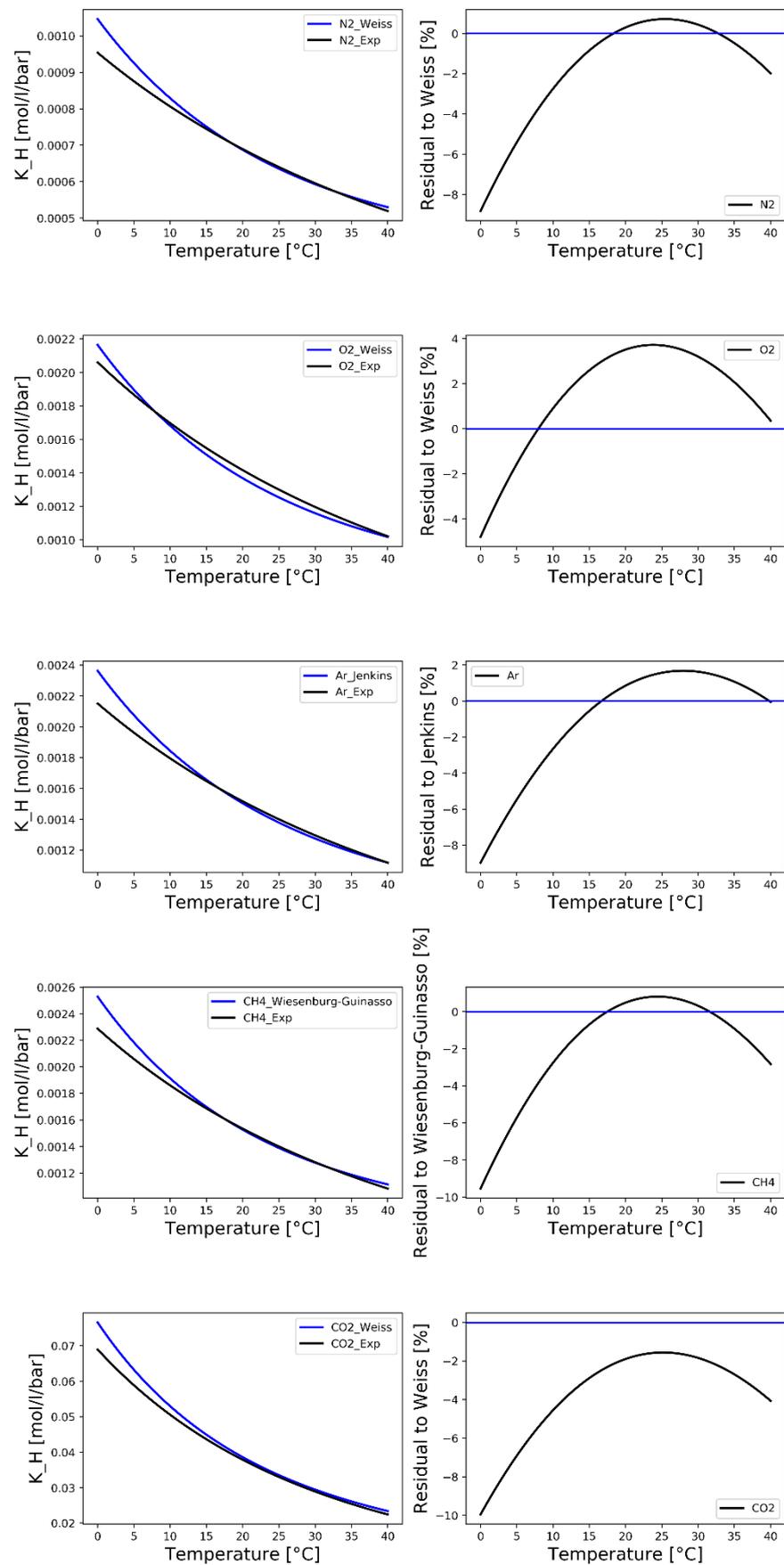


Figure S1. solubilities of the most relevant gases for gas pressure in lakes: left column: solubilities in mol/l/bar: simple exponential fits from Sander (2015) [19] in comparison to accurate parametrizations for N₂ and O₂ (Weiss 1970 [23]), Ar

(Jenkins et al. 2019 [24]), CH₄ (Wiesenburg and Guinasso 1979 [25]) and CO₂ (Weiss 1974 [26]). Right column: difference between approaches.

S.7 Water vapour

In addition to the dissolved gases, water itself develops a vapour pressure which contributes to total gas pressure. The maximum vapour pressure water can develop at some given temperature is called the saturation vapour pressure $E(T)$ and is governed by the Clausius-Clapeyron equation:

$$\frac{dE}{dT} = \frac{LE}{RT^2}, \quad (S7)$$

Where L is the latent heat of vaporization, R is the gas constant and T is in Kelvin (Koutsoyiannis, 2012 [115]). If L is approximated by a linear function of the form $L = m - nT$, integration of equation S7 produces:

$$E(\theta) = \frac{\exp\left(A - \frac{B}{\theta + 273.15}\right)}{(\theta + 237.15)^C}, \quad (S8)$$

Where θ is temperature in Celsius and $E(\theta)$ is in Pa (Huang, 2018 [35]). Since more regression coefficients bring more degrees of freedom and a more accurate fit, one can instead write:

$$E(\theta) = \frac{\exp\left(A - \frac{B}{\theta + D_1}\right)}{(\theta + D_2)^C}, \quad (S9)$$

and perform regression analysis on accurate data to obtain $A = 34.494$, $B = 4924.99$, $C = 1.57$, $D_1 = 237.1$ and $D_2 = 105$ (Huang, 2018 [35]). This equation determines $E(\theta)$ to high accuracy even for high temperatures exceeding 40°C where the improved Magnus formula (Alduchov & Eskridge, 1996 [33]) becomes increasingly inaccurate (~2%) (see Fig. S2)

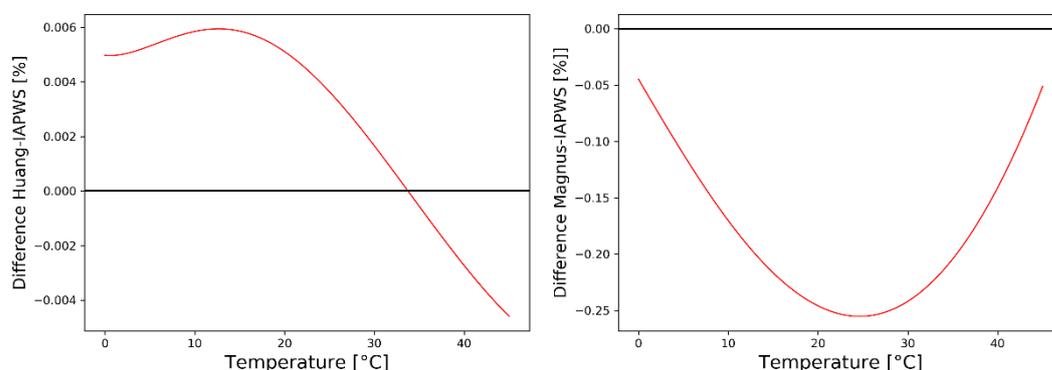


Figure S2. Vapour pressure against temperature. Left panel: Huang (2018) compared to the IAPWS recommended curve (Wagner and Pruss, 1993 [34]); right panel: Magnus equation compared to the recommendation of IAPWS (Wagner and Pruss, 1993 [34]).

S.8 Other gases

Active geological structures also transport gases H₂S, SO₂ and HCl. There may be cases where such reactive gases may play a relevant role even for gas pressure in highly

active volcanic lakes. We refer the interested reader to the special and competent literature (Christenson and Tassi 2015 [30]; Lee et al. 2018 [116]). Sulphate reduction (eq. S5) forms S^{2-} , which is transferred into HS^- and finally H_2S . The latter is highly toxic and greatly undesirable in the environment (Guidotti 1996 [108]; Lewis 2010 [117]), especially as it enters bubbles and hence is released into the atmosphere. Even small concentration result in an unpleasant smell. Sulphides can precipitate with a suitable (mostly double charged) cation, and hence is removed from the water phase and sequestered (Lewis 2010 [117]; Sobolewski 1996 [128]).

There is a large number of other gases detectable in lakes. They may be used for dating or tracing water, such as noble gases, chlorofluorocarbons (CFC) or sulfurhexafluorid SF_6 (Kipfer et al. 2002 [29]; von Rohden et al. 2009 [95], Aeschbach-Hertig et al. 1999b [59]; Chambers et al. 2019 [101]; Bärenbold et al. 2020 [97]). In addition, ecologically relevant gases, like H_2 and climate relevant gases, such as N_2O , can be quantified in water (e.g. Poissant et al. 2007 [122]; Baulch et al. 2011 [98]). Some of them are short lived and others are produced at such low rates that their concentrations do not amount enough to contribute to total gas pressure considerably. As a consequence, they could be neglected for our present purposes.

References

All the references cited here are in the maintext.