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## Carbon Dioxide Supersaturation in the Surface Waters of Lakes

Jonathan J. Cole, Nina F. Caraco, George W. Kling, Timothy K. Kratz

Data on the partial pressure of carbon dioxide ( $\text{CO}_2$ ) in the surface waters from a large number of lakes (1835) with a worldwide distribution show that only a small proportion of the 4665 samples analyzed (less than 10 percent) were within  $\pm 20$  percent of equilibrium with the atmosphere and that most samples (87 percent) were supersaturated. The mean partial pressure of  $\text{CO}_2$  averaged 1036 microatmospheres, about three times the value in the overlying atmosphere, indicating that lakes are sources rather than sinks of atmospheric  $\text{CO}_2$ . On a global scale, the potential efflux of  $\text{CO}_2$  from lakes (about  $0.14 \times 10^{15}$  grams of carbon per year) is about half as large as riverine transport of organic plus inorganic carbon to the ocean. Lakes are a small but potentially important conduit for carbon from terrestrial sources to the atmospheric sink.

Processes that add and remove  $\text{CO}_2$  occur simultaneously in the surface waters of lakes. Lakes can thus act either as sources or as sinks for  $\text{CO}_2$ . Earlier studies have shown that Arctic lakes are strongly supersaturated in  $\text{CO}_2$  and therefore are sources to the overlying atmosphere (1, 2). In the Arctic the transport of tundra organic matter to surface waters leads to  $\text{CO}_2$  supersaturation (1, 2). Other regions that lack the vast soil carbon storage of the Arctic may behave differently. In fact, detailed studies on a limited number of temperate and boreal lakes have suggested that these lakes are net sinks for atmospheric  $\text{CO}_2$  (3), but no comprehensive analysis exists. We report data from lakes with a worldwide distribution that show that boreal, temperate, and tropical lakes are typically supersaturated with  $\text{CO}_2$  and thus are net sources to the atmosphere.

Data were obtained both from the literature and from our own direct measurements of the partial pressure of  $\text{CO}_2$  ( $P_{\text{CO}_2}$ ). The value of  $P_{\text{CO}_2}$  was calculated from pH and dissolved inorganic carbon (DIC) or acid-neutralizing capacity (ANC) with corrections for other physical and chemical variables (4). For the direct measurement of  $P_{\text{CO}_2}$ , we collected water from 0.1 to 0.25 m below the surface into a thermally insulated

2-liter glass bottle and equilibrated it with 50 ml of ambient air (5). Gas chromatography was used to measure  $\text{CO}_2$  on the equilibrated head space. Simultaneously ambient air 1 m above the lake surface was collected for the measurement of atmospheric  $\text{CO}_2$ .

The lakes analyzed range in size from  $8.2 \times 10^6$  ha (Lake Superior) to 0.4 ha, span latitudes from  $60^\circ\text{S}$  to  $62^\circ\text{N}$ , and include both hard and soft waters (Table 1). For each data set there are differences in the type of measurements made, the intensity of those measurements over time, and geographic location (Table 1). For these reasons we discuss the data in terms of a series of individual data sets.

Of the 37 lakes (390 samples) where direct measurements of  $P_{\text{CO}_2}$  were made, 16 lakes (43%) were supersaturated at all samplings. Data for a persistently super-

saturated lake are shown in Fig. 1. The mean measured  $P_{\text{CO}_2}$  for the 37 lakes was  $801 \pm 67 \mu\text{atm}$  (mean  $\pm$  standard error), about 2.2 times the measured atmospheric value (Fig. 2A). Only 7% of the samples were within  $\pm 20\%$  of atmospheric equilibrium (Fig. 2A).

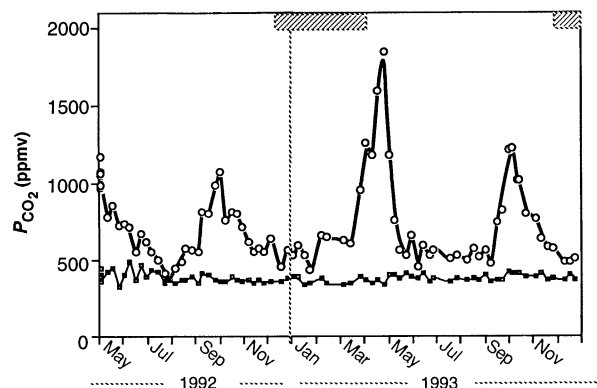
In the larger data sets for which  $P_{\text{CO}_2}$  was calculated, we also see a consistent tendency toward supersaturation. For the 1612 lakes sampled in autumn [eastern lakes survey (6) (Fig. 2B)], mean  $P_{\text{CO}_2}$  was  $1031 \pm 19.4 \mu\text{atm}$  or three times the atmospheric equilibrium value. Relatively few lakes (6.6%) were within  $\pm 20\%$  of the atmospheric equilibrium value.

Because of thermal mixing, autumn may be a time of elevated  $P_{\text{CO}_2}$  in surface waters. Nevertheless, a similar pattern of supersaturation was seen for 69 lakes from all over the world with full seasonal data for the entire ice-free season (Fig. 2C). For lakes with ANC-based data, calculated mean  $P_{\text{CO}_2}$  averaged  $1122 \mu\text{atm}$ ; for lakes with DIC-based data, calculated mean  $P_{\text{CO}_2}$  was  $1039 \mu\text{atm}$ . Both of these values are well above atmospheric equilibrium (7) and similar to that from the lakes sampled only in autumn (Fig. 2B). For 34 of these 69 lakes, 100% of the samples were supersaturated, and for every lake the time-weighted average was above the atmospheric value.

The 60 lakes (179 samples) sampled only during summer stratification, a time of lower-than-average  $P_{\text{CO}_2}$ , were also supersaturated. The distribution is broader and the mean lower ( $680 \pm 65 \mu\text{atm}$ ) than for the other data sets (Fig. 2D). For these samples also, only 12.8% were within  $\pm 20\%$  of the atmospheric equilibrium value.

Tropical African lakes were strongly supersaturated with the mean  $P_{\text{CO}_2}$  being about six times ( $2296 \pm 409 \mu\text{atm}$ ) the atmospheric value; few samples (11%) were within  $\pm 20\%$  of atmospheric equilibrium (Fig. 2E).

For the lakes for which we both directly measured and calculated  $P_{\text{CO}_2}$ , we found relatively good agreement between measured and calculated values (8), but such agreement



**Fig. 1.** Seasonal cycle of direct measurements of the  $P_{\text{CO}_2}$  in the surface water of Mirror Lake (circles) and in the overlying air (squares), showing persistent supersaturation. Mirror Lake is a soft water lake in New Hampshire (15); ppmv, parts per million by volume. The hatched areas represent ice cover.

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may not be universal. Electrode-based measurements of pH in lakes with high concentrations of dissolved organic carbon may be biased low by about 0.2 pH unit, which would lead to overestimates of  $P_{CO_2}$  (9). Recalculating our data with the assumption that the reported pH was in error by 0.2 pH unit lowers the mean  $P_{CO_2}$  to 797  $\mu\text{atm}$  but still leads to the conclusion that lakes are generally supersaturated in  $CO_2$ .

Whether  $P_{CO_2}$  in the surface waters of lakes is measured directly or calculated from other chemical measurements, most of the lakes that we surveyed were out of equilibrium with the atmosphere and were supersaturated. Only 7% of the samples in the combined data set were within  $\pm 20\%$  of equilibrium with the atmosphere, and 87% were supersaturated. Our analysis suggests that the surface water of lakes is rarely at equilibrium with the atmosphere. Furthermore, lakes showed an enormous range of  $CO_2$  concentrations, from 175-fold below to 57-fold above atmospheric equilibrium at the extremes and 3.1-fold below to 16-fold above equilibrium for the means of the upper and lower 10% of the samples.

Lakes from boreal, temperate, and tropical regions appear to be similar to those of the Arctic in overall  $CO_2$  supersaturation. The mean  $P_{CO_2}$  from the surface waters of Arctic lakes averaged  $1162 \pm 132 \mu\text{atm}$  (1, 4), which compares closely to the mean  $P_{CO_2}$  of 1036  $\mu\text{atm}$  for lakes from other regions. The Arctic lakes also show a small percentage (8%) of samples within  $\pm 20\%$  of atmospheric equilibrium and a large range in  $P_{CO_2}$  [93 to 2758  $\mu\text{atm}$  (1, 4)]. Analyzing our data set by broad regions, we see supersaturation of comparable magnitude within each region. Lakes from boreal (non-Arctic) Sweden, for example, have a mean  $P_{CO_2}$  of  $1469 \pm 38 \mu\text{atm}$ ; South

American lakes,  $1520 \pm 101 \mu\text{atm}$ ; non-Arctic lakes from North America,  $1087 \pm 23 \mu\text{atm}$ ; and lakes from somewhat higher, tropical Africa,  $2296 \pm 409 \mu\text{atm}$ .

In the specific case of Arctic tundra lakes, the large accumulation of organic matter in the tundra and its respiration in soil or lake water is a probable explanation for the excess  $CO_2$  (1, 4). Our data suggest that the phenomenon of excess  $CO_2$  in lake water is quite general and occurs in other regions without these accumulations. Lakes must either import excess  $CO_2$  (derived from plant-root or soil respiration) in inflowing ground or surface waters or produce internally more  $CO_2$  than they consume (that is, ecosystem respiration exceeds ecosystem primary production). If excess respiration within the lake is the cause, the organic matter that supports this process must come either from previously deposited

lake sediments or from new inputs from the catchment. Either model would be at odds with published carbon budgets for some lakes (10), but both agree with some recent

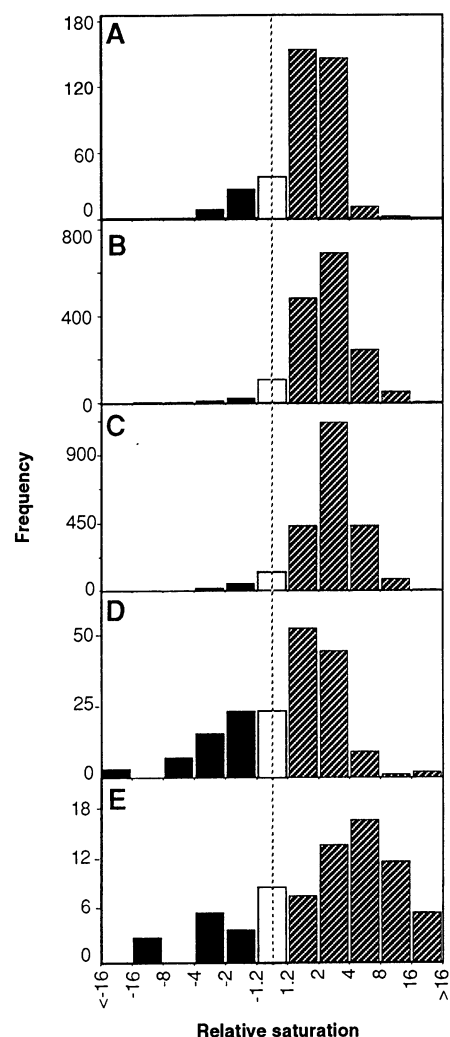
**Fig. 2.** Frequency diagram (by numbers of samples) for calculated  $P_{CO_2}$  in the surface waters of lakes from five different, nonoverlapping data sets: (A) direct measurements, (B) autumn survey, (C) full seasonal data, (D) summer survey, and (E) tropical Africa. Only values from the ice-free season are shown. Relative saturation (RS) is the degree of supersaturation (hatched bars) or undersaturation (solid bars) relative to atmospheric equilibrium. For supersaturation,

$$RS = P_{CO_2}(\text{water})/P_{CO_2}(\text{air})$$

For undersaturation,

$$RS = -P_{CO_2}(\text{air})/P_{CO_2}(\text{water})$$

On this scale, water with twice the  $P_{CO_2}$  of the atmosphere has a value of 2; water with half the value of the atmosphere has a value of -2. The vertical dotted line represents equilibrium with the atmosphere ( $RS = 1.0$ ), and the open bars represent the samples in near equilibrium with the atmosphere ( $\pm 20\%$  of equilibrium). See Table 1 for characteristics of the data sets.



**Table 1.** Some characteristics of lakes in each data set. Only data from the ice-free period are included. The five data sets are nonoverlapping and are kept distinct because of the different information available in each. Letters refer to the panels in Fig. 2.

Parameter	Data set				
	A	B	C	D	E
	Direct $P_{CO_2}$ measurements	Lakes in autumn	Full seasonal cycles	Lakes in summer	African lakes
Lakes (n)	37	1612	69	60	59
Samples (n)	390	1612	2395	179	79
Latitude (range)	44°25'N–41°21'N	47°13'N–27°14'N	62°00'N–60°43'S	44°5'N–28°00'N	7°26'S–23°17'S
Area (ha) (range)	$1.5 \times 10^6$ – $5.8 \times 10^6$	1–89,358	$0.5 \times 10^6$ – $8.2 \times 10^6$	0.4–3,075	1–59,900
pH (range)	4.7–9.5	3.8–9.4	4.2–9.8	4.9–9.3	6.0–9.9
DIC ( $\mu\text{M}$ ) (range)	4.9–2,500	13.3–4,077	6.6–4,800	11–3,578	43–145,790
$P_{CO_2}$ ( $\mu\text{atm}$ ) (mean)	801	1031	1064	680	2296
$P_{CO_2}$ ( $\mu\text{atm}$ ) (range)	107–4,128	20–9,789	1–7,845	5–7,991	32–20,249
Basis of $P_{CO_2}$ estimate	Direct measurement	pH, DIC	pH, DIC pH, ANC	pH, DIC	pH, ANC
Sampling intensity	Weekly to quarterly	Each once in autumn	Varied but more than 10 samples per year	Summer period only; each lake two to three times	One to three times
Source	This study	(5)	(17)	(16)	(18)

reassessments of the balance between pelagic production and respiration in lakes (11). Our data suggest that the transport of carbon from land to water is an important control on the carbon budget in most lakes.

We can use the frequency distribution of  $P_{CO_2}$  to estimate the potential contribution of  $CO_2$  from lakes to the atmosphere. We assume an evasion coefficient of  $0.5 \text{ m day}^{-1}$  for all lakes, and for undersaturated lakes an enhancement factor of 3 (12). Globally, lakes (an area of  $2 \times 10^{12} \text{ m}^2$ ) could contribute  $CO_2$  to the atmosphere in the amount of  $0.14 \times 10^{15} \text{ g}$  of carbon per year. This flux is slightly less than half as great as the total export of organic plus inorganic carbon from rivers to the sea (13), is larger than recent estimates of total organic carbon burial in lake sediments [ $0.06 \times 10^{15} \text{ g}$  (14)], and is comparable to organic carbon burial in reservoirs [ $0.2 \times 10^{15} \text{ g}$  (14)]. Lakes have longer hydrologic residence times than do flowing waters, which may allow for both the degassing of  $CO_2$  derived from soil respiration and possibly for increased respiration of organic materials derived from the catchment.

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- During the calculation of  $P_{CO_2}$  from pH and ANC, overestimation of true  $P_{CO_2}$  may be caused by the presence of noncarbonate ANC. This effect is strongest at low values of ANC; we excluded from

our ANC-based calculations samples with ANC below  $40 \mu\text{eq}$  to minimize this effect.

- We found a strong, unbiased relation between  $P_{CO_2}$  directly measured versus  $P_{CO_2}$  calculated from pH and DIC. A linear regression of measured versus calculated  $P_{CO_2}$  ( $N = 330$  samples) has an  $r^2$  of 0.88 and a slope of  $1.03 \pm 0.01$ .
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- Evasion of  $CO_2$  from supersaturated water was calculated as:

$$\text{Flux} = D/z[(CO_2)_{aq} - K_h(P_{CO_2})_{air}]$$

where  $K_h$  is Henry's constant,  $D$  is the temperature-dependent diffusion coefficient, and  $z$  is the surface boundary layer. An evasion coefficient ( $D/z$ ) of  $0.5 \text{ m day}^{-1}$  would be equivalent to  $z = 300 \mu\text{m}$  at  $22^\circ\text{C}$  (or  $z = 200 \mu\text{m}$  at  $10^\circ\text{C}$ ) and is well within published values for lakes. In undersaturated water, atmospheric  $CO_2$  may react chemically with hydroxyl or carbonate ions more rapidly than it would diffuse passively [S. Emerson, *Limnol. Oceanogr.* **20**, 743 (1975)]. We used an enhancement factor of 3 to compute flux into undersaturated waters.

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## Fossil Evidence for Early Hominid Tool Use

Randall L. Susman

Although several Plio-Pleistocene hominids are found in association with stone and bone tools, it has been generally assumed that at any one time the hominid with the largest brain was the toolmaker. Fossils recovered over the last decade suggest that early hominids subsequent to 2.5 million years ago all might have used tools and occupied "cultural" niches. A test for humanlike precision grasping (the enhanced ability to manipulate tools) is proposed and applied to australopithecines and early *Homo*. The results indicate that tools were likely to have been used by all early hominids at around 2.0 million years ago. The earliest australopithecines, which predate the appearance of stone tools in the archaeological record, do not show signs of advanced precision grasping.

Approximately 2 million years ago (Ma) Africa was home to at least two, and probably more, hominid species (1). At least one, but perhaps all, early hominids at this time used implements of bone and stone, but the question of which Plio-Pleistocene hominids engaged in tool behavior (2) has been unresolved since the early 1960s (3–5). Oldowan tools are found throughout Africa beginning around 2.5 to 2.7 Ma. In 1960, the discovery of a partial hand of *Homo habilis* (Olduvai Hominid 7) from Bed I, Olduvai Gorge, prompted the inference that early *Homo* was a toolmaker (6) on the basis of anatomical features shared with modern humans. No diagnostic hand fossils of other fossil hominids from East or South Africa were then known. As a result, and because *H. habilis* had a large brain (7)

and more advanced, humanlike teeth (8) and feet (9), *H. habilis* was considered to be the principal toolmaker in Bed I times, roughly 2 Ma (10).

The idea that *H. habilis*, and not the australopithecines, was the exclusive toolmaker of the Plio-Pleistocene (11) was based on the assumption that the first stone toolmakers had relatively large brains (5–7). This idea has persisted up to the present (12). In this report, I test the assumption that brain size is somehow linked to tool behavior and that only one hominid could be a toolmaker at any one point in time, by an analysis of the functional morphology of ape and human hands and relevant hominid fossils. A major problem in determining which hominids made tools stems from a poor knowledge of which traits in the bones of living animals might be diagnostic of tool behavior. After a discussion of morphological correlates of precision grasping in hu-

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