

Weiss et al, 2018, <https://doi.org/10.1016/j.cub.2017.12.022>

ENV-200

Chemistry of natural waters II: Effect of CO_2 increase on lakes

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Processes affecting CO₂ budget of a lake

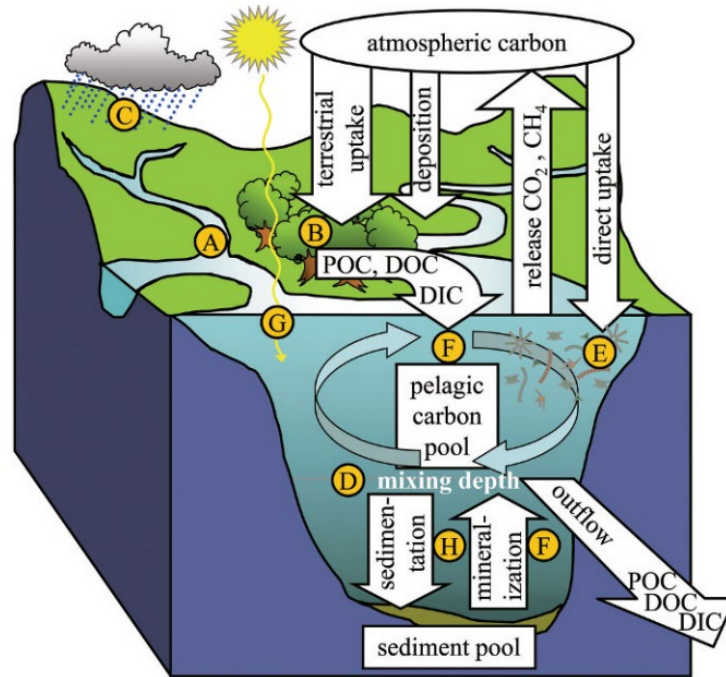


Fig. 2. Schematic diagram showing pathways of carbon cycling mediated by lakes and other continental waters. The letters correspond to rows in Table 1.

Source: Tranvik et al., *Limnol. Oceanogr.*, 2009

Processes affecting CO₂ budget of a lake

CO₂ sources:

- Atmospheric input
- Respiration: $(\text{CH}_2\text{O})_n + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$
- Abiotic oxidation of (imported) organic matter, e.g., $\text{MnO}_2 + (\text{CH}_2\text{O})_n + \text{H}^+ \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{Mn}^{2+}$
- Input from groundwater or rivers

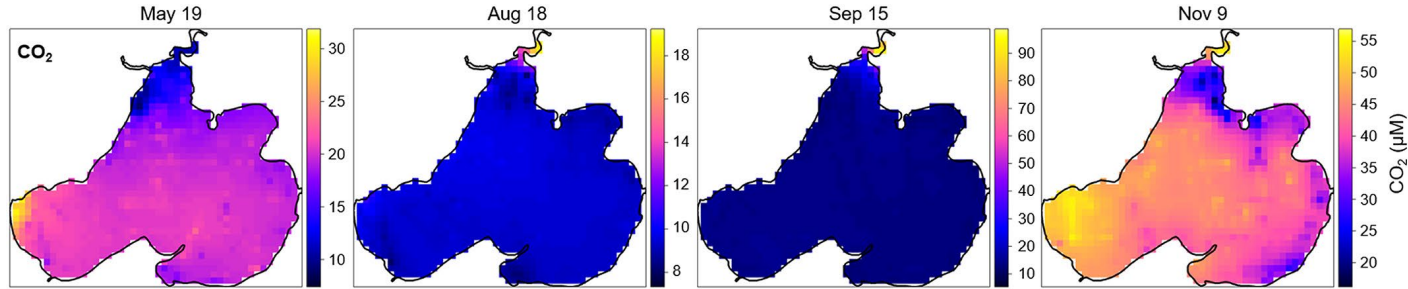
CO₂ sinks:

- Evaporation into atmosphere
- Photosynthesis: $\text{CO}_2 + \text{H}_2\text{O} \rightarrow (\text{CH}_2\text{O})_n + \text{O}_2$
- Mineral weathering, e.g.: $\text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{Ca}^{2+} + \text{HCO}_3^-$
- Export to downstream ecosystems

Human influences affect CO₂ budget in various ways:

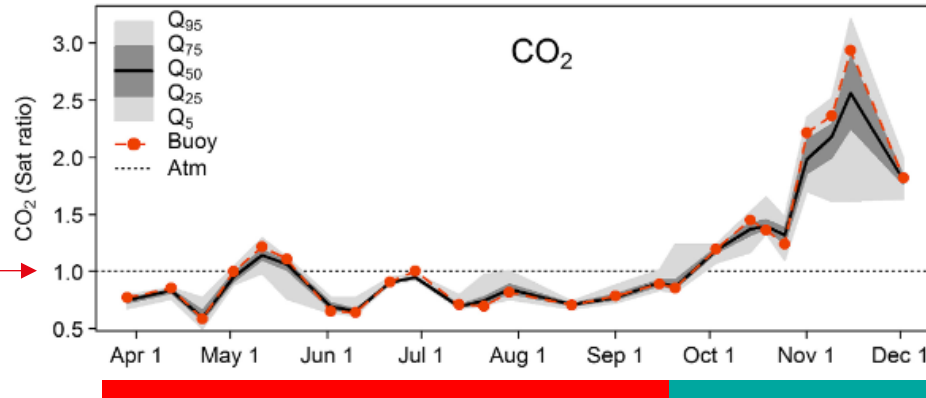
- Nutrient input by agriculture or wastewater → eutrophication → increased algal growth / decomposition
- Climate change → higher temperature → lower CO₂ solubility in water column, enhanced microbial activity and respiration rates.
- Land use changes → deforestation and urban development alter the inflow of organic matter and nutrients

Lake CO₂ levels and saturation vary by season



Source: Loken et al, 2019: <https://doi.org/10.1029/2019JG005186>

Equilibrium w
atmospheric CO₂ →



photosynthesis > respiration
(lake is undersaturated, a CO₂ sink)

respiration > photosynthesis
(lake is oversaturated, a CO₂ source)

Lake Geneva is a net CO₂ emitter (ca. 12 Gg C per year). Why?

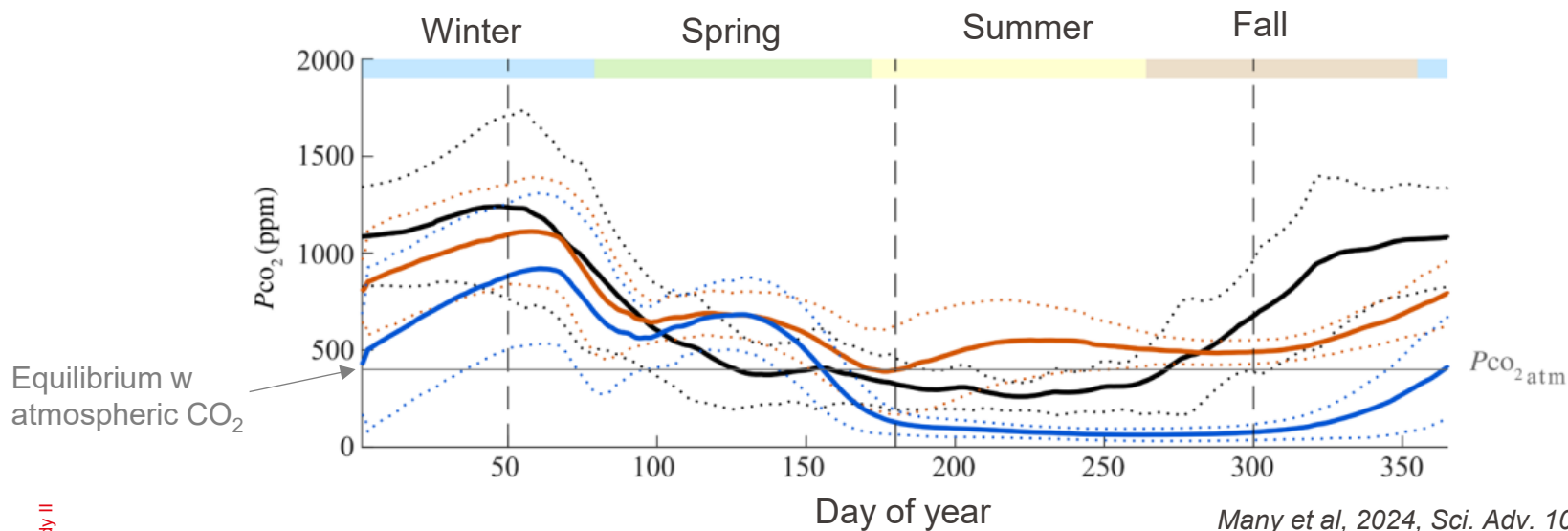
Only little input of organic matter from the shore, so respiration of imported organic material is not a relevant CO₂ source.

Alternative, newly discovered, chemical explanation:

- Input of calcium and carbonate by erosion of the rock on the upper shore of the lake (dissolution of CaCO₃ by rain water).
- In summer, the combination of photosynthesis (pH increase) and heat promote supersaturation of Ca²⁺
- Calcite microparticles precipitate, releasing CO₂: $\text{Ca}^{2+} + 2 \text{HCO}_3^- \leftrightarrow \text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O}$
- The release of CO₂ compensates a large fraction of the CO₂ incorporated by photosynthetic algae, minimizing CO₂ undersaturation during summer

For more info, see *Many et al, 2024, Sci. Adv. 10, eado5924*

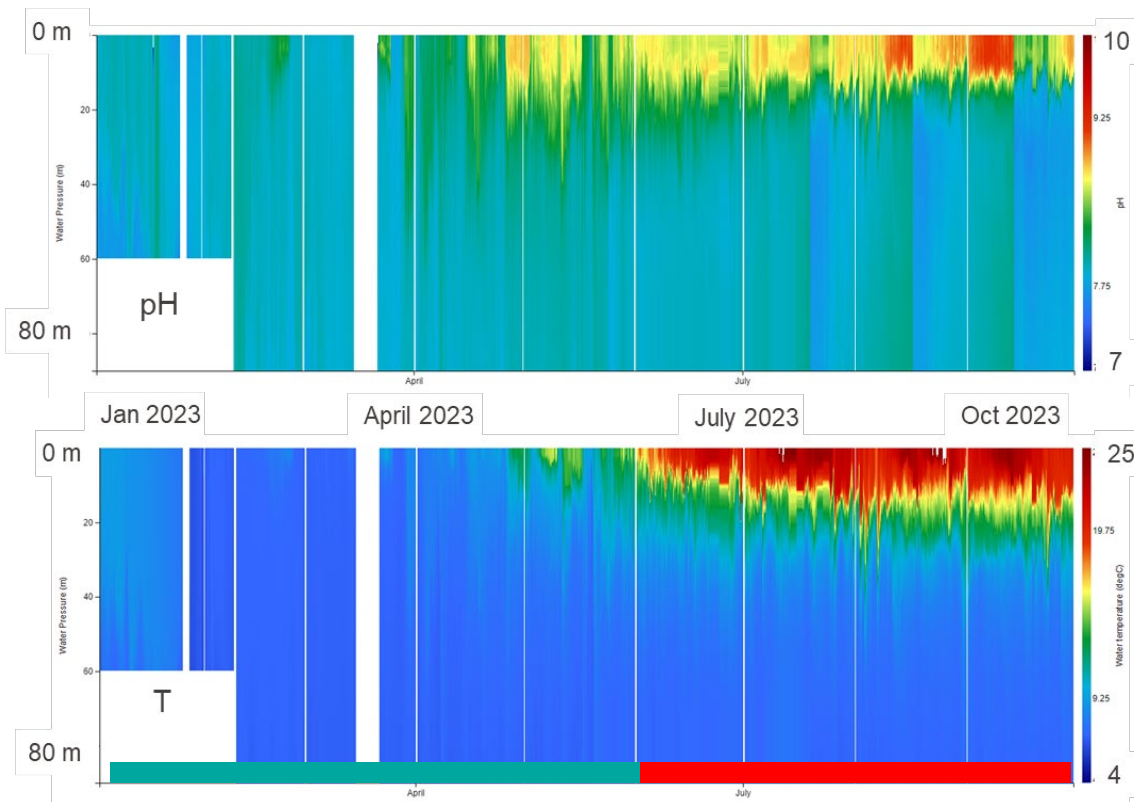
Data are averaged from 0 to 10m depth



Black line: measured pCO₂

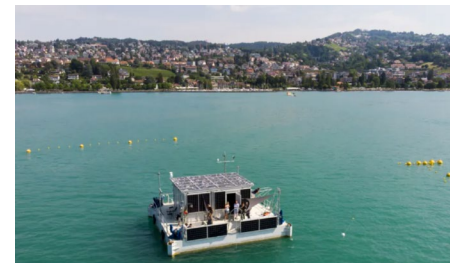
Red line: modelled pCO₂ considering calcite precipitation

Blue line: modelled pCO₂ without calcite precipitation



Data source:

<https://www.datalakes-eawag.ch/>



*LÉXPLORE experimental platform
near Pully*

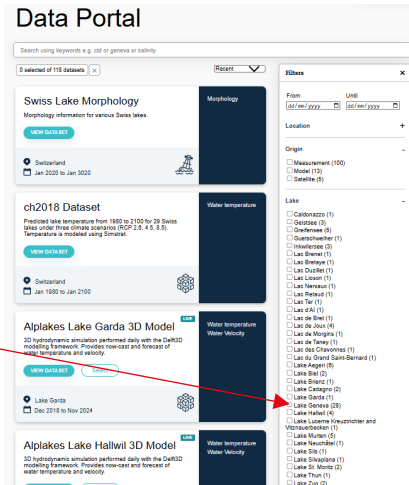
Source: [swissinfo.ch](https://www.swissinfo.ch)

Cold water, respiration > photosynthesis →
large CO₂ oversaturation, CO₂ emission

Warm water, CO₂ consumption by photosynthesis → pH
increase, calcite precipitation → CO₂ release
→ only slight CO₂ undersaturation

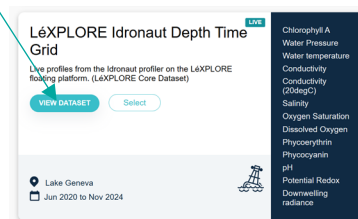
Find the T profile for Lake Geneva in 2024 on www.datalakes-eawag.ch

- 1 Open datalakes → data portal
- 2 Under “Lake” select Lake Geneva
- 3 Find “Lexplore Idronaut depth time grid” and click on “view dataset”
- 4 Select “water pressure” on the y-axis (reflects depth)
- 5 Select “water temperature” on the z axis
- 6 Under “Time Range”, select the year 2024
- 7 Under “Display options” you can re-scale the axes

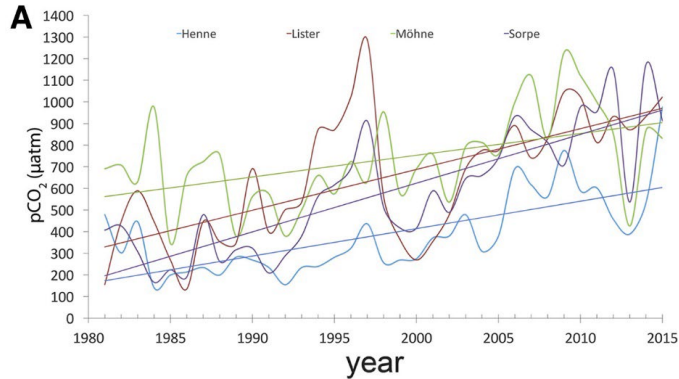


Discuss with your neighbor:

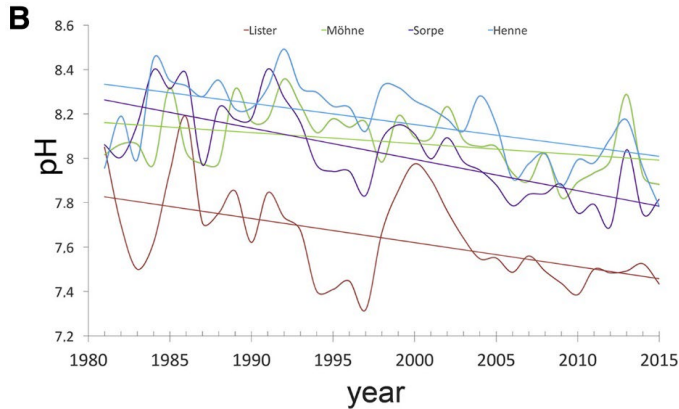
- how does the temperature profile of 2024 compare to that of 2023?
- Do you think the lake emitted more or less CO₂ in 2024 than in 2023?
- When atmospheric pCO₂ increases, will lakes still acidify, even though they are often emitters of CO₂ rather than sinks?



Observation: pH and CO₂ in 4 German lakes over 35 years



Average increase of $p\text{CO}_2$ by 561.21 μatm during the 35 year monitoring period. (Note: this is the dissolved CO₂ concentration, in an unusual unit).



Average decrease in pH from 8.13 to 7.82 over the 35 year monitoring period

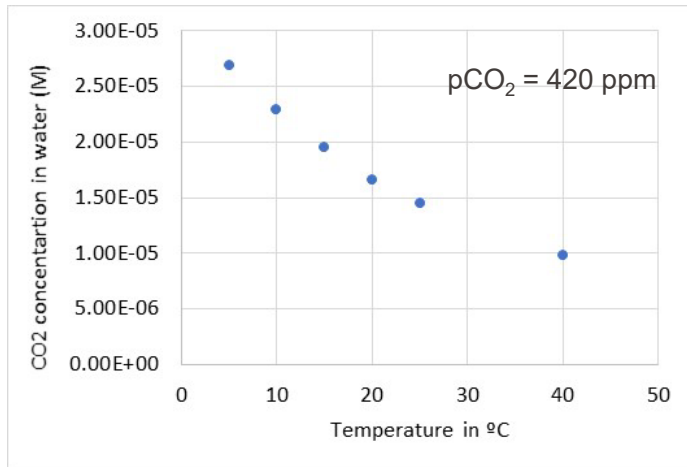
Source: Weiss et al, 2018, <https://doi.org/10.1016/j.cub.2017.12.022>

EPFL Possible causes for decrease in pH and increase in dissolved CO₂

1. Increase in water temperature?

Recall: $p_{\text{CO}_2} / [\text{H}_2\text{CO}_3^*(\text{aq})] = K_{\text{H}} \quad (\text{atm/M}) \quad \log[\text{H}_2\text{CO}_3^*] = \log[p_{\text{CO}_2}] + pK_{\text{H}}$

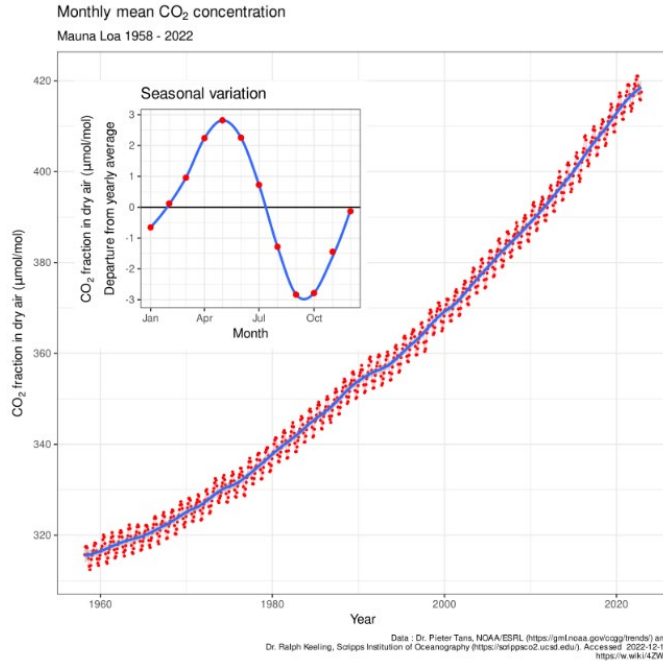
	pK _H					
	5 °C	10 °C	15 °C	20 °C	25 °C	40 °C
CO ₂ (g) + H ₂ O ↔ H ₂ CO ₃ *	-1.20	-1.27	-1.34	-1.41	-1.47	-1.64



No! Increasing water temperature leads to less dissolved CO₂

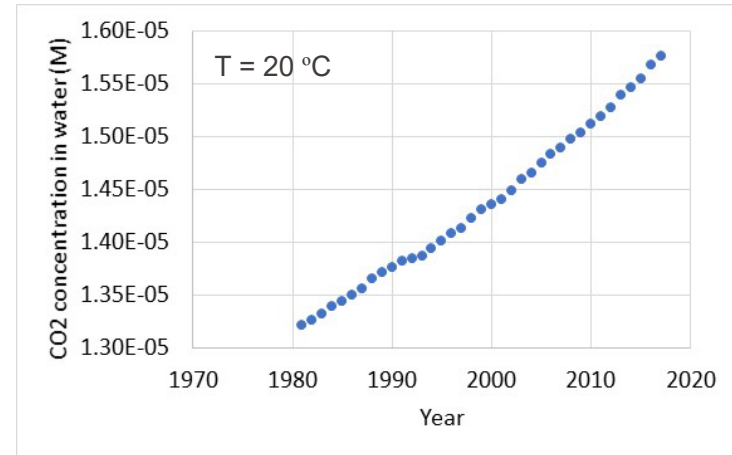
Possible causes for decrease in pH and increase in dissolved CO₂

2. Increase in atmospheric pCO₂ due to fossil fuel burning?



Source: Wikipedia

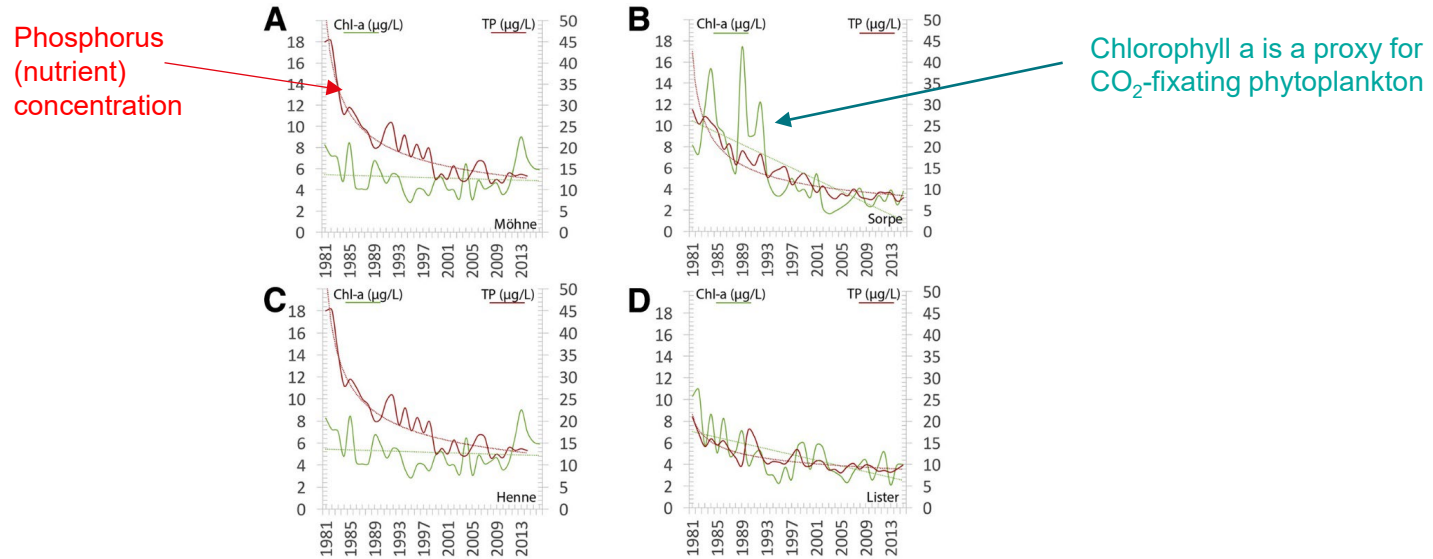
$$\log[\text{H}_2\text{CO}_3^*] = \log[\text{p}_{\text{CO}_2}] + \text{p}K_{\text{H}}$$



Correct trend in dissolved CO₂

EPFL Possible causes for decrease in pH and increase in dissolved CO₂

3. Decrease in nutrient input leading to less CO₂ fixation?

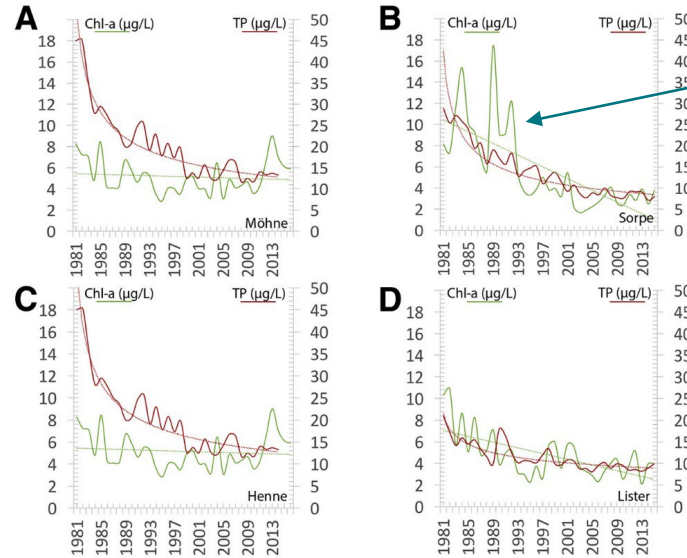


Source: Weiss et al, 2018, <https://doi.org/10.1016/j.cub.2017.12.022>

No! Nutrients were reduced in all lakes but CO₂ fixation only went down in two.

EPFL Possible causes for decrease in pH and increase in dissolved CO₂

4. Decrease in the abundance of CO₂-fixing phytoplankton?



Chlorophyll a is a proxy for CO₂-fixing phytoplankton

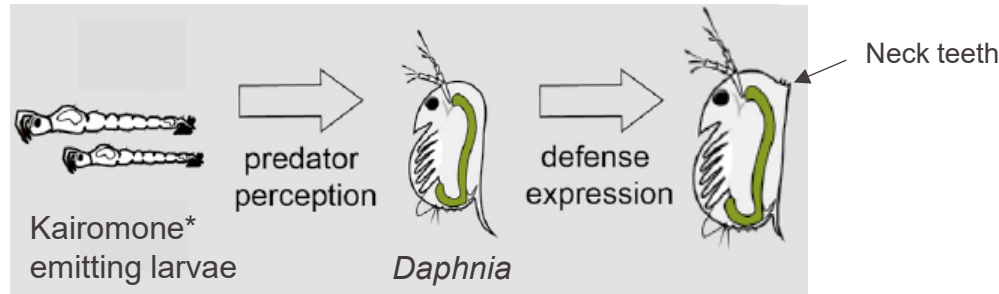
Source: Weiss et al, 2018, <https://doi.org/10.1016/j.cub.2017.12.022>

No! Chl-a only decreases in two lakes (and only over first 20 years), but CO₂ increases in all four lakes and for entire monitoring period.

Ecological effects on *Daphnia*

Daphnia is a water flea that is often used as a model organism in ecotoxicological studies. They serve as prey for fish and invertebrates. They are ca. 1 mm in size and present in many water bodies and are highly sensitive to xenobiotics.

Daphnia has different defense mechanisms. When predators (e.g., kairomone-emitting larvae) excrete chemical signals (kairomones), they are sensed by *Daphnia* and elicit a defense response (development of neck teeth and increase in body size).



Adapted from: Weiss et al, 2018, <https://doi.org/10.1016/j.cub.2017.12.022>

*Kairomones = signaling chemicals that transfer information between organisms

Ecological effects on *Daphnia*

Test 1: effect of pCO₂ on neck teeth and body size, **with** and **without** a predator.

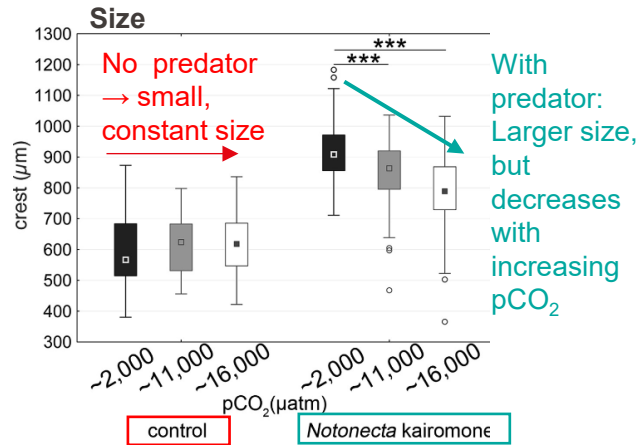
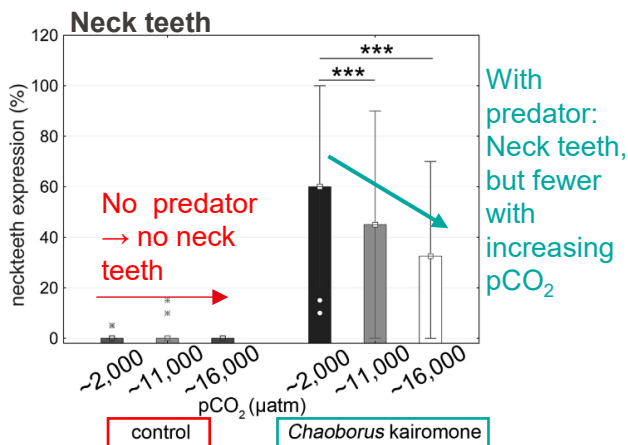
Approach: increase pCO₂, measure if and how neck teeth and size (crest) change.

pCO₂/pH conditions tested:

2000 µatm CO₂/pH 7.5

11'000 µatm CO₂/pH 6.9

16'000 µatm CO₂/pH 6.7



Conclusion1 : CO₂ affects the ability of *Daphnia* to sense a predator.

The higher the pCO₂, the weaker the defense mechanism when a predator is present.

Ecological effects on *Daphnia*

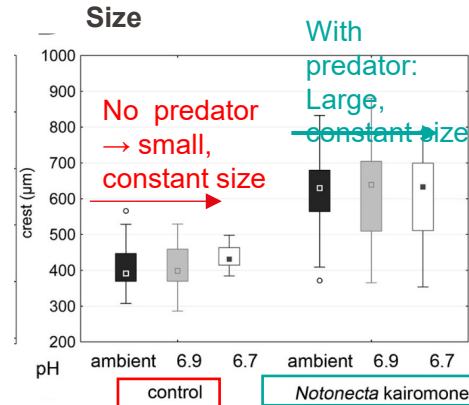
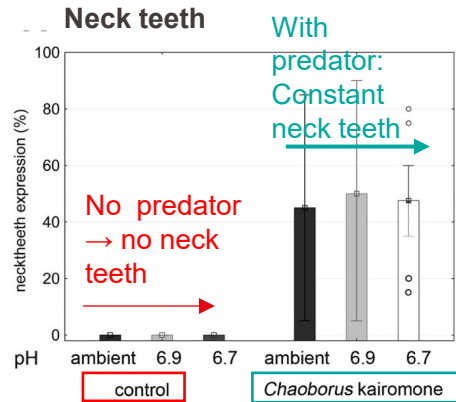
Test 2: is it the change in $p\text{CO}_2$ or the associated change in pH that reduces defense?

Approach: vary pH, but not $p\text{CO}_2$ (by adding hydrochloric acid)

~ 2000 $\mu\text{amt CO}_2$ /pH 7.5

~ 2000 $\mu\text{amt CO}_2$ /pH 6.9

~ 2000 $\mu\text{amt CO}_2$ /pH 6.7



Conclusion 2: The defense mechanism is not affected by pH.
The reduction in defense mechanism must be due to the increase in $p\text{CO}_2$ itself.

- Lakes have a complex CO₂ budget, which is affected by increasing CO₂ levels, but also other mechanisms (both natural and human-made)
- Even though lakes are often supersaturated in CO₂, they are acidifying as a result of increasing CO₂ levels.
- The lake pH is dropping, so far by about 0.3 units over 35 years (though large differences in lakes can be expected!)
- The increase in CO₂ has ecological effects, which are not necessarily related to pH, but also to CO₂ itself.
- The effects of climate change on lake biogeochemistry and ecology are highly complex and are not well understood. This is an interesting and highly interdisciplinary field of study for future environmental scientists and engineers.