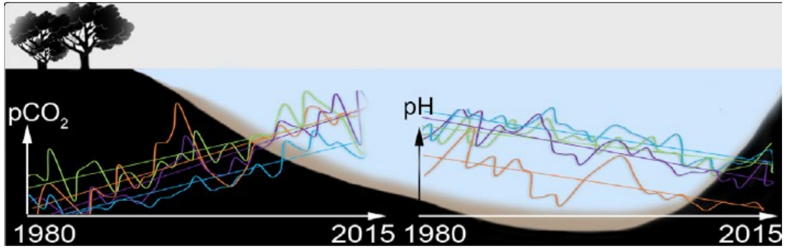

Weiss et al, 2018, https://doi.org/10.1016/j.cub.2017.12.022

ENV-200
Chemistry of natural waters I : Effect of CO_2 increase on lakes

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Processes affecting CO_2 budget of a lake

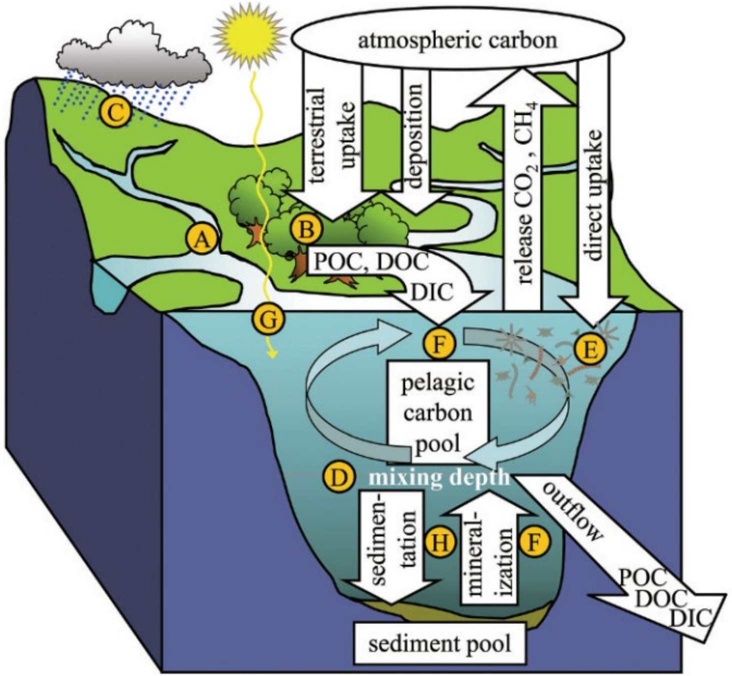


Fig. 2. Schematic diagram showing pathways of carbon cycling mediated by lakes and other continental waters. The letters correspond to rows in Table 1.

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

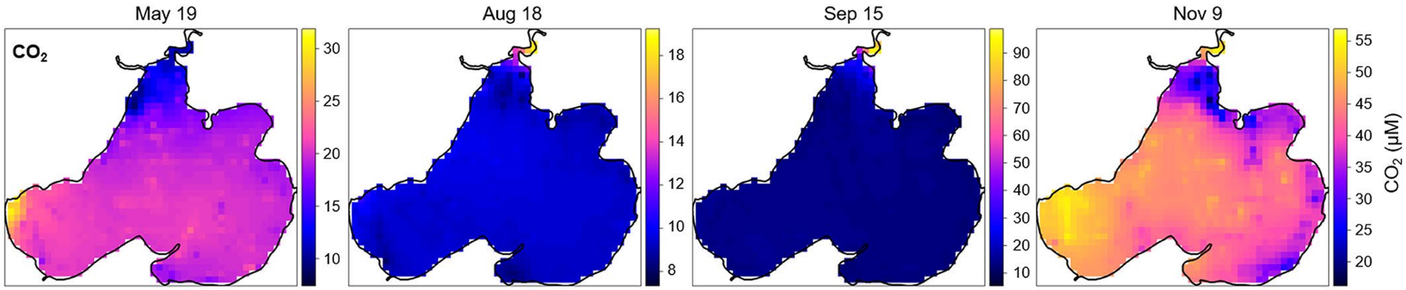
Processes affecting CO_2 budget of a lake

CO_2 sources:
- Atmospheric input
- Respiration: $(CH_2O)_n + O_2 \rightarrow CO_2 + H_2O$
- Abiotic oxidation of (imported) organic matter, e.g., $MnO_2 + (CH_2O)_n + H^+ \rightarrow CO_2 + H_2O + Mn^{2+}$
- Input from groundwater or rivers

CO_2 sinks:
- Evaporation into atmosphere
- Photosynthesis: $CO_2 + H_2O \rightarrow (CH_2O)_n + O_2$
- Mineral weathering, e.g.: $CaCO_3 + CO_2 + H_2O \rightarrow Ca^{2+} + 2\ HCO_3^-$
- Export to downstream ecosystsems

Human influences affect CO_2 budget in various ways:
- Nutrient input by agriculture or wastewater → eutrophication → increased algal growth / decomposition
- Climate change → higher temperature → lower CO_2 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

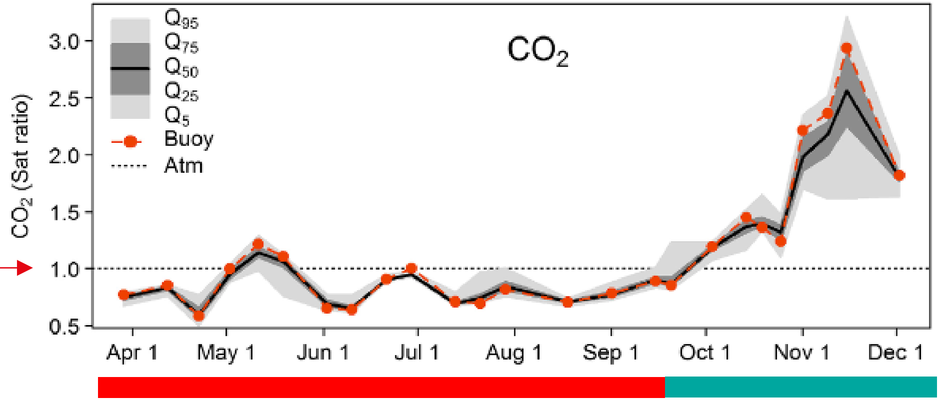
Lake CO_2 levels and saturation vary by season



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

Lake Mendota (USA)

Equilibrium w atmospheric CO_2



photosynthesis > respiration
(lake is undersaturated, a CO_2 sink)

respiration > photosynthesis
(lake is oversaturated, a CO_2 source)

CO_2 budget of Lake Geneva

Lake Geneva is a net CO_2 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 CO_2 source.

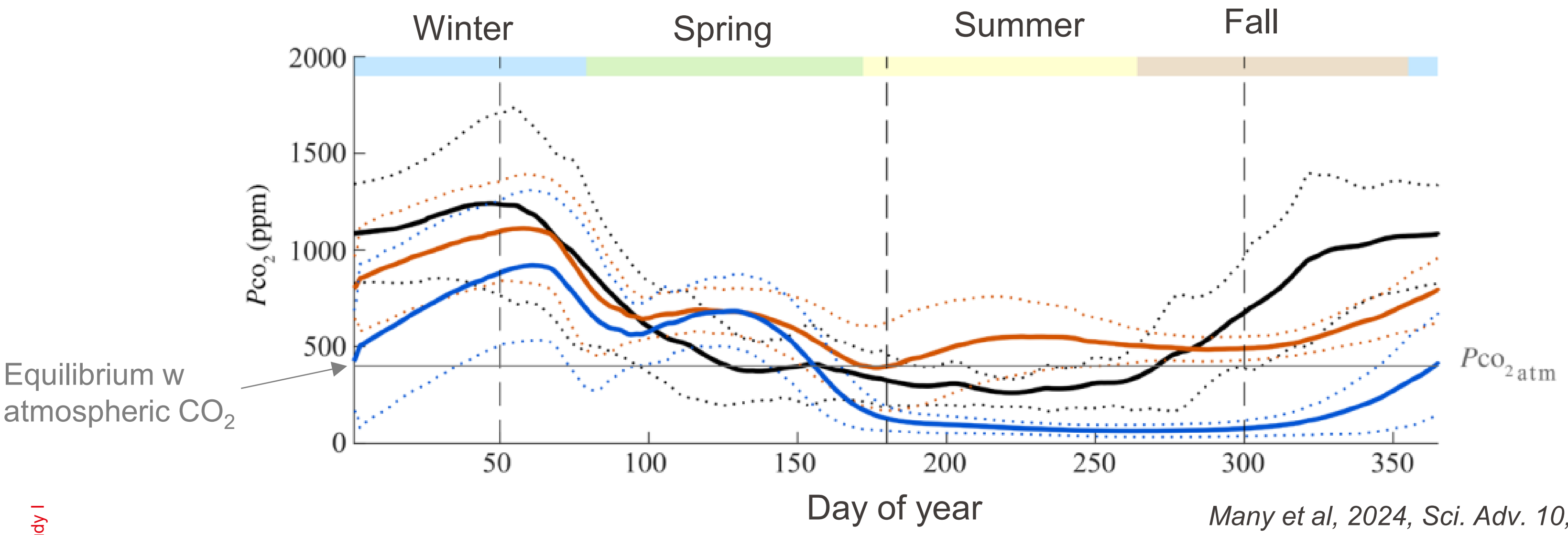
Alternative, newly discovered, chemical explanation:

- Input of calcium and carbonate by erosion of the rock on the upper shore of the lake (dissolution of $CaCO_3$ by rain water).
- In summer, the combination of photosynthesis (pH increase) and heat promote supersaturation of Ca^{2+}
- Calcite microparticles precipitate, releasing CO_2 : $Ca^{2+} + 2\ HCO_3^- \leftrightarrow CaCO_3 + CO_2 + H_2O$
- The release of CO_2 compensates a large fraction of the CO_2 incorporated by phtosynthetic algae, minimizing CO_2 undersaturation during summer

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

pCO_2 in Lake Geneva

Data are averaged from 0 to 10m depth



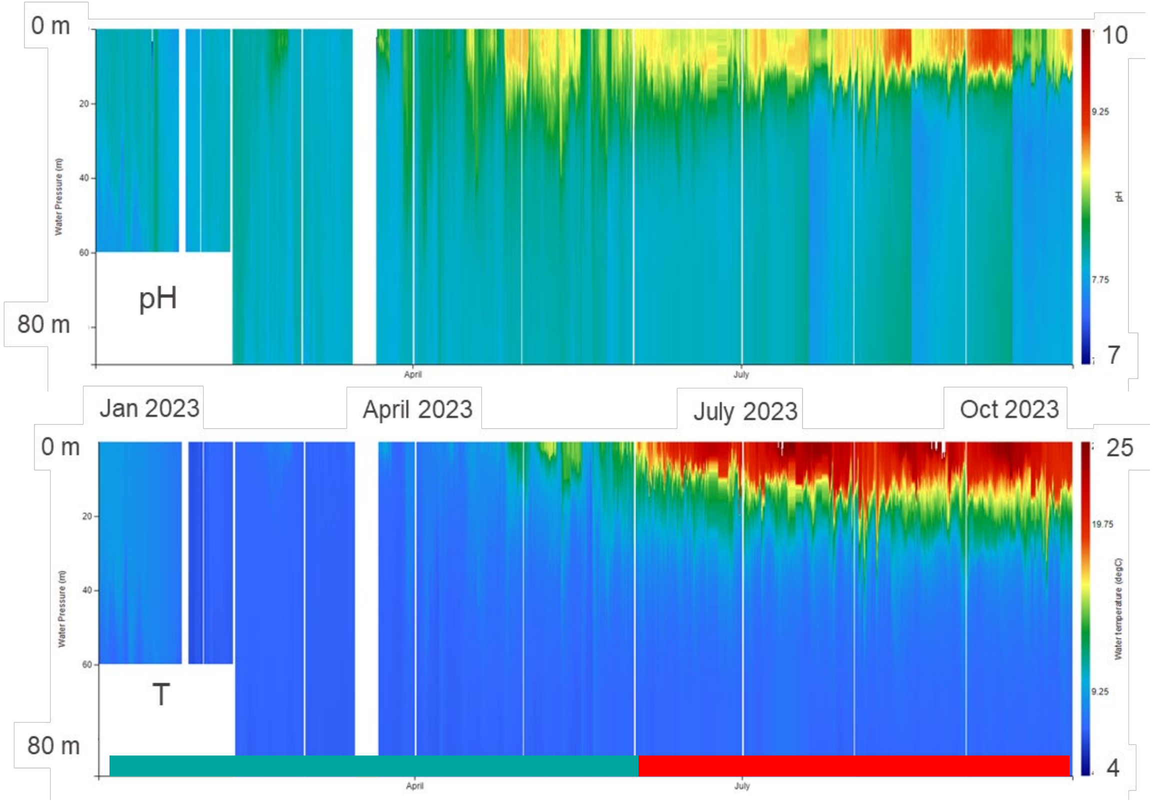
Many et al, 2024, Sci. Adv. 10, eado5924

Black line: measured pCO_2

Red line: modelled pCO_2 considering calcite precipitation

Blue line: modelled pCO_2 without calcite precipitation

Lake Geneva in 2023



Cold water, respiration > photosynthesis → large CO_2 oversaturation, CO_2 emission

Warm water, CO_2 consumption by photosynthesis → pH increase, calcite precipitation → CO_2 release → only slight CO_2 undersaturation

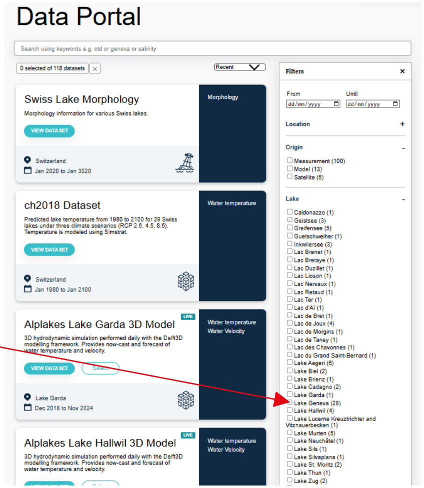
Data source:
https://www.datalakes-eawag.ch/

LéXPLORE experimental platform near Pully
Source: swissinfo.ch

Exercise

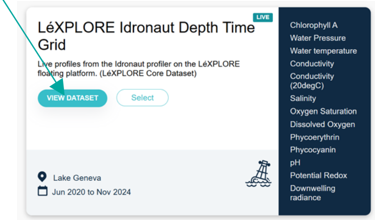
Find the T profile for Lake Geneva in 2024 on www.datalakes-eawag.ch

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

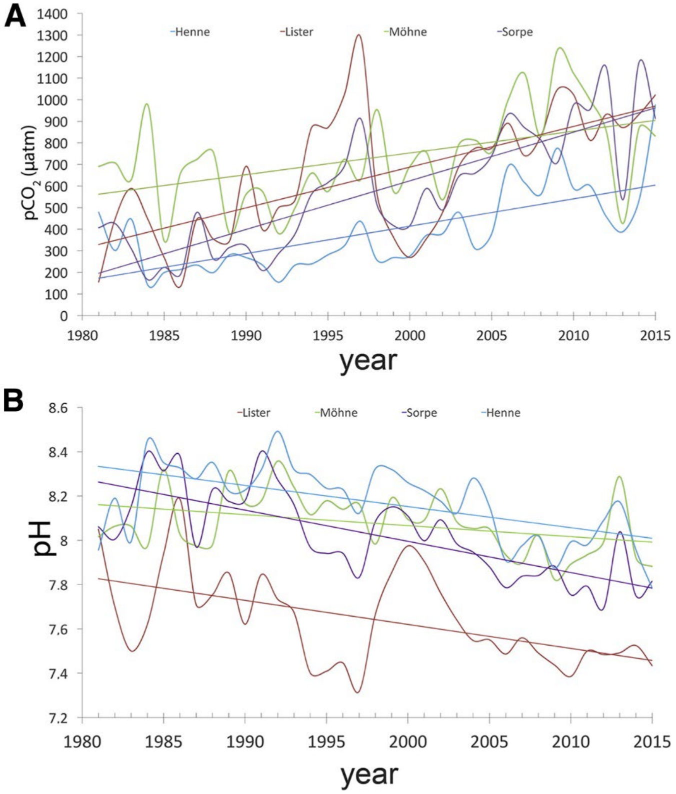


Discuss with your neighbor:

- how does the temperature profile of 2024 compare to that of 2023?
- Do you think the lake emitted more or less CO_2 in 2024 than in 2023?
- When atmospheric pCO_2 increases, will lakes still acidify, even though they are often emitters of CO_2 rather than sinks?



Observation: pH and CO_2 in 4 German lakes over 35 years



Average increase of pCO_2 by 561.21 µatm during the 35 year monitoring period. (Note: this is the dissolved CO_2 concentration, in an unusual unit).

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

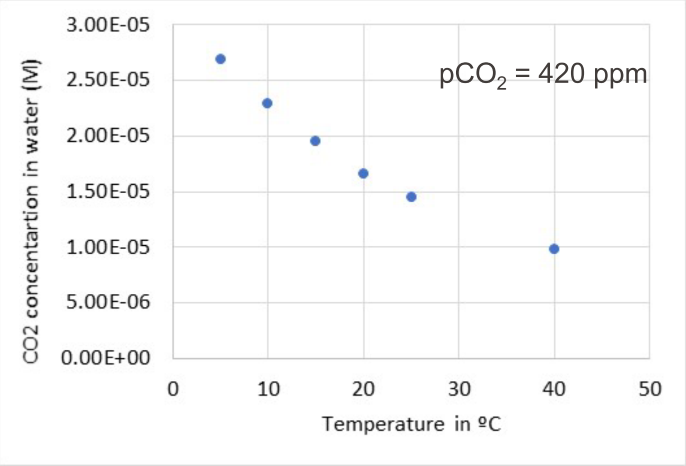
Source: Weiss et al, 2018, https://doi.org/10.1016/j.cub.2017.12.022

Possible causes for decrease in pH and increase in dissolved CO2

1. Increase in water temperature?

Recall: $p_{CO_2}/[H_2CO_3^*(aq)] = K_H$ (atm/M) $\log[H_2CO_3^*] = \log[p_{CO_2}] + pK_H$

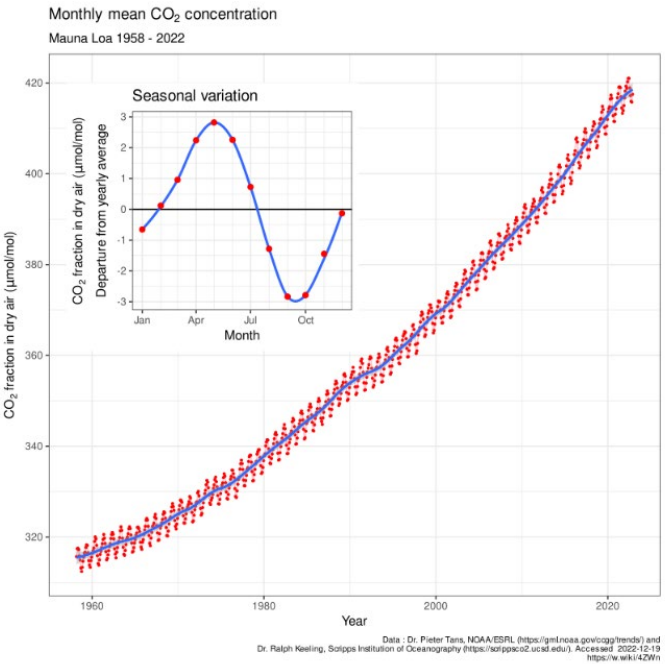
	pK_H					
	5 °C	10 °C	15 °C	20 °C	25 °C	40 °C
CO_2 (g) + $H_2O \leftrightarrow H_2CO_3^*$	-1.20	-1.27	-1.34	-1.41	-1.47	-1.64



No! Increasing water temperature leads to less dissolved CO_2

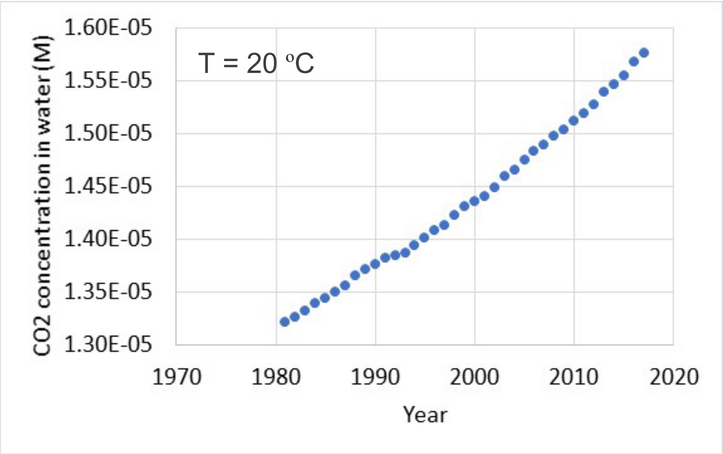
Possible causes for decrease in pH and increase in dissolved CO2

2. Increase in atmospheric pCO_2 due to fossil fuel burning?



Source: *Wikipedia*

$$\log[H_2CO_3^*] = \log[p_{CO_2}] + pK_H$$

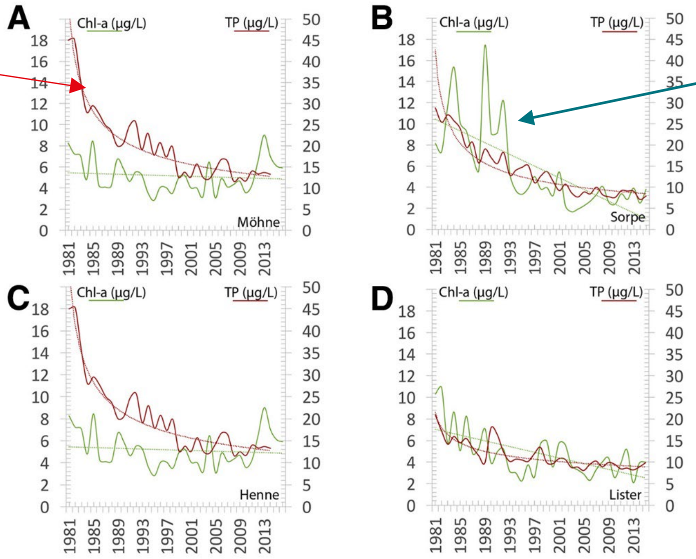


Correct trend in dissolved CO_2

Possible causes for decrease in pH and increase in dissolved CO2

3. Decrease in nutrient input leading to less CO_2 fixation?

Phosphorus (nutrient) concentration



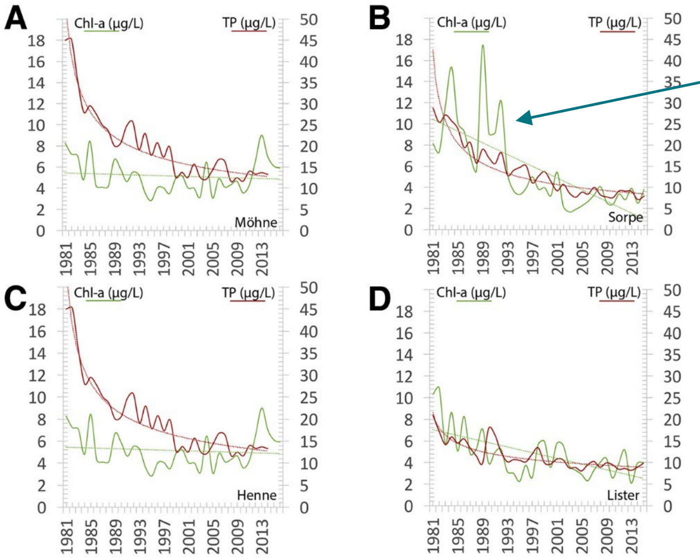
Chlorophyll a is a proxy for CO_2-fixating phytoplankton

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

No! Nutrients were reduced in all lakes but CO_2 fixation only went down in two.

Possible causes for decrease in pH and increase in dissolved CO2

4. Decrease in the abundance of CO_2-fixating phytoplankton?



Chlorophyll a is a proxy for CO_2-fixating phytoplankton

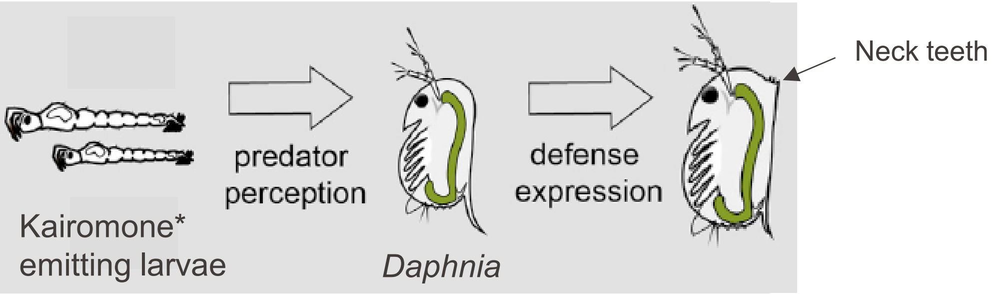
Source: Weiss et al, 2018, https://doi.org/10.1016/j.cub.2017.12.022

No! Chl-a only decreases in two lakes (and only over first 20 years), but CO_2 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.

Daphia 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).

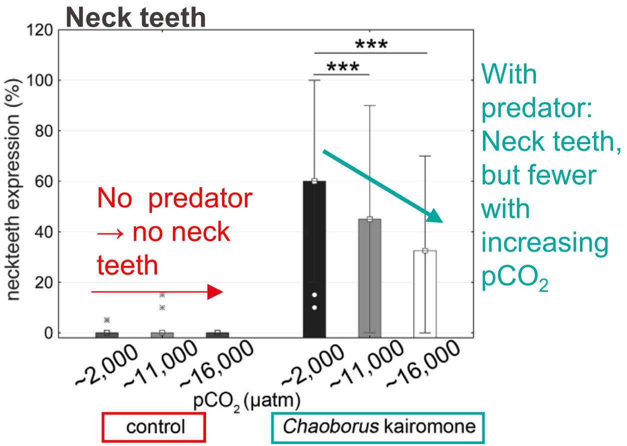


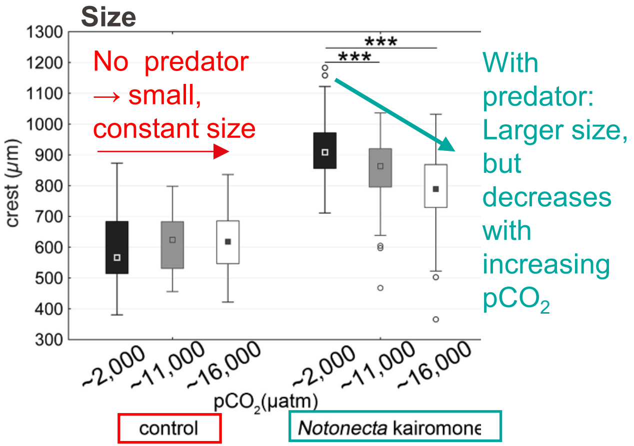
Adapted from: Weiss et al, 2018, https://doi.org/10.1016/j.cub.2017.12.022

*Kairomones = signaling chemicals that transfer information between organisms

Ecological effects on *Daphnia*

Test 1: effect of pCO_2 on neck teeth and body size, with and without a predator.
Approach: increase pCO_2, measure if and how neck teeth and size (crest) change.
pCO_2/pH conditions tested:
2000 µamt CO_2/pH 7.5
11'000 µatm CO_2/pH 6.9
16'000 µatm CO_2/pH 6.7



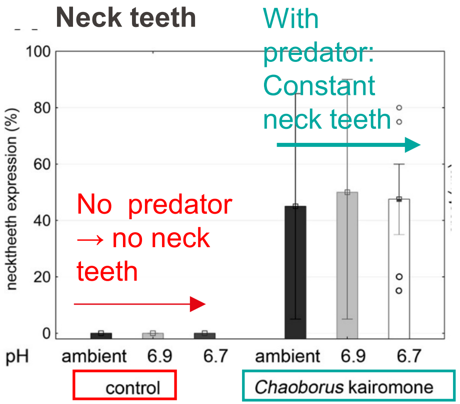


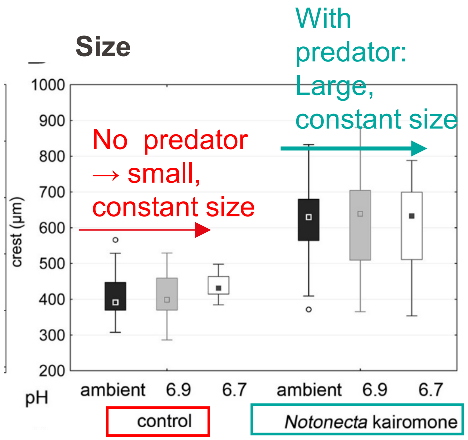
Conclusion1 : CO_2 affects the ability of Daphnia to sense a preditor.
The higher the pCO_2, the weaker the defense mechanism when a predator is present.

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

Ecological effects on *Daphnia*

Test 2: is it the change in pCO_2 or the associated change in pH that reduces defense?
Approach: vary pH, but not pCO_2 (by adding hydrochloric acid)
~ 2000 µamt CO_2/pH 7.5
~ 2000 µamt CO_2/pH 6.9
~ 2000 µamt 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 pCO_2 itself.

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

Summary

- Lakes have a complex CO_2 budget, which is affected by increasing CO_2 levels, but also other mechanisms (both natural and human-made)
- Even tough lakes are often supersaturated in CO_2 , they are acidifying as a result of increasing CO_2 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 CO_2 has ecological effects, which are not necessarily related to pH, but also to CO_2 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.