An atmosphere-ocean paradox? Brian Durham and Christian Pfrang

- **1.** The question Given Earth's ocean-atmosphere gas equilibrium, why do measured atmospheric CO₂ curves (Fig. 1) rise more steeply against solvent temperature than predicted by Henry's Law (Fig. 4), over a temperature range that may be as little as 1°C (Kent and Kennedy 2021) (our Fig. 2)?
- 2. Background The classic determinations of the seawater-headspace partition (Henry constant) were by Li and Tsui 1971 and Weiss 1974. By convention the measurements were performed with a headspace of 100% CO₂, giving a Henry constant that is conventionally extrapolated/intrapolated linearly across a wide range of partial pressures of the gas.

But does that linearity necessarily hold across partial pressures relevant to Earth atmosphere?

1. Simple lab tests at Earth atmosphere pressures - We therefore ran some tests on seawater twinned (in water-bath) with pure water controls, to simulate the





Fig. 1 Above: Mauna Loa atmospheric CO2 chart

Juxtaposed with: Fig. 2 Below: Sea Surface temperature (Kent and Kennedy 2021)

Fig. 3 Experimental setup: Both samples were preconditioned for 1 hour at 0.1°C with an airstream pre-adjusted to 290ppm CO₂ (from $1m^3$ PTFE gasbag).,

before closing headspace and adjusing

bath temperature.



headspace CO₂ curve seen at a range of atmospheric monitoring stations (Yuan et al 2019). Complications exist – in our experience even pure water is slow to equilibrate with its headspace, and seawater is slower still, behaving as if there is a slow-release chemical bond that might have been removed by reported pre-treatment in the 1970s analyses (Li and Tsui 1971; Weiss 1974).

- 2. Catalytic release of dissolved gas We speed our CO₂ release using a surfactant (sodium dodecyl sulphate (SDS) following gas hydrate studies), coupled with a short chain silicone as anti-foaming agent. We have yet to tackle the presumed chemical bond (above) in seawater, and suggestions of a catalyst would be welcome – our first choice will be a natural zinc-based CO₂ anhydrase.
- 3. Preliminary observations We report here trial runs, illustrated by a Campbell Science LoggerNet screenshot (20 March 2023 Fig. 4 opposite). From this and similar runs we derive:
 - 1. six data points for pure water:
 - 2. Six data points for seawater:
 - 3. Respective Weiss curves of Henry Constant intrapolated to 405 ppm CO₂.

It will be seen that the pure water curve is flatter than Weiss intrapolated, and seawater is higher and steeper than Weiss 35‰ intrapolated, in the latter case without the individual analyses showing any sign of approaching respective equilibrium asymptote (Fig. 4 green trace).

To improve on both we propose:



Fig. 4 Typical run: First hour is preconditioning (as above) to 11:30. Thereafter bath kept at 0.1'C till 13:05; raised progressively to 10'C; 15;'C and 20'C (temperature right axis). The hike in pure water (blue) at 20'C was repeated in another run, when it continued for several hours unexplained. Green trace (seawater) never approached equilibrium (eight hours).



- Extend PTFE tubing into the Li-Cor analysers to reduce drift;
- Confirm the pureness of the control samples (presently proprietary de-ionised water);
- Find a catalyst for the HCO₃ -> CO₂ release, 3.
- Span both analysers at respective ranges;
- Calibrate temperature probes; 5.
- Confirm salinity of UK Atlantic coastal water samples; 6.
- Control condensation at higher temperatures;
- 8. Identify a glitch in cell-pressure values from the CO₂ analysers. (Fig. 4: 11:30)

6. Inferences? – The closest we come to conclusions are:

- **a.** Pure Water The temperature slope of the pure water samples is substantially flatter than found by the 1970s papers. This may steepen as we develop add runs at higher temperatures (avoiding condensation). Otherwise it becomes a consideration in the extent to which the Henry Constant can be intrapolated linearly to atmospheric partial pressure, which for CO₂ is only 4 orders lower than the Henry determinations.
- **b.** Non-acidified seawater Even without any sign of approach to an asymptote, the headspace above seawater shows a substantially greater differential from pure water than that reported for (acidified) seawater by Li and Tsui and by Weiss, a differential likely to increase with use of an anhydrase or other CO_2 -release catalyst.
- c. Relationship to atmospheric measurements Given the rising trend in the six non-acidified seawater samples, there is a possibility that seawater holds a previously un-suspected store of available CO_2 .

Fig. 5 Provisional results: Values from this work plotted against published Henry Constant data for pure water and seawater 35‰ salinity (Weiss 1974), adjusted to 405ppm CO2

Ye Yaun et al 2019 On the diurnal, weekly, and seasonal cycles and annual trends in atmospheric CO2 at Mount Zugspitze, Germany, during 1981–2016, Fig. 6

- *d. The `paradox'? -* Hence there may be no paradox.
- 7. Wider implications (Fig. 6) Two possible considerations have been run past Munich TUM:
 - a. Continental v oceanic? Continental stations (i.e. terrestrial) in Fig. 6 show an annual cycle that is offset relative to the Mauna Loa station. Mauna Loa is more than 3000km from any extensive terrestrial photosynthetic horizon, and might be expected to show the effect of equilibration with the ocean surface.
 - b. Is `altitude' of reporting station to be measured from sea level or from *local photosynthetic surface?* This will logically need more global stations than those used by TUM.



Yaun et al 2019, Figure 6. Mean CO₂ seasonal cycles from the STL seasonal component at each measurement site or location. Uncertainties at the 95% confidence interval are shown by the shaded areas with corresponding colors. Atmos. Chem. Phys., 19, 999–1012, 2019 https://doi.org/10.5194/acp-19-999-2019 © Author(s) 2019.



- For continental stations, the amplitude of the seasonal cycle of CO₂ tends to reduce with increasing height (altitude) of the recording station (m asl);
- The same trend extends to the oceanic station at Mauna Loa, Hawaii, which is 440m higher than highest continental station (Mt Zugspitze Summit, 2962m asl);
- The spring peak at continental stations (February-March) is more than two months earlier than at the quoted oceanic station (May);
- The autumn trough at continental stations (August) is more than one month earlier than at the quoted oceanic station (September-October).



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