A revised look at the oceanic sink for atmospheric carbon tetrachloride (CCl_4)

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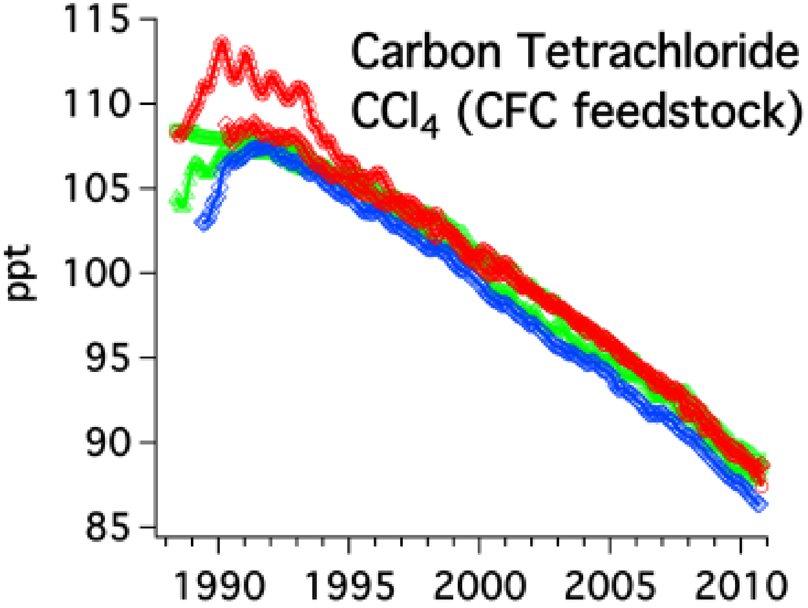
Why is this important?

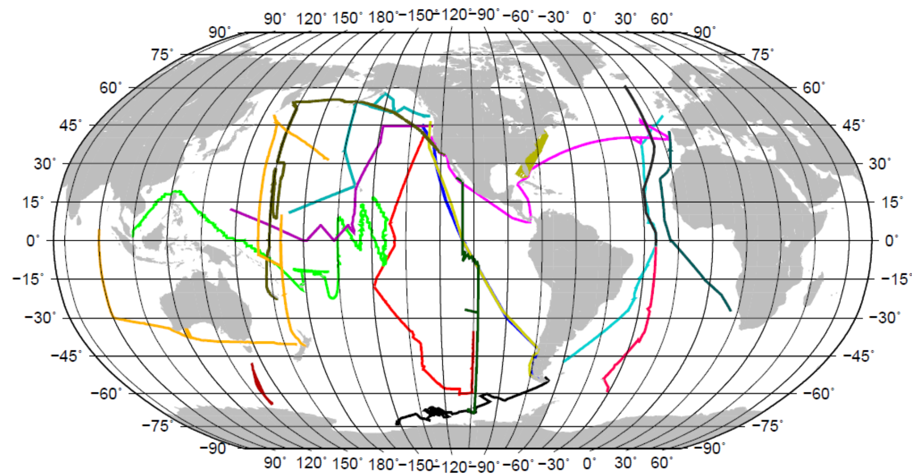
- CCl_4 is a strong ozone-depleting gas for which most production has ceased.
- Although its amount is declining In the atmosphere, the rate of decline is slower than its limited production and atmospheric lifetime (~26 y) suggest.
- The oceanic sink is typically treated as a significant contributor to the lifetime of CCl_4 in the atmosphere, along with reaction in the stratosphere and loss to soils.



Purpose of this study

- Re-examine the oceanic sink to provide more confidence in our ability to estimate the rate of atmospheric CCl_4 removal by the ocean.
  - ➢ With data from 16 cruises, this allows us to provide a much more representative picture of oceanic removal rates.

Research cruises contributing to this study

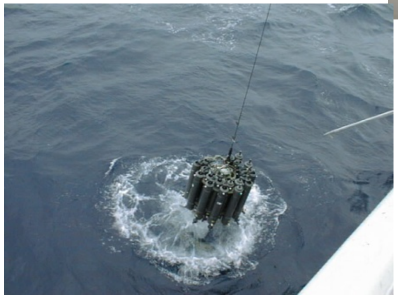


SAGA-2, RITS89, SAGA-3, OAXTC, BLAST1, BLAST2, BLAST3, GasEx98, RB9906, CLIVAR01, A16N, A16S, PHASE, P18, GOMECC, HalocAST-P, HalocAST-A

- 16 cruises
- All oceans
- All seasons
- 23 years (1987-2010)

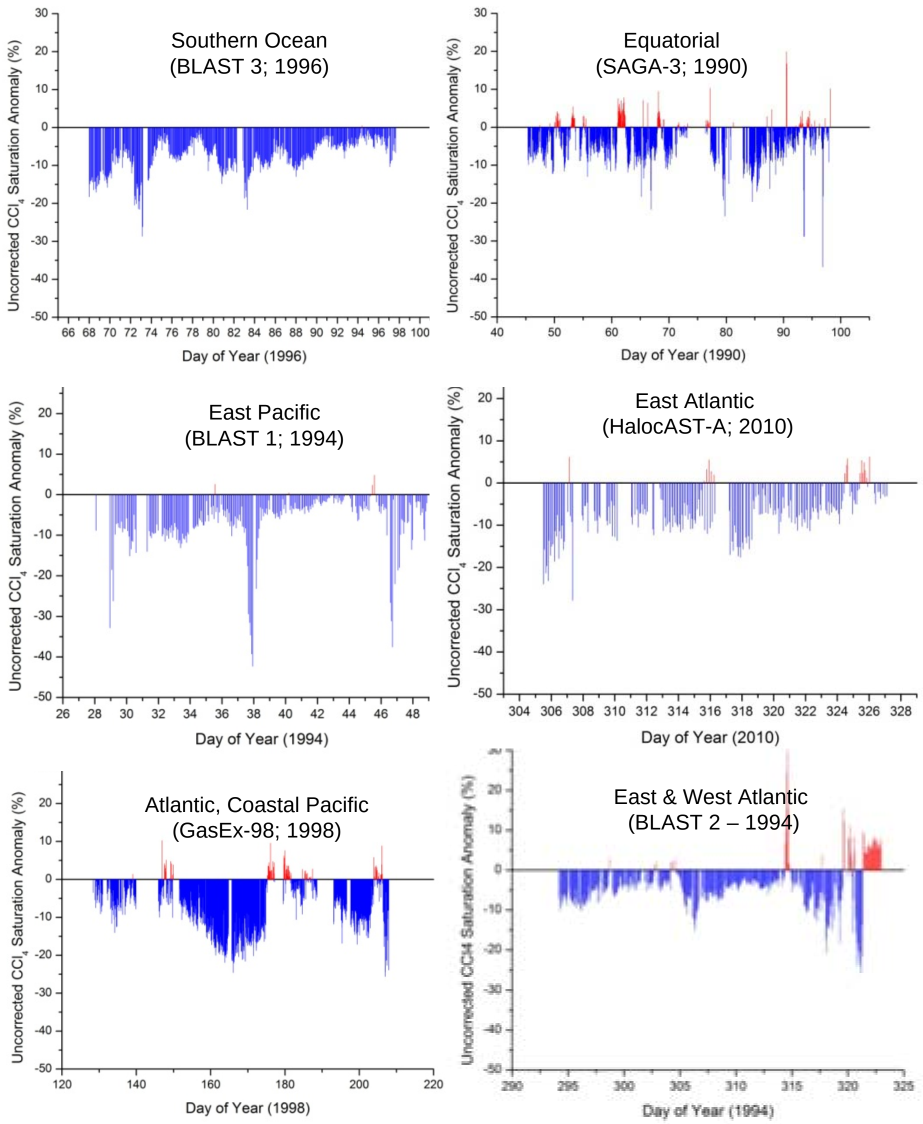
How did we do it?

- Air samples were collected from the ship's bow, surface samples were obtained with an underway, Weiss-type equilibrator, and, on many cruises, samples from hydrocasts were analyzed as well.
- Samples were analyzed by gas chromatography with both ECD and mass spectrometric detection to evaluate potential analytical biases.
- Depth profiles of CCl_4 were obtained on some cruises to identify potential zones of CCl_4 loss.
- The minimum, pseudo-1st-order degradation rate constant was used in the oceanic uptake model to determine the global uptake and partial atmospheric lifetime.



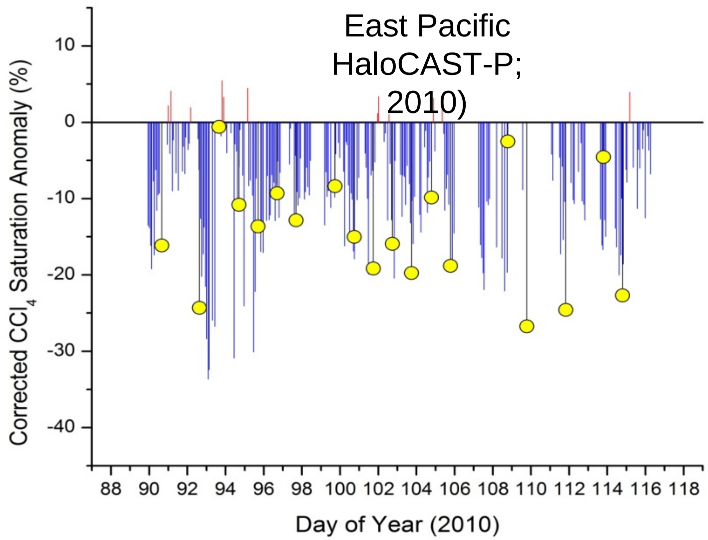
What did we find out?

- CCl_4 is undersaturated in the surface ocean nearly everywhere, virtually all the time.
- This undersaturation exceeds that which might be expected from physical effects, such as mixing of water masses.
- The minimum, pseudo-1st-order degradation rate constants needed to support the observed undersaturations, assuming no *in situ* production, differ by only small amounts in various oceanic regions.

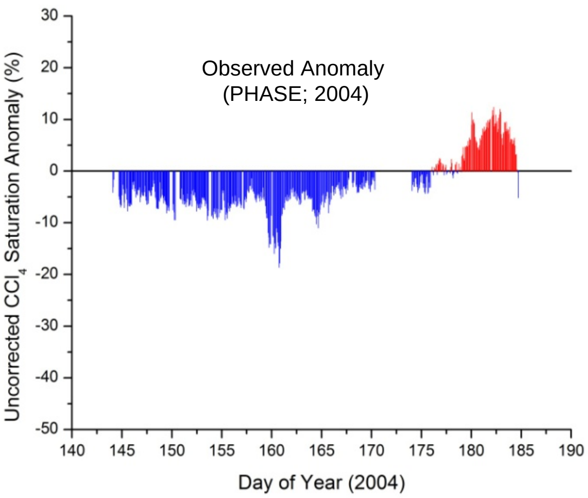


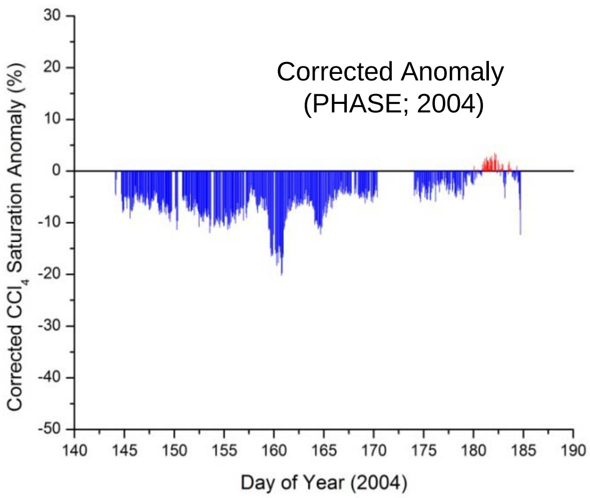
Are we sure?

- Surface samples from hydrocasts (circles) vs. equilibrator measurements (spikes) suggest no sampling bias



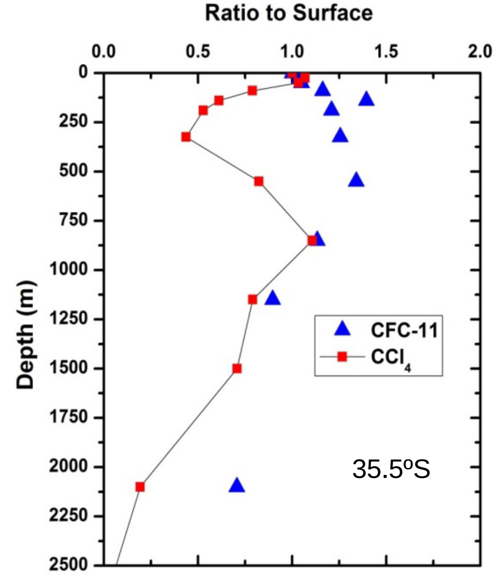
- Often, but not always, influences of physical effects make the anomaly positive or less negative.
  - For calculating fluxes, these effects from air injection, mixing, and thermal changes are corrected by subtracting observed CFC-11 surface anomalies.

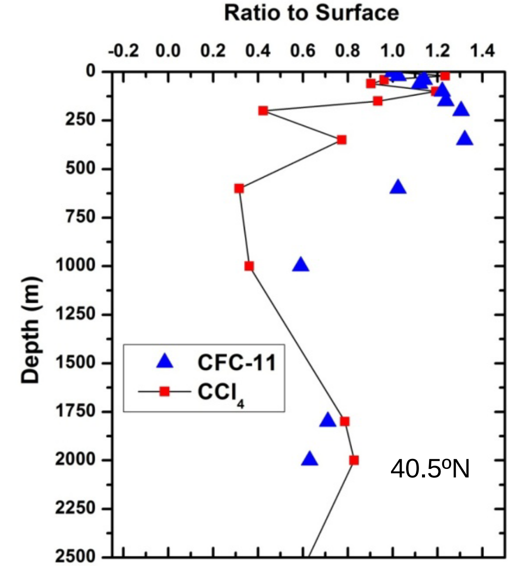




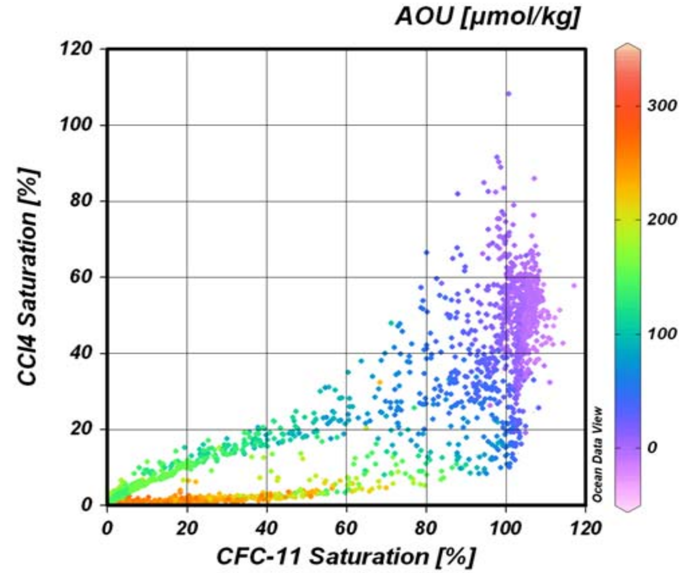
What's causing this undersaturation?

- Relative concentrations of CCl_4 are consistently less than CFC-11 at intermediate depths, suggesting consumption as oxygen declines



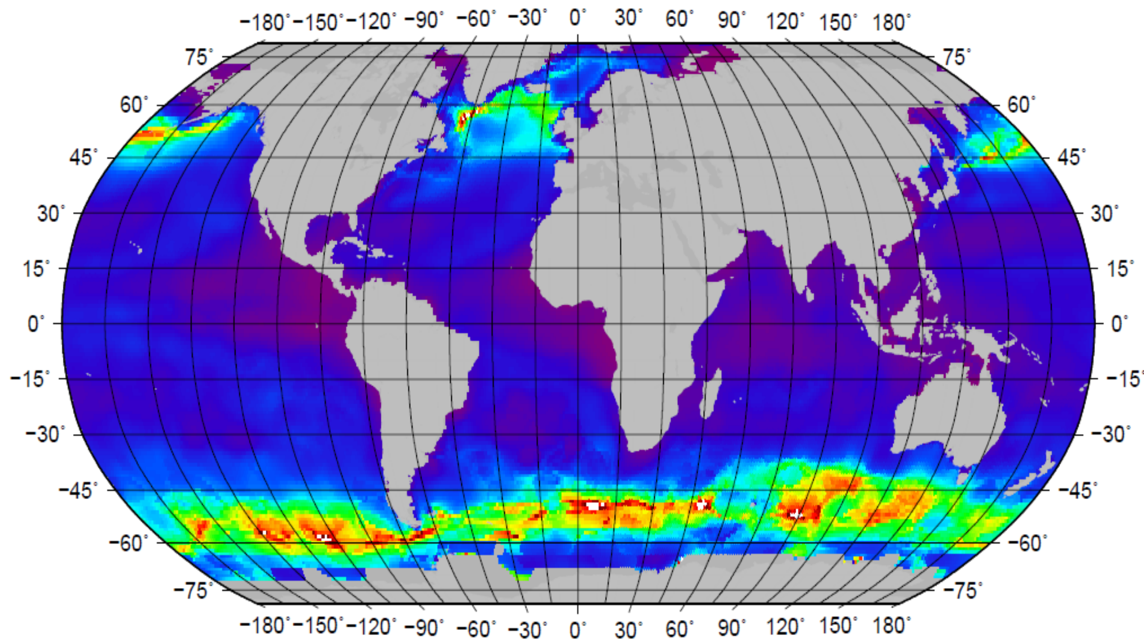


- CCl_4 seems to be consumed most rapidly in low-oxygen waters
  - Data from the P18 cruise in the eastern Pacific show dramatically lower CCl_4 saturations vs CFC-11 saturations, especially in sub-surface waters with high Apparent Oxygen Utilization (AOU).



What did we find out?

- The oceanic sink is responsible for removing ~30% of the CCl_4 from the atmosphere, representing a partial atmospheric lifetime of 81y (vs 94y used in the WMO/UNEP Scientific Assessments).



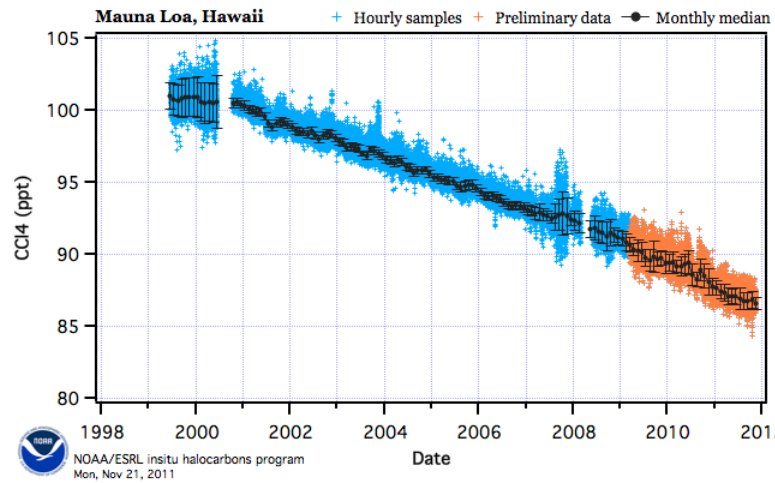
- Considering this sink and the removal of CCl_4 in the stratosphere, the mid-range estimate of the atmospheric lifetime of CCl_4 would be 25y (formerly 26y in the WMO/UNEP Scientific Assessments).

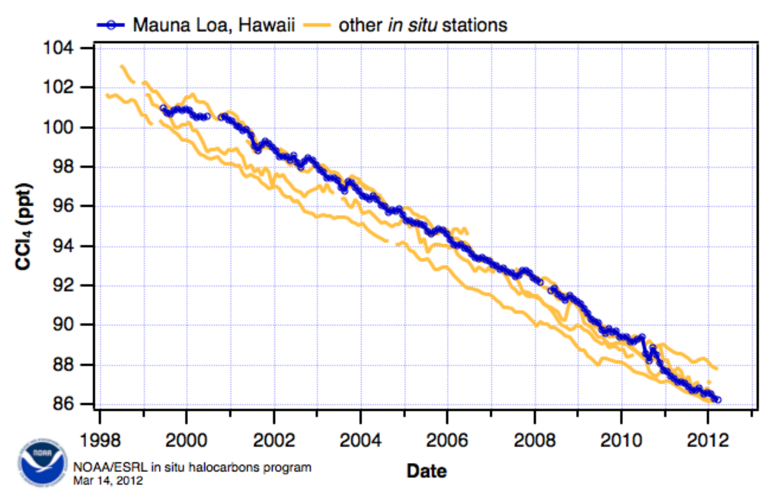
What does this all mean?

- Irreversible removal of CCl_4 by processes within the ocean has a significant impact (~30%) on the lifetime of CCl_4 in the atmosphere reducing the length of time that stratospheric ozone would otherwise be impacted by Cl from this molecule.

- CCl_4 removal could take place in the surface ocean, but there is considerable evidence in depth profiles that it is removed more rapidly at depth near the oxygen minimum.

- The influence of the oceanic sink on the atmospheric lifetime is robust and well supported by observations and models.





Questions?