An overview of opportunities and challenges for atmospheric O_2/N_2 measurements

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Talk outline

Large-scale applications

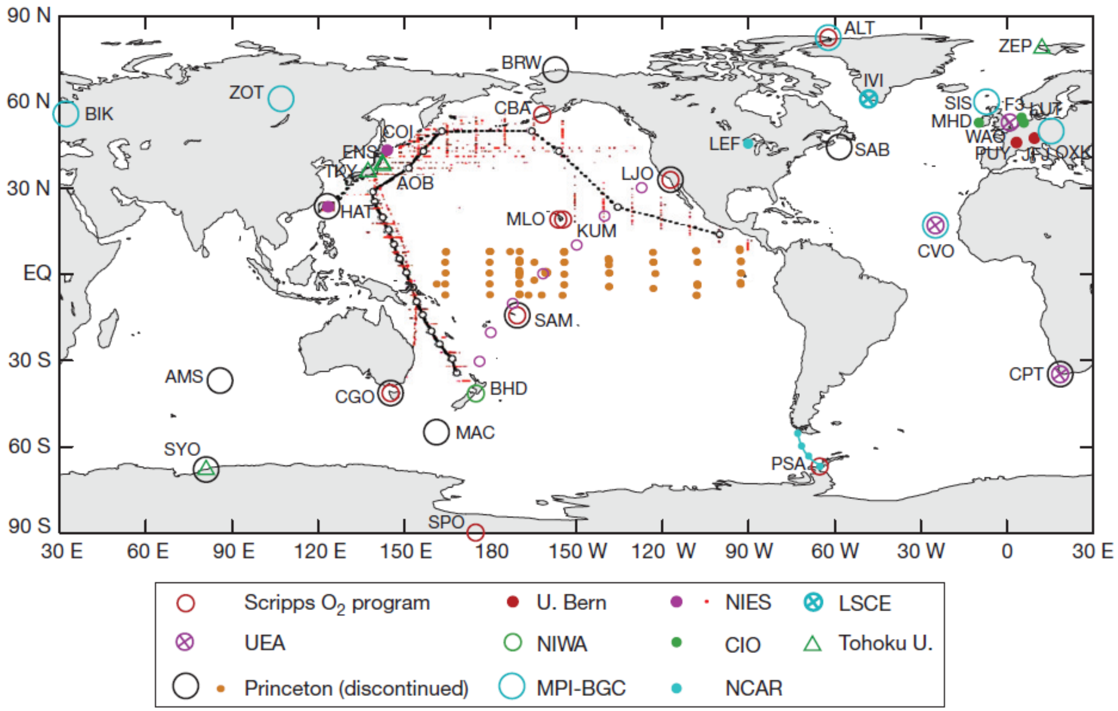
- Quantification of CO_2 sources and sinks.
- Response of planet to changing climate, ocean heat uptake, biogeochemical changes (especially oceans).

Smaller-scale applications

- Quantification of fossil-fuel emissions
- Terrestrial ecology applications

Obstacles and Challenges

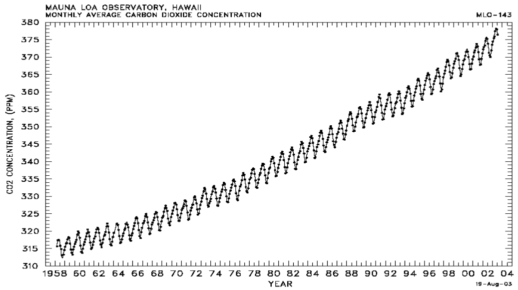
O_2/N_2 measurement network circa 2013

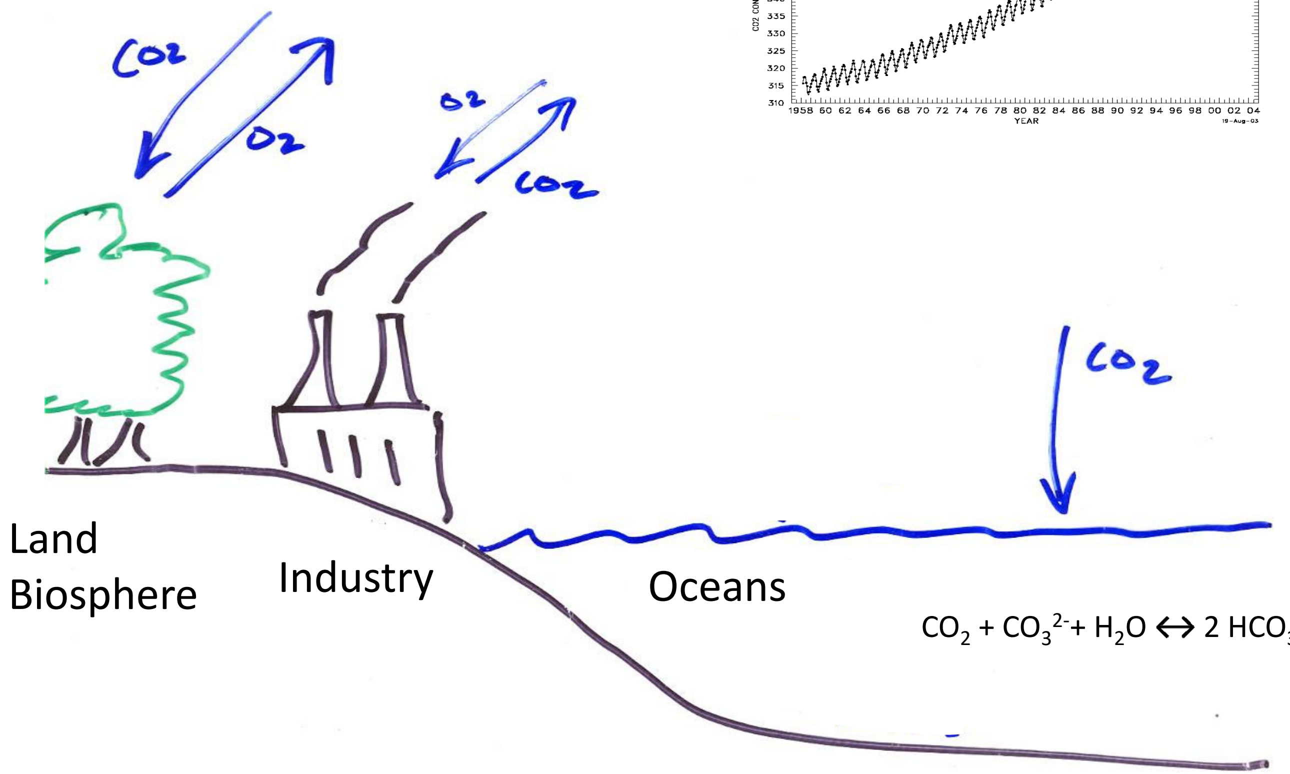


Other additions:

Atlantic ship-based, UEA
Airborne, AIST

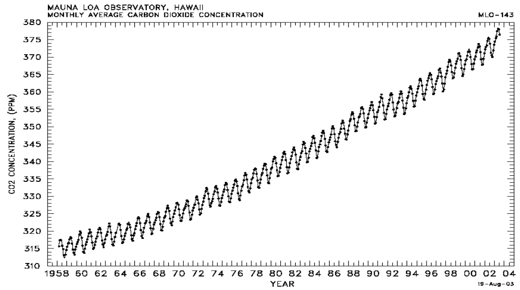
Large-scale applications

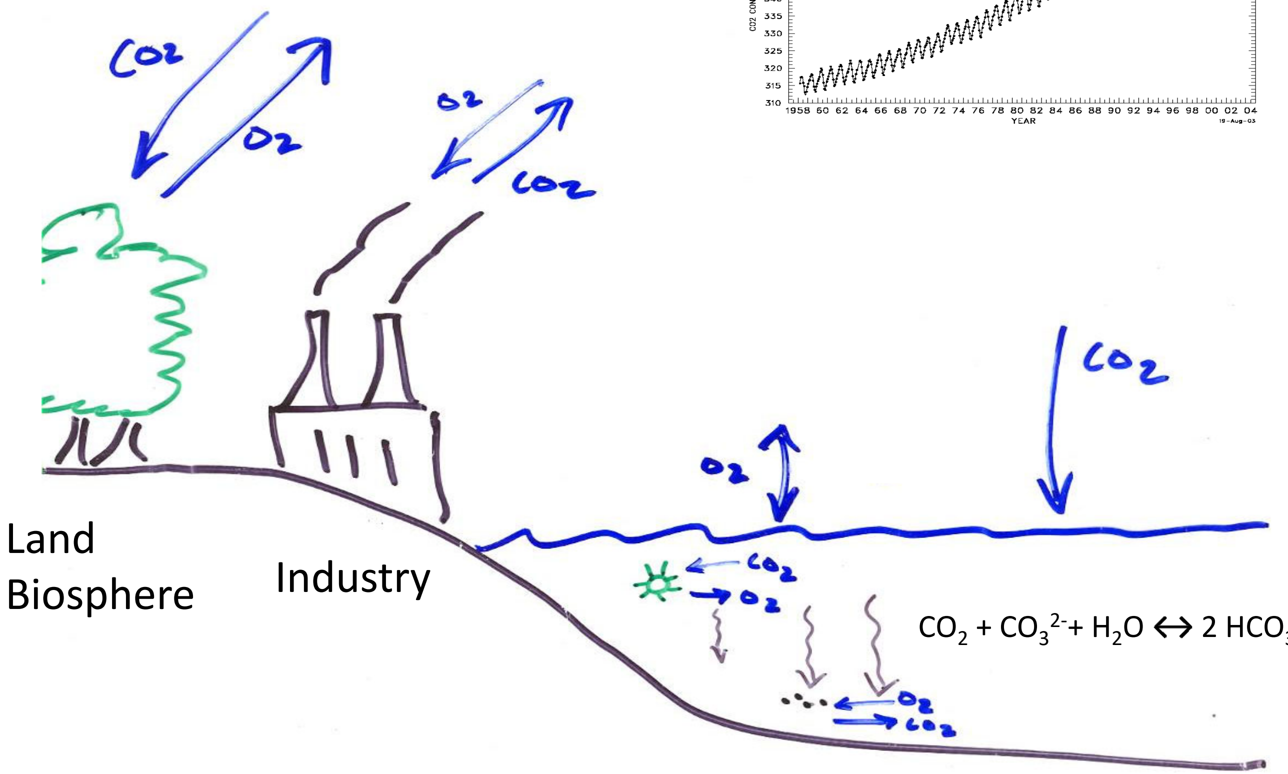




$$CO_2 + CO_3^{2-} + H_2O \leftrightarrow 2\ HCO_3^{-}$$

Large-scale applications





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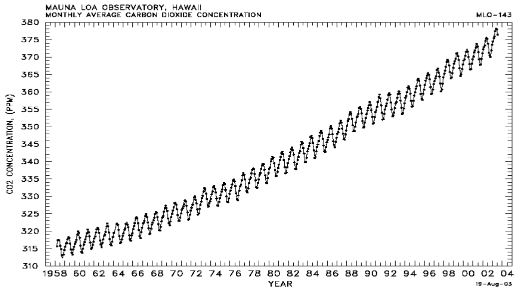
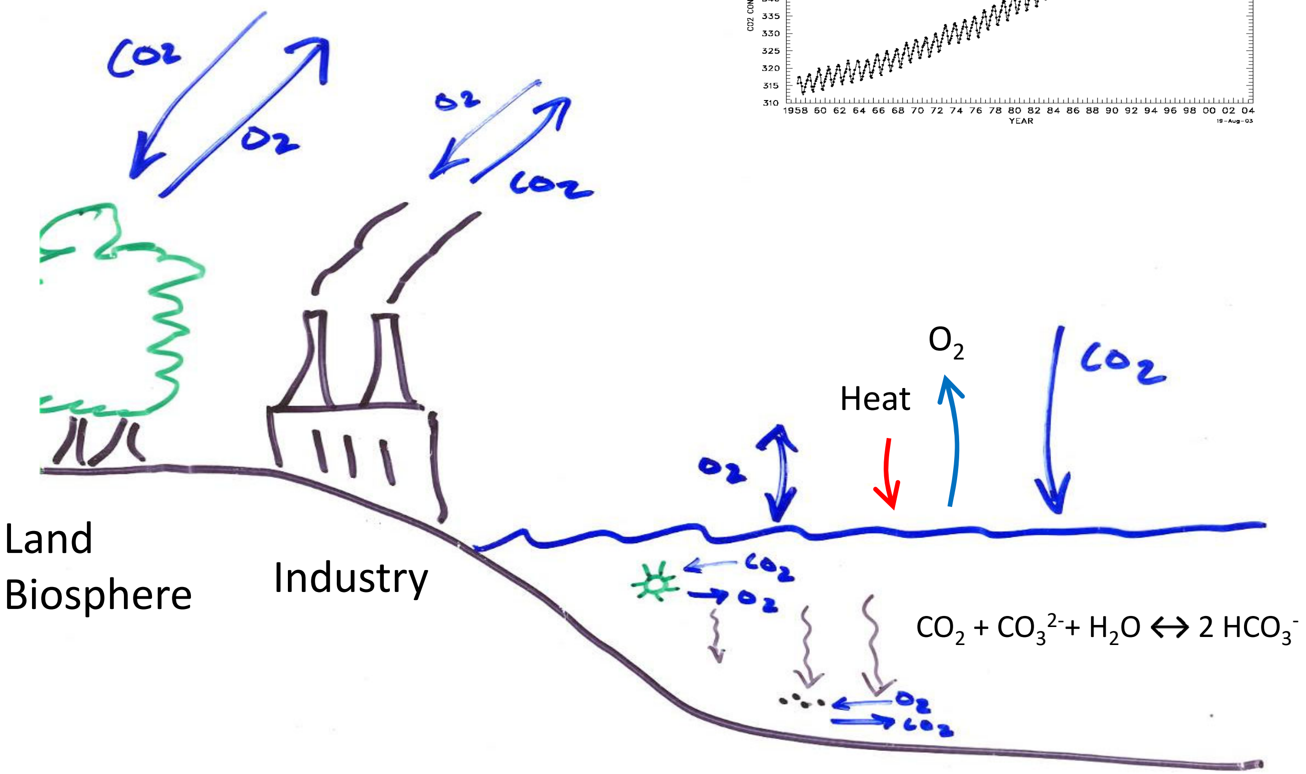
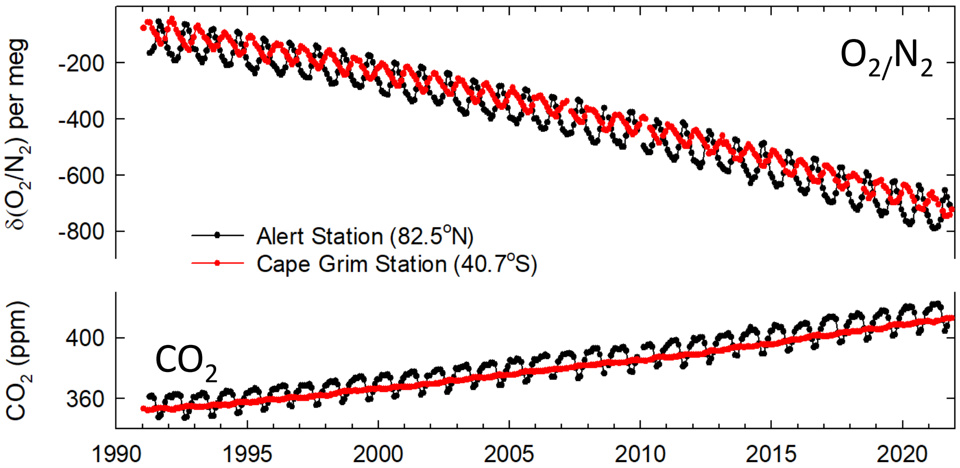
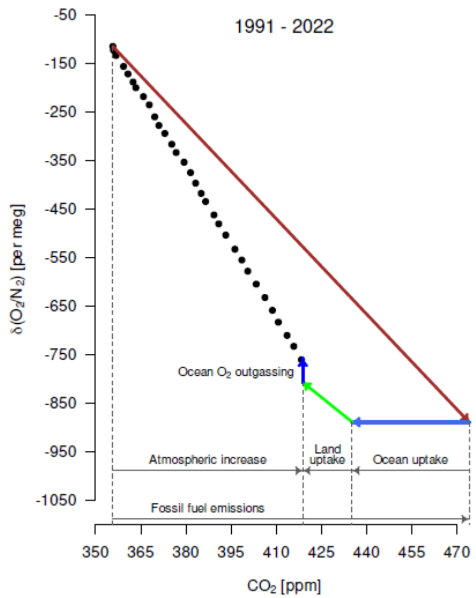
Large-scale applications





Constraining global land and ocean carbon sinks



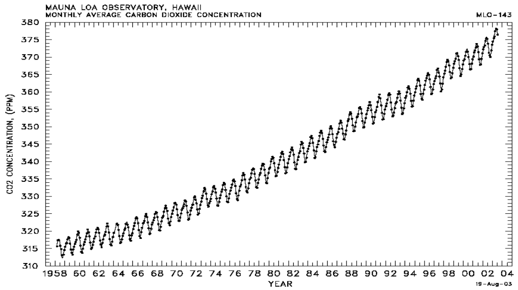


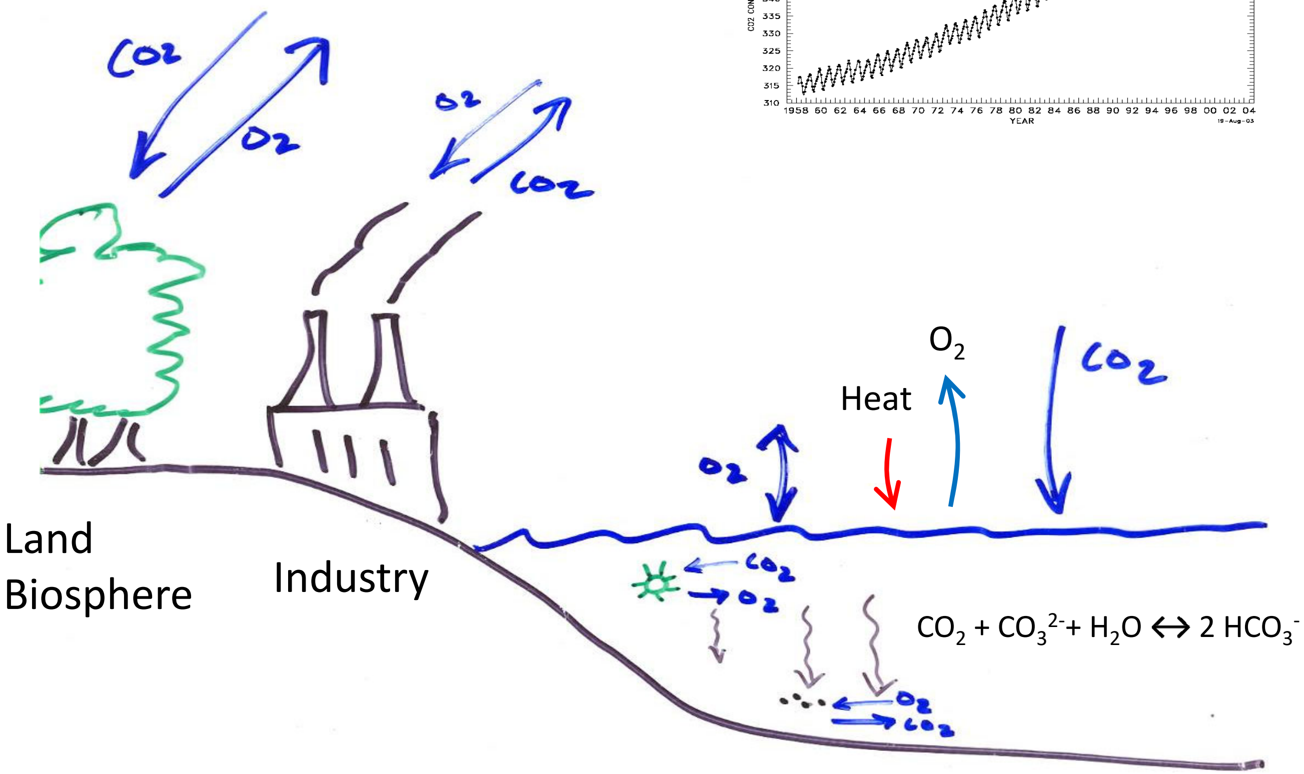
Long-term O_2 and CO_2 trends anchor estimates of global land and ocean carbon sinks.

Years	Emissions	Atmosphere	Land	Ocean
1990–1999	6.3 ± 0.6	3.2 ± 0.2	1.2 ± 1.0	1.9 ± 0.7
2000–2009	7.8 ± 0.7	4.0 ± 0.2	1.3 ± 1.1	2.6 ± 0.6
2010–2019	9.6 ± 0.9	5.0 ± 0.2	1.4 ± 1.3	3.1 ± 0.6

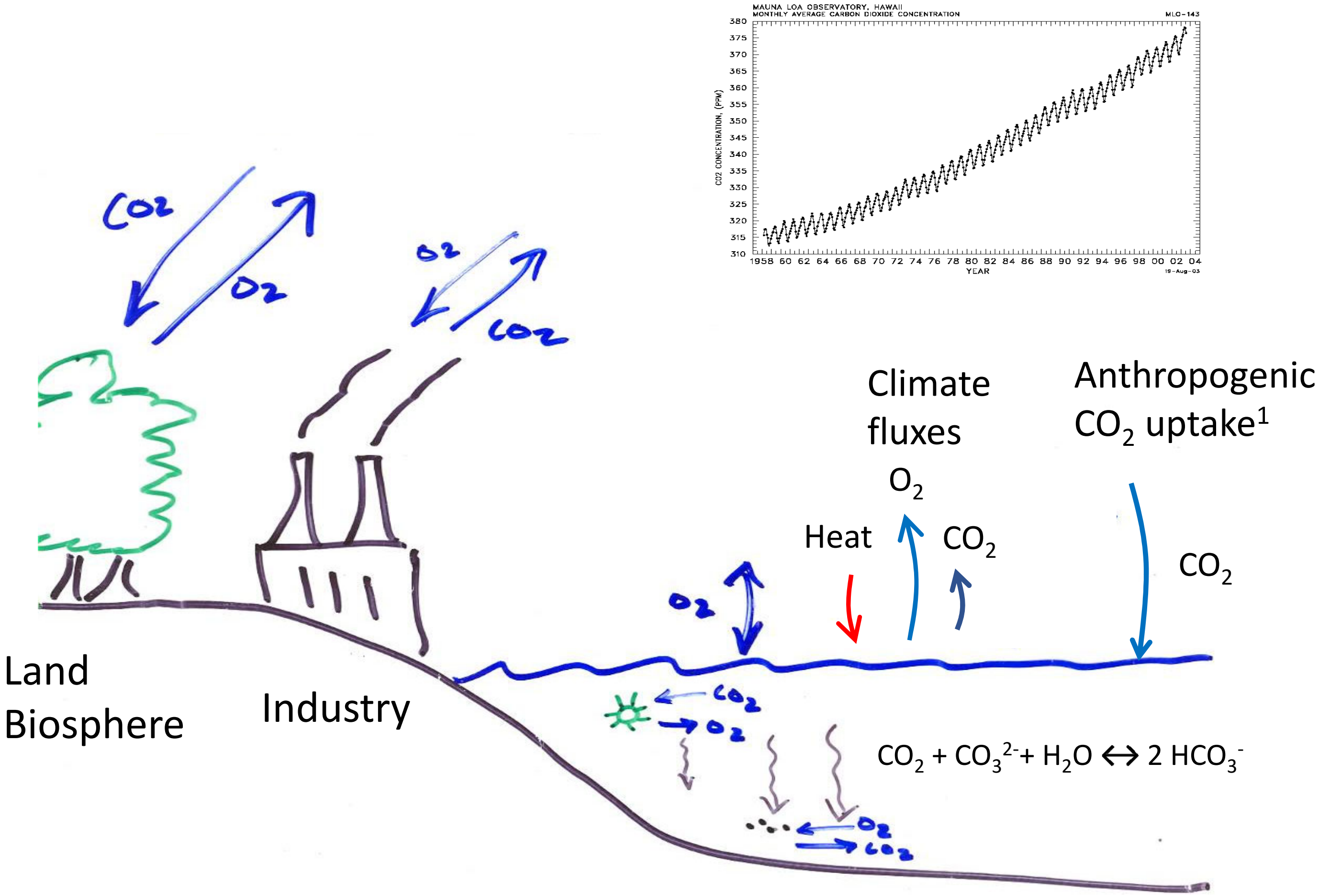
Global carbon budget in PgC yr^{-1}, based on trends in δAPO, with $\alpha_B = 1.05$ and $\gamma_{O_2} = 4.9$ nmol J^{-1}

Controls on atmospheric CO_2 and O_2





Controls on atmospheric CO_2 and O_2



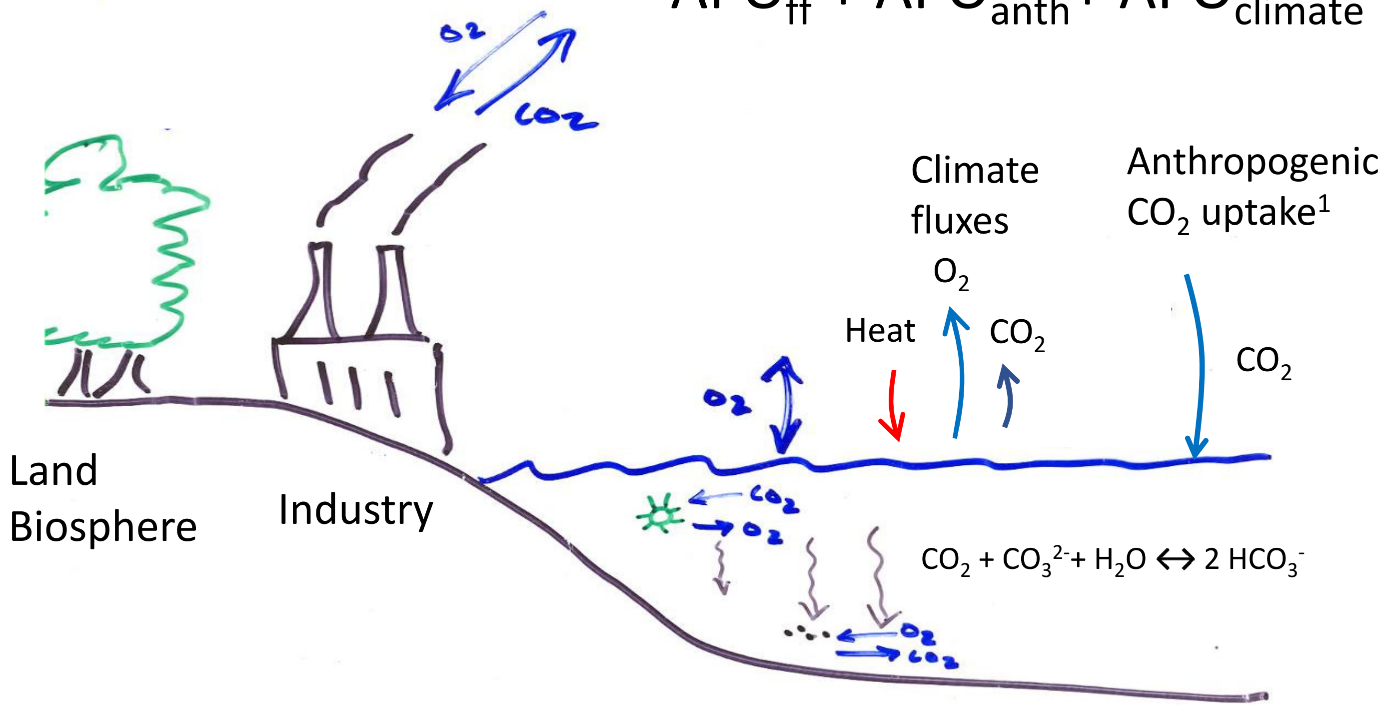
[1]Constrained by CFC data and CO_2 history

Controls on atmospheric CO_2 and O_2

Atmospheric Potential Oxygen

$$APO \sim O_2 + 1.1 * CO_2$$

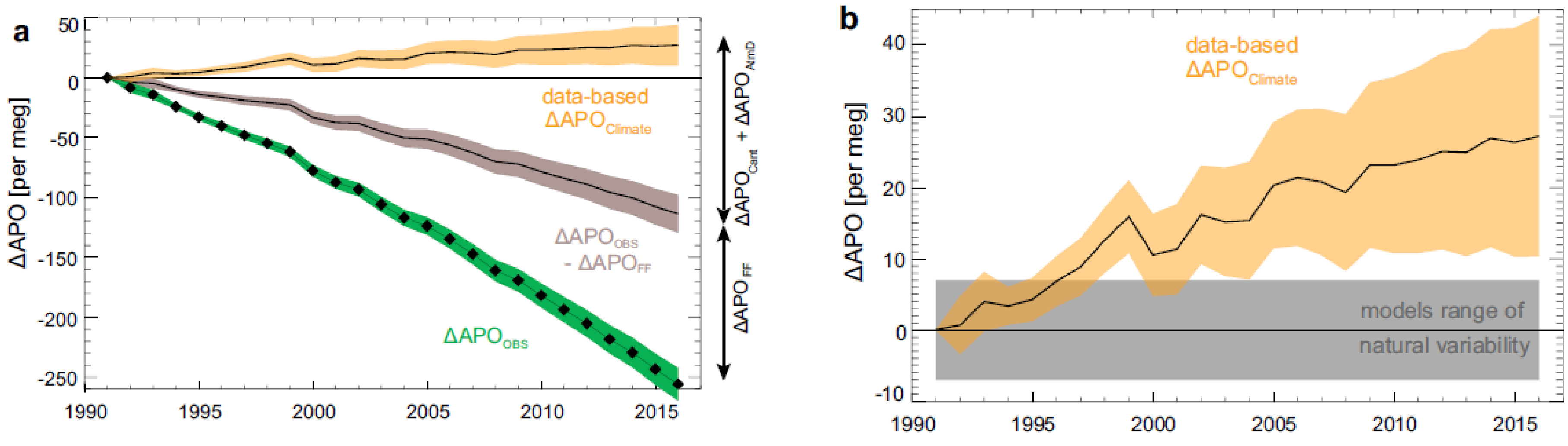
$$= APO_{ff} + APO_{anth} + APO_{climate}$$



[1]Constrained by CFC data and CO_2 history

Atmospheric potential oxygen (APO) trend

Resplandy et al, 2019



C_{anth} estimate: DeVries (2014). Global Biogeochemical Cycles **28(7): 631-647.**

Small-scale applications

1. Local fossil-fuel emissions assessment

<u>Oxidative ratios</u>

Petroleum ~ 1.44

Natural gas ~ 1.95

Coal ~ 1.17

Measuring APO in urban setting allows detecting signal of fossil-fuel burning without impact from vegetation fluxes.

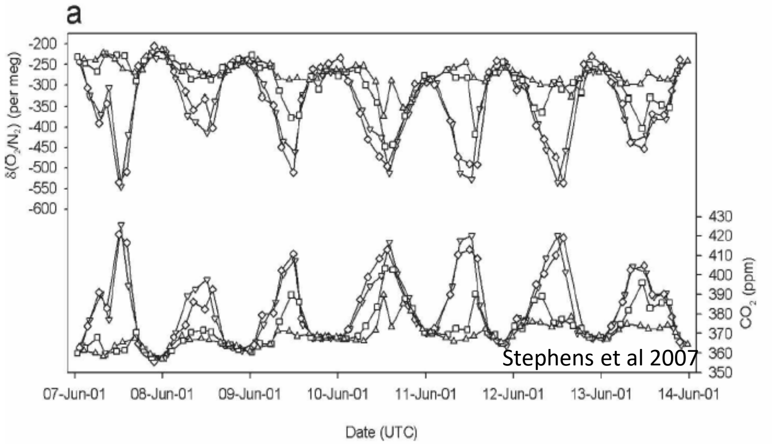
Affordable alternative to using ^{14}C, which requires flask sampling and expensive analyses.

Detection of COVID lockdown drop in emissions:

Pickers et al , P. A., A. C. Manning, C. L. Quéré, G. L. Forster, I. T. Luijkx, C. Gerbig, L. S. Fleming and W. T. Sturges (2022). "Novel quantification of regional fossil fuel CO2 reductions during COVID-19 lockdowns using atmospheric oxygen measurements." Science Advances 8(16): eabl9250.

Small-scale applications

2. Ecosystems



Measure correlations between O_2 and CO_2 to establish O_2:CO_2 exchange ratio (ER).

Stephens et al (unpublished ~1997) *Harvard Forest*; Seibt et al (2004) - *Harvard Forest, Griffin Forest, Hainich*
Stephens et al (2007) *WLEF*; Kozlova et al (2008) *Zontino;* Ishidoya et al (2013, 2015), *Takayama*; van der Laan et al (2014) *Fyodorovskoye*; Faassen et al. (2023) *Hyytiälä*;

Potential applications:

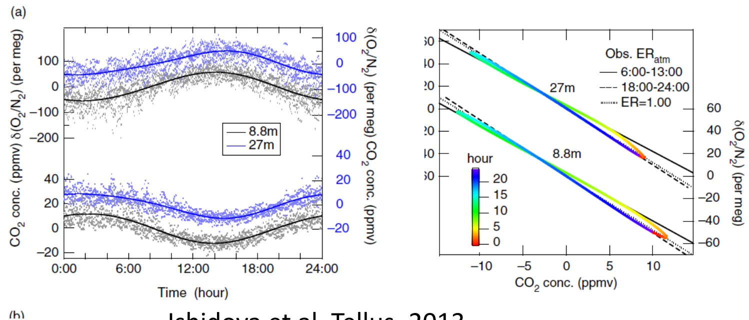
- Understand better controls on exchange ratio (ER) to use for larger scales (e.g. APO calculations)
- Partition ecosystems fluxes into photosynthesis (GPP) and respiration (RECO)
- Something about nitrogen cycling?

Small-scale applications

2. Ecosystems

What have we learned so far?

- Daytime ratios lower than nighttime ratios (Ishidoya, 2013,2015; Battle 2019; Faassen 2023) tied ER for photosynthesis
  ER for photosynthesis ~ 1.0, Respiration ~ 1.1.
  Complicated by different processes occurring simultaneously
- Temporal O_2:CO_2 ratio may not equal flux ratio (Faassen 2023)



Ishidoya et al, Tellus, 2013

- Several studies have found ER ~ 0.9 for seasonal uptake (Ishidoya, 2014; van der Laan 2014), much lower than oxidative ratios of 1.03-1.10 for leaves and stems (Gallagher, 2017). What carbon pools are actually building up seasonally?

Opportunities:

- Studies demonstrating closure by combining ER and plant tissue measurements. Does it all add up?
- Studies combining O_2/N_2 and ^{14}C to better resolve regional ER for APO calculation

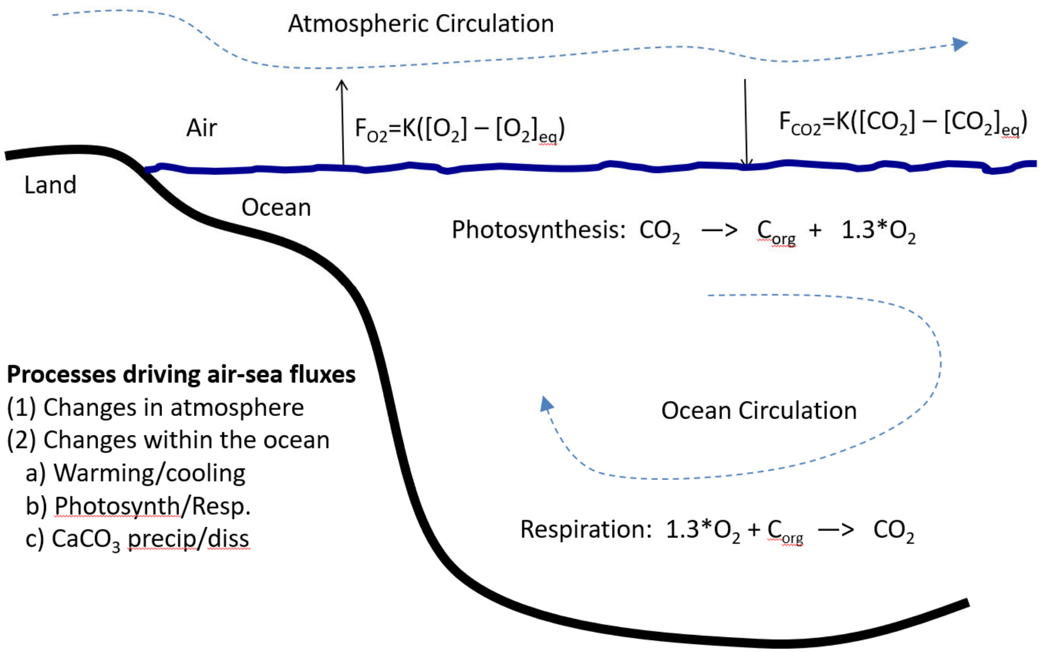
Challenges:

- How to refine ER for APO calculation? Can ecosystems scale measurements help with this?
- How to relate ecosystem-scale ER to relevant ecological measures? (Could be viewed as opportunity.)

Obstacles and challenges

1. We lack modelling tools to integrate O_2 and CO_2 constraints on ocean processes.

Linking air-sea O_2 and CO_2 fluxes



Processes driving air-sea fluxes

(1) Changes in atmosphere

(2) Changes within the ocean

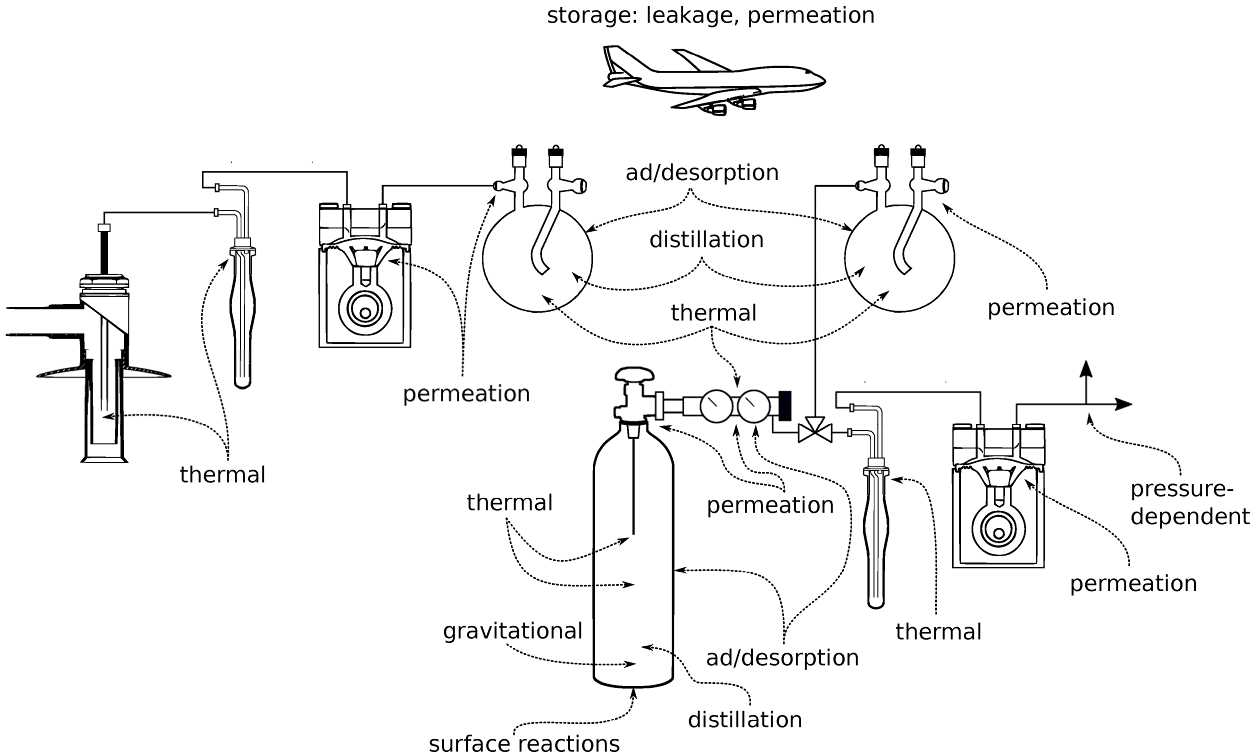
a) Warming/cooling

b) Photosynth/Resp.

c) $CaCO_3$ precip/diss

Obstacles and challenges

2. Measurements are hard, many sources of fractionation:



...and potential leaks everywhere.

Art credit: Eric Morgan

Obstacles and challenges

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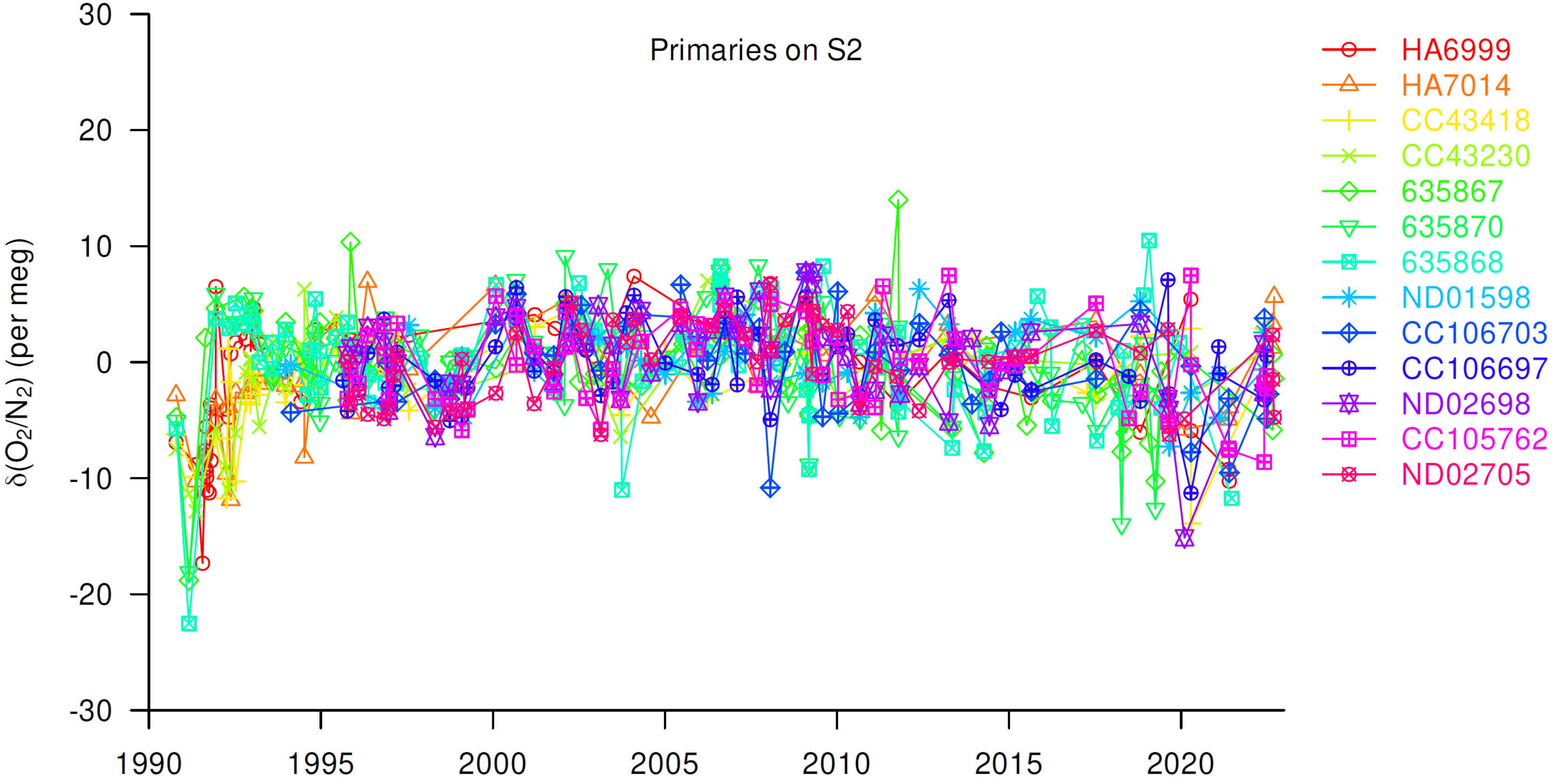


Obstacles and challenges

3. Potential for long-term drift in compressed air referenes necessitates having absolute standards

Intercomparison of O_2 / N_2 ratio scales among AIST, NIES, TU, and SIO based on a round-robin exercise using gravimetric standard mixtures

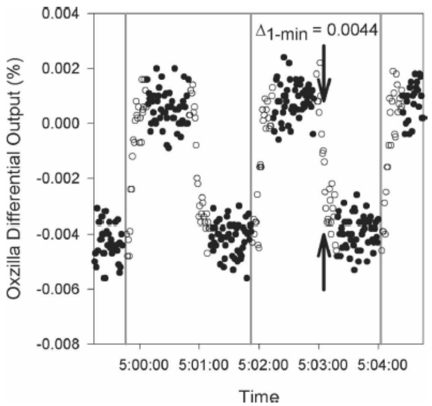
Nobuyuki Aoki[1], Shigeyuki Ishidoya[2], Yasunori Tohjima[3], Shinji Morimoto[4], Ralph F. Keeling[5], Adam Cox[5], Shuichiro Takebayashi[4], and Shohei Murayama[2]

[1]National Metrology Institute of Japan (NMIJ), National Institute of Advanced Industrial Science and Technology (AIST), 1-1-1 Umezono, Tsukuba 305-8563, Japan
[2]Research Institute for Environmental Management Technology (EMRI), National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba 305-8569, Japan
[3]Center for Environmental Measurement and Analysis, National Institute for Environmental Studies, Tsukuba 305-8506, Japan
[4]Center for Atmospheric and Oceanic Studies, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan
[5]Scripps Institution of Oceanography, La Jolla, CA 92093-0244, USA

Atmos. Meas. Tech., 14, 6181–6193, 2021
https://doi.org/10.5194/amt-14-6181-2021

Obstacles and challenges

4. Requires custom installations and lots of calibration gas



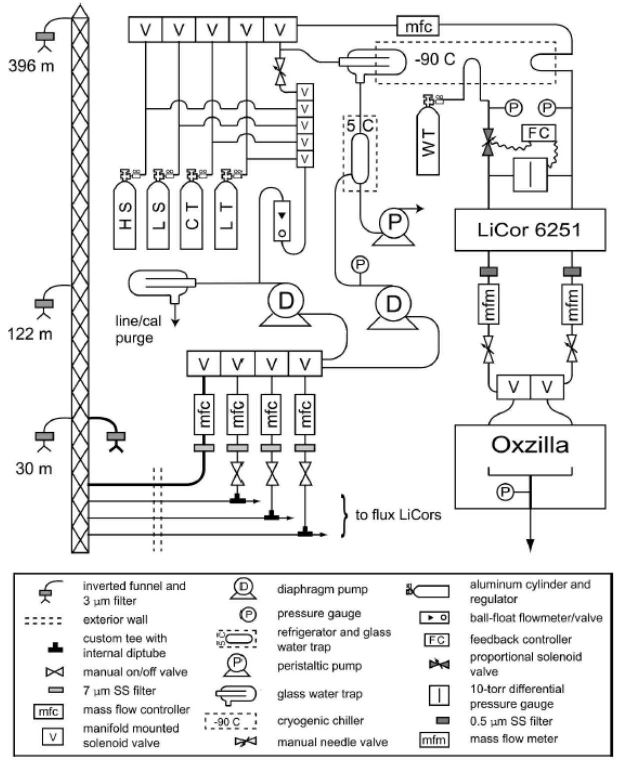


FIG. 1. Schematic and legend showing the gas-handling arrangement as implemented at the WLEF tall tower. Components are included for air sampling, air drying, calibration, regulator and sample line purging, active flow and pressure control, and O_2 and CO_2 analysis.

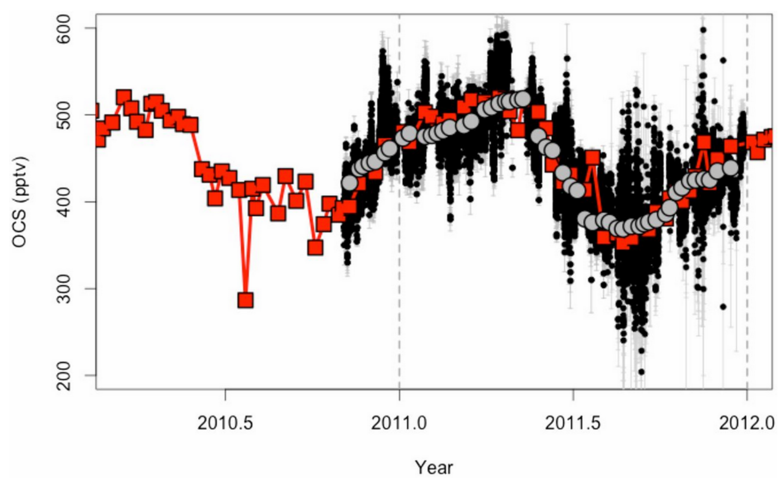
Stephens et al (2007). Journal of Atmospheric and Oceanic Technology **24(1): 82-94.**

Obstacles and challenges

Contrasting example: rapid adoption of COS measurements largely tied to availability of simper analysis methods.

Aerodyne Research

Fig. S1.



Comparison of OCS (pptv; pmol·mol^{-1}) measured by the TILDAS [30-min average (black) with 1σ SDs shown in gray], NOAA flask pair means [red points; 1σ SDs shown as red line error bars (barely visible)], and cosampled TILDAS OCS [3-h average at the time of the flask sample (gray circles)]. The flasks were sampled weekly followed by analysis by GC-MS in Boulder as part of the NOAA flask sample network (1).

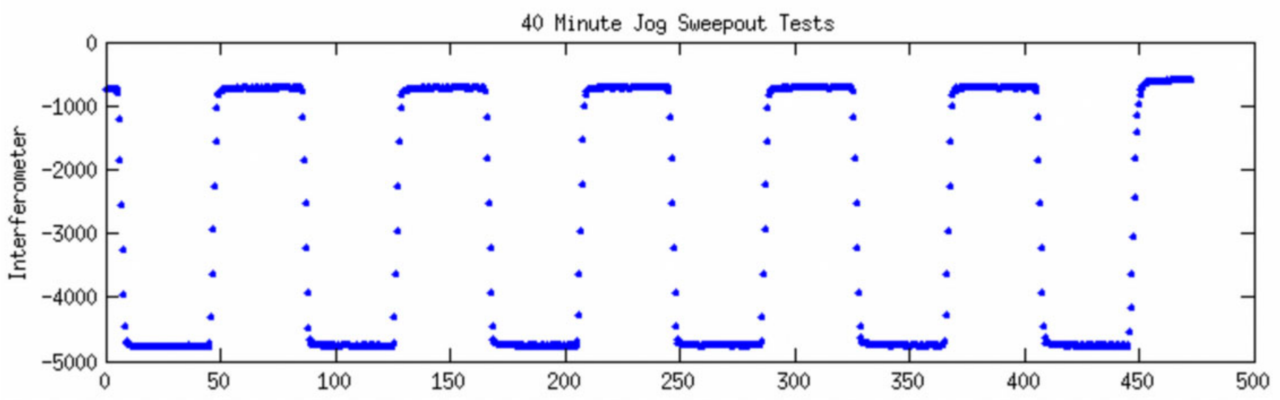
Commane et al, "Seasonal fluxes of carbonyl sulfide in a midlatitude forest." PNAS, 2015

Insert: 2023 span update of Scripps scale

2020 Technical report[1]

Reduced O2/N2 changes by ~ 2% (but time dependent). Did not fully address scale contraction from incomplete sample/reference sweepout

2023 technical report in preparation. Addresses incomplete sweepout



- 2023 correction increases previously reported O_2/N_2 differences by 0.96%.
- Reprocessed all data on new scale: "SIO2023 scale"
- SIO2023 scale is highly consistent with Aoki et al (2021) which identified offset of 0.95% based on comparison with AIST gravimetric scale.

[1]Keeling, R. F., S. J. Walker and B. Paplawsky (2020). Scripps Institution of Oceanography Technical Report, Span Sensitivity of the Scripps Interferometric Oxygen Analyzer. SIO Reference Series, Scripps Institution of Oceanography, UC San Diego**: 1-4**

Opportunities

- Operationalize O_2/N_2 constrain on global carbon and heat budgets (with further improvements, e.g. metallurgy)
- Improved estimating of global and regional O2:C exchange ratios
- Incorporate O_2/N_2 (APO) data assimilation systems to constrain ocean carbon fluxes and biogeochemical processes
- Further improve gas handling methods including further development of gravimetric standards and scale propagation
- Further develop regional applications for fossil-fuel emissions, ecosystem processes, and CCS leakage detection
- Develop “off-the shelf” O_2, CO_2 system that less calibration gas