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

ABSTRACT: High precision measurements of the atmospheric O_2/N_2 ratio have now been made for more than three decades, and have provided great insight into ocean and land biogeochemistry and carbon cycling, particularly via the tracer atmospheric potential oxygen (APO). As the records have grown in length and coverage has improved, the applications have evolved to span not just global and large-scale constraints on carbon cycling, but also regional applications, such as quantifying near-field fossil-fuel emissions, or for studying aspects of ecosystem metabolism. Measurement capabilities have continued to advance, including recent development of highly accurate gravimetric standards for O_2/N_2. While progress has been significant, there are also major obstacles to wider adoption of these methods and wider use of the data.

Many potential applications depend on the feasibility of making high-precision O_2/N_2 measurements directly in the field, using fuel cell or other types of analyzers. But these capabilities are available only to users who are able to build and maintain custom instrumentation and who have a steady supply of calibration gas. Wider adoption will probably require an off-the shelf instrument achieving ~5 per meg precision and much lower usage rates of calibration gas.

Even for groups with long-term O_2/N_2 measurement experience, various obstacles stand in the way of improving data quality, both within and between labs. A better understanding is needed of the sources of variability in the O_2/N_2 (and Ar/N_2) ratios in the gas delivered from high pressure cylinders. The GOLLUM tank intercomparison program is critical to these efforts, but it would help if individual labs experimented with alternate protocols to seek improved methods.

The use of O_2/N_2 data by a wider community is also hampered by the difficulty of incorporating O_2/N_2 data into carbon data assimilation systems, such as NOAA's Carbon Tracker. O_2/N_2 measurements easily resolve signals of ocean processes that are not seen or barely resolvable in atmospheric CO_2 and its isotopes. But to exploit the oceanic signals in O_2/N_2 (or APO), we need assimilation systems with a different architecture, that allow for optimizing ocean interior processes (mixing, circulation, photosynthesis, respiration) which mechanistically link O_2 and CO_2 cycling within the oceans.

Constraints from stable and radio carbon isotope ratios of atmospheric CO_2 on fossil and terrestrial biospheric processes

John Miller

The airborne fraction, and its past and future trajectory, is governed by anthropogenic fossil CO_2 inputs and resultant uptake of atmospheric by land and ocean net sinks. CO_2 mole fraction measurements provide information on the combined effect of fossil emissions and the sinks, and (somewhat weakly) their geographical distribution. As a complement, the ^{14}C:C and ^{13}C:^{12}C ratios of atmospheric CO_2 (expressed as $\Delta^{14}C$ and $\delta^{13}C$), provide a window into the mechanisms driving the net effect. In this talk I will discuss developments over the past decade in applying $\Delta^{14}C$ and $\delta^{13}C$ to better quantify and understand fossil CO_2 emissions, via $\Delta^{14}C$, and some of the mechanisms responsible for terrestrial net ecosystem exchange, via $\delta^{13}C$. Along with our collaborators, we have developed regional and global measurement and modeling programs focused on these tracers. In addition to describing the evolution and current state of these programs, I will discuss the challenges and opportunities for effectively applying these tracers for understanding carbon cycling. One intriguing question that I will touch on is, what is the most profitable way to combine the information contained within atmospheric oxygen, CO_2 mole fraction, and CO_2 isotopic ratio measurements?

Improvements to reference gas cylinder production and calibration at Scripps.

Tim Lueker, Ralph Keeling.

Scripps Institution of Oceanography

In the last few years, we have made several changes to our cylinder filling, spiking, and data management systems that have reduced our turnaround time for providing service to the community, including cylinder filling, mixing, calibration, and delivery.

This presentation will provide updates on:

1) The improved performance of our RIX air compressor (post rebuild).
2) The expansion of our filling station to include 4 more cylinder filling ports.
3) The performance of our new MEECO ™ H_2O analyzer.
4) Improved methodology for minor adjustments to concentrations.
5) Ability to provide standard gases containing calibrated concentrations of N_2O, CO, CH_4 as well as CO_2, O_2/N_2, and Ar/N_2.
6) Computerized database for RIX filling, Corblin compressor transfers, cylinder spiking (concentration adjustments), and cylinder valving.
7) Cylinder inventory including sniff and analysis results and historical gas cylinder collection with tagged cylinders for improved tracking and monitoring.
8) Preparation and calibration of standard cylinders for field projects, using examples of the “LA megacities” and the Barrow AK O2/N2 field instrument.

Evaluation of an influence of the atmospheric minor components on the precise atmospheric oxygen measurements

Nobuyuki Aoki[1], Shigeyuki Ishidoya[1], Yasunori Tohjima[2]

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We developed the standard mixtures for atmospheric oxygen measurements with less than 1 μmol/mol standard uncertainty by using an improved gravimetric method, in which cylinder mass can be measured with a standard uncertainty of 0.8 mg (Aoki et al. 2019), and then conducted a round robin excise among AIST, NIES, TU and SIO using the standard mixtures (Aoki et al. 2021). The intercomparison experiment revealed the relationship in the O_2/N_2 scales among the respective laboratories. However, since the standard mixtures only consist of N_2, O_2, Ar and CO_2 gases, the influence of the atmospheric minor components such as rare noble gases (Ne, He, Kr and Xe), CH_4, and so on, on the precise O_2/N_2 measurements is unclear. To understand the influence of minor components on the precise O_2/N_2 measurements, we prepared gravimetric standard mixtures including not only N_2, O_2, Ar and CO_2, but also minor components of Ne, He, Kr, Xe and CH_4. The pure N_2, O_2, Ar, CO_2 and CH_4 gases were purchased from gas manufactures and then their impurities were determined in our laboratory. The gravimetric mixture of rare gases (Ne, He, Kr and Xe) was also purchased from a gas manufacture. We prepared four gravimetric gas mixtures according to the following procedure: 1) The gravimetric mixture of rare gases, pure CO_2 and CH_4/N_2 were prepared (CH_4/N_2 was also prepared by mixing pure CH_4 and pure N_2). 2) The above prepared mixture and pure Ar were mixed. 3) The mixture prepared in the second step, pure O_2 and pure N_2 were mixed. Mass of source gases filled in cylinders were calculated from the difference in cylinder mass before and after filling the respective source gases. The standard uncertainty of oxygen molar fraction in the above gravimetric gas mixture including the minor components was about 0.7 μmol/mol which was almost same as that in our previously developed standard mixtures of N_2, O_2, Ar and CO_2. To investigate the influences of the minor components on the O_2/N_2 measurement, we compared the measured O_2/N_2 values between the gravimetric mixtures with and without above minor components. In this study, we examined three types of analyzers; a paramagnetic O_2 analyzer (Aoki and Shimosaka, 2018), a mass spectrometer (Ishidoya and Murayama, 2014), and a gas chromatograph equipped with a thermal conductivity detector (Tohjima, 2000). We will discuss the results obtained from the three analyzers in the presentation.

Improving the precision of the Bowdoin/Harvard Forest dataset *ex post facto*

Edie Salzig & Mark Battle (Bowdoin College)

We have recently been revisiting the processing of our data from Harvard Forest, both the already-published dataset and recently collected data. This presentation will focus on the details of this reanalysis of the Harvard Forest CO_2 and O_2 datasets. While specific to our instrument, we hope that the lessons we have learned will be of interest to, and useful for, a broader audience.

Our system at Harvard Forest uses an Oxzilla II fuel cell analyzer for oxygen measurements and a LiCor Li7000 for CO_2 measurements. To monitor the system, pressures and flows are actively managed and recorded. These data are useful in investigating the quality of measurements produced by the Oxzilla and LiCor. Our work focuses on three possible techniques for improving the precision and accuracy of these measurements. First, we examine the role of pressure variations between the two fuel cells of the Oxzilla. We then consider the method by which we calculate the CO_2 values after initiating a calibration run. Finally, we look at the impact that flow imbalances have on Oxzilla precision.

Since our instrument is in constant use at the field site, we base our assessment of performance on the measurements of standard tanks (calibration runs), that are conducted at least four times daily during routine sampling. As we will show, these data provide us with insight into both the intrinsic instrumental limitations and the impact of gas handling on measurement precision.

Markus Eritt

O2/N2 measurements in the ICOS network

ICOS is a European network for the measurement of greenhouse gases. Within ICOS, O2/N2 measurements are performed on flask samples in the Flask and Calibration Laboratory of the Central Analytical Laboratory (CAL-FCL) in Jena.
The presentation will focus on three topics:
- introduction of our newly built mass spectrometric setup for O2/N2 measurements at the ICOS CAL-FCL in Jena and its capabilities.
- flask samples within ICOS are taken with a standardised, automated flask sampling system developed and built in our laboratory. Among other possibilities, our Flasksampler allows the collection of over one hour averaged air samples by adjusting the flask purge rate. The adjustment of the sample air flow through the flasks comprises a T-connection. I will explain our flask sampling setup, which shows no measurable O2/N2 fractionation effects.
- our Flasksampler is drying the sample air down to a dew point of only -40°C. I will present first results of humidification experiments showing the influence of sample humidity on mass spectrometric O2/N2 measurements.

Results from the "GOLLUM" O_2 intercomparison programme

Andrew C. Manning, Marica Hewitt, Alex Etchells, Mai Hong,

and participants from all high-precision atmospheric O_2 laboratories

Centre for Ocean and Atmospheric Sciences, School of Environmental Sciences, University of East Anglia, Norwich, United Kingdom

There is currently no single international calibration scale for reporting atmospheric O_2/N_2 measurements, making it difficult to use O_2/N_2 data sets collected by different laboratories in collaborative projects and joint modelling efforts. Quality control of the data sets is also compromised without an international scale. The "Global Oxygen Laboratories Link Ultra-precise Measurements" (GOLLUM) programme was established to help address these deficiencies, by quantifying laboratory offsets for the different O_2/N_2 calibration scales. Even if two organisations are nominally on the same scale, it is nevertheless essential to quantify laboratory offsets, and to establish possible time-varying or mole fraction dependencies for such offsets.

The GOLLUM programme first ran for eleven years (2004-2015), resuming in 2021 with eleven laboratories involved. The programme consists of repeated analyses of six high pressure cylinders of air, in two sets of three, which are circulated sequentially and continuously to all participating laboratories. We present the results that have been collated from the O_2/N_2 analyses of these cylinders from all participants, and include results from CO_2 analyses, where available. We discuss possible drifts in the cylinders' O_2/N_2 (and CO_2) values over time and how to address this. We also examine potential changes in offsets over time at any of the participating laboratories, as well as mole fraction dependencies of these offsets. Finally, we discuss possible next steps that the community might like to consider with regard to combining O_2/N_2 data sets, including soliciting advice from the modelling community.

Using atmospheric oxygen in the global carbon budget and monitoring systems

Ingrid Luijkx

There is a growing interest in using atmospheric oxygen measurements in greenhouse gas monitoring and verification systems, as well as in the annually updated global carbon budget (GCB) papers. In this talk, I would like to show the current use of atmospheric oxygen in the GCB methods and discuss future additional analyses that our community can offer. Currently, atmospheric O_2 is used as a validation metric for both the ocean and land components of the global carbon budget. Here, there are some key challenges and assumptions that are made, which are related to the interpretation of the land and ocean sinks estimated by the O_2 method. I would like to discuss the adjustments that need to be made to compare top-down and bottom-up methods, which are related to the lateral transport of carbon by rivers from land to ocean, and that are also applied to other components in the budget, including the atmospheric inversions. Furthermore, I would like to discuss the possibilities for having a larger visibility for the O_2 based land and ocean sink estimates, for which the GCP core team expressed a large interest at the recent GCP workshop in Exeter. At WAO4, I would like to update on the outcomes and possibilities for the O_2 community, and I will give an update of two recently started EU projects in which O_2 is going to be used for CO_2 emission verification (PARIS and CORSO).

What can Atmospheric Potential Oxygen tell us about the evolution of the ocean carbon sink?

E. A. Kozlova, A. J. Watson, University of Exeter, UK

R. F. Keeling, Scripps Institution of Oceanography, USA

M. Heimann, Max Planck Institute for Biogeochemistry, Germany.

Abstract:

We examine the magnitude and evolution of the global ocean sink for atmospheric carbon dioxide over the last 30 years through the analysis of atmospheric CO_2 and O_2/N_2 observations from Scripps Institution of Oceanography and Max Planck Institute for Biogeochemistry flask networks. We derive a latitude- and time-varying product describing global surface atmospheric potential oxygen (APO), and from this an estimate of the CO_2 sinks, particularly the flux into the ocean. This independent estimate can be compared to the more widely used methods of ocean biogeochemical models or surface ocean CO2 observation products, which are the techniques currently used by the Global Carbon Project to derive the ocean sink in their annual budgets. Those methods, however, do not agree as to the rate of change of the ocean sink over recent decades and predict increasingly divergent values. The APO observations indicate a rapid increase in the ocean sink through the years 2000-2015, similar to the surface ocean data products, and faster than that indicated by models. However, over the period of 2015-2020 they suggest this increase had stalled.

Global budget imbalances in O_2 and APO

and

Constraining the Southern Ocean CO_2 sink variability with observation-based O_2 fluxes

Nico Mayot[1], Corinne Le Quéré[1], Christian Rodenbeck[2], and Andrew C. Manning[1]

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The concept of a global carbon budget imbalance (BIM_{CO2}) was first introduced in Le Quéré et al. (2018: https://doi.org/10.5194/essd-10-405-2018). It refers to the mismatch between estimated fossil fuel (FF) and land-use change (LUC) CO_2 emissions, and the estimated land (L) and ocean (O) carbon sinks plus the observed accumulation of CO_2 in the atmosphere (ΔCO_2). In other words:
$BIM_{CO2} = FF + LUC - L - O - \Delta CO_2$. We present an extension of this concept, introducing BIM_{O2} and BIM_{APO}, adapted from the global budget equations of O_2 and APO, respectively. Our preliminary analyses suggest that the main driver of variability in both BIM_{O2} and BIM_{APO} is variability in estimates of ocean O_2 outgassing. We also found a small but statistically-significant upward trend in both BIM_{O2} and BIM_{APO} (over the period 1993-2020), which we think is owing to an overestimation of ocean O_2 outgassing, and/or an underestimation of the ocean carbon sink coupled with an overestimation of the land carbon sink.

The Southern Ocean is a major sink of atmospheric CO_2, but the nature and magnitude of its variability remains uncertain and debated. Estimates based on observations suggest substantial variability that is not reproduced by process-based ocean models, with increasingly divergent estimates over the past decade. We examined potential constraints on the nature and magnitude of climate-driven variability of the Southern Ocean CO_2 sink from observation-based air–sea O_2 fluxes. On interannual time scales, the variability in the air–sea fluxes of CO_2 and O_2 estimated from observations is consistent across the two species and positively correlated with the variability simulated by ocean models. Our analysis suggests that variations in ocean ventilation related to the Southern Annular Mode are responsible for this interannual variability. On decadal time scales, the existence of significant variability in the air–sea CO_2 flux estimated from observations also tends to be supported by observation-based estimates of O_2 flux variability. However, the large decadal variability in air–sea CO_2 flux is absent from ocean models. Our analysis suggests that issues in representing the balance between the thermal and non-thermal components of the CO_2 sink and/or insufficient variability in mode water formation might contribute to the lack of decadal variability in the current generation of ocean models.

Toward a more complete global oxygen budget: The impact of processing metal oxides and sulfur.

Mark Battle, Raine Raynor, Ralph Keeling and Stephen Kesler.

Over the last three decades, our characterization of the long-term, global atmospheric oxygen budget and its connections to the carbon cycle has become increasingly nuanced. Originally including just fossil fuel combustion and the terrestrial biosphere, the budget has been updated to include fluxes driven by ocean warming, both directly (solubility) and indirectly (stratification). However, to date, the community has largely ignored oxygen fluxes associated with the processing of minerals for industrial and manufacturing purposes. Said differently, we have been ignoring the small fraction of fossil fuel oxidation by oxide ores that occurs during refining of metals, and thereby overestimating losses of atmospheric O_2. Here, we address this deficiency by quantifying the effective O_2 fluxes associated with the processing of iron, aluminum and copper. We also consider the potential impact of sulfur.

We find that consideration of the oxygen mobilized during metal processing (equivalent to a net O_2 flux of $12.0^{+0.2}{}_{-0.4}$ Tmol a^{-1}) leads to an increased estimate of ocean carbon uptake in the years 2000-2010 of $0.144^{+0.002}{}_{-0.005}$ Pg a^{-1} of carbon with a corresponding decrease in estimated land uptake. A rough estimate of oxygen uptake due to sulfur chemistry during fossil fuel combustion (2.4Tmol a^{-1}) decreases ocean carbon uptake but by a much smaller amount. We will also briefly discuss the possibility of a more sophisticated estimate of the impacts of sulfur.

These corrections are small compared to existing estimates of the fluxes and their uncertainties ((2.27±0.60) and (1.05±0.84) Pg a^{-1} of carbon for ocean and land respectively (Keeling and Manning, 2014)) but should be employed in future analyses.

The APO Forward model intercomparison experiment

Britton Stephens, Matt Long, Frederic Chevallier, Yuming Jin, Ralph Keeling, Ingrid Luijkx, Shamil Maksyutov, Eric Morgan, Yosuke Niwa, Prabir Patra, Christian Roedenbeck, Jesse Vance

We are conducting a forward transport model intercomparison based on simulation of atmospheric potential oxygen (APO) and its components (O_2, CO_2, and N_2), using different models and source fields. This effort was initially motivated by a need for a diverse set of transport simulations to support hemispheric scale APO flux estimates from spatially and temporally sparse airborne campaign, surface station, and shipboard observations, but has grown to support other applications. These include evaluation of transport biases in models used for global inversions of APO and other species, support for CO2 and APO flux estimates over the Southern Ocean, and assessments of oceanic and fossil-fuel contributions to O2 and CO2 signals, and their ratios, observed at terrestrial sites.

A total of seven international modeling groups have contributed output from eight unique forward transport simulations. The base set of required simulations used 10 flux tracers, including air-sea APO fluxes from the Jena APO inversion, air-sea CO2 fluxes from both a pCO2 climatology and CESM, air-sea O2 fluxes from both a dissolved gas climatology and CESM, air-sea N2 fluxes derived from two different heat flux reanalyses, two fossil fuel CO2 flux products, and one fossil fuel O2 flux product. All contributors submitted concentration output matching ObsPack records for a common set of 10 Scripps O2 Program stations, a series of global aircraft campaigns, the AIST/JMA aircraft record, and the ARSV L.M. Gould shipboard record. Many modelers provided additional optional contributions, including: daily mean 3D fields; output matching the full set of NOAA ObsPack records; hourly time series at a list of 58 fixed sites; output matching three additional shipboard records; temperature, pressure, and humidity values; and concentration output from terrestrial CO2 and independent inversion fluxes.

We plan to make all output available to the community. We will describe the intercomparison experiment and report on preliminary results.

Intensified oxygen uptake in the Southern Ocean revealed by bubble-mediated model

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The oxygen exchange across the atmosphere-ocean interface (i.e. air-sea O_2 flux) has been recognized as a potentially crucial factor influencing oxygen distributions in the ocean. Nevertheless, our understanding of the underlying processes remains insufficient, leading to systematic discrepancies between observation and model simulations. Here we integrate the buble-miediated parameterization into the Community Earth System Model (CESM) to investigate the role of bubbles in the abovementioned air-sea gas transportation. Our results reveal an intensified oxygen uptake associated with bubble injection in the widespread Southern Ocean regions. Furthermore, a stronger response of the air-sea O_2 flux to global warming has been found under the bubble-mediated model. These findings emphasize the significance of the bubble injection effect in explaining air-sea oxygen exchange. The absence of gas transfer descriptions associated with collapsing bubbles in current models might lead to a severe underestimate in sensitivity of ocean oxygen cycle to climate change.

The suitability of atmospheric oxygen measurements to constrain Western European fossil-fuel CO_2 emissions and their trends

Christian Rödenbeck[1], Karina E. Adcock[2], Markus Eritt[1], Maksym Gachkivskyi[3], Christoph Gerbig[1], Samuel Hammer[3], Armin Jordan[1], Ralph F. Keeling[4], Ingeborg Levin[3], Fabian Maier[3], Andrew C. Manning[2], Heiko Moossen[1], Saqr Munassar[1], Penelope A. Pickers[2]*, Michael Rothe[1], Yasunori Tohjima[5], and Sönke Zaehle[1]

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Atmospheric Potential Oxygen (APO) data over continents have been proposed as a constraint on CO_2 emissions from fossil-fuel burning. Here we assess the suitability of such APO data to constrain anthropogenic CO_2 emissions in Western Europe, with particular focus on their decadal trends. We use an inversion of atmospheric transport to estimate spatially and temporally explicit scaling factors on a bottom-up fossil-fuel emissions inventory. Based on the small number of currently available observational records, our CO_2 emissions estimates show relatively large apparent year-to-year variations, exceeding the expected uncertainty of the bottom-up inventory and precluding the calculation of statistically significant trends. We were not able to trace the apparent year-to-year variations back to particular properties of the APO data. Inversion of synthetic APO data, however, confirms that data information content and degrees of freedom are sufficient to successfully correct a counterfactual prior. Larger sets of measurement stations, such as the recently started APO observations from the Integrated Carbon Observation System (ICOS) European research infrastructure, improve the constraint and may ameliorate possible problems with local signals or with measurement or model errors at the stations. We further tested the impact of uncertainties in the O_2:CO_2 stoichiometries of fossil-fuel burning and land biospheric exchange and found they are not fundamental obstacles to estimating decadal trends in fossil-fuel CO_2 emissions, though further work on fossil-fuel O_2:CO_2 stoichiometries seems necessary.

Atmospheric Potential Oxygen over the Atlantic Ocean

Dieu Anh Tran[1], Penelope A. Pickers[2], Andrew C. Manning[2], Christian Rödenbeck[1], and Leigh S. Fleming[2,3].

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Abstract

We present continuous observations of Atmospheric Potential Oxygen (APO), a tracer derived from carbon dioxide (CO_2) and oxygen (O_2) measurements, collected from a commercial container ship operated by Hamburg Süd Group, sailing between Hamburg, Germany (53.6°N, 10.0°E) and Buenos Aires, Argentina (34.6°S, 58.4°W). The ship operates continuously and takes 8 weeks to travel from Hamburg to Buenos Aires and back to Hamburg. Our dataset provides unique information, as it represents the only meridional transects of continuous atmospheric O_2 and CO_2 over the Atlantic Ocean, collected from 2014 to 2019. The data show a step change in both atmospheric O_2 and CO_2 time series corresponding to the (seasonally-varying) position of the Intertropical Convergence Zone (ITCZ), which we determined independently from the Global Precipitation Climatology Project (GPCP) daily precipitation data. Our updated Atlantic Ocean APO data also show significant equatorial outgassing bulges in most years, but not during 2015 and 2016. The suppression of the equatorial bulge during these two years could be owing to the development of El Niño conditions. Modelled APO from "Jena CarboScope" (https://www.bgcjena.mpg.de/CarboScope/) using the TM3 atmospheric transport model does not exhibit a bulge over the Atlantic in any year. This model-observation mismatch suggests that either there are inaccuracies in the oceanic flux data products in the equatorial Atlantic Ocean region, or that there are atmospheric transport inaccuracies in the model, or a combination of both. The Hamburg Süd APO dataset has the potential to constrain modelled meridional transport of heat and carbon in the Atlantic Ocean, since the thermally-induced gas fluxes of O_2 and CO_2 are closely tied to the net air–sea heat flux.

Average seasonal cycles of atmospheric potential oxygen (APO) in the Pacific region: possible autumn oceanic O_2 emissions

Yasunori Tohjima[1], Tomoko Shirai[1], Misa Ishizawa[2], Hitoshi Mukai[1], Toshinobu Machida[1], Motoki Sasakawa[1], Yukio Terao[1], Kazuhiro Tsuboi[3], and Shin-ichiro Nakaoka[1]

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To investigate spatiotemporal variations in atmospheric O_2 and CO_2 concentrations in the Asia-Pacific region, we have been collecting air samples into glass flasks at Hateruma Island (HAT; lat. 24.1°N, long. 123.8°E) since July 1997, at Cape Ochi-ishi (COI; lat. 43.2°N, long. 145.5°E) since December 1999, and at Minamitorishima (MNM; lat. 24.3°N, long. 154.0°E) since September 2011. Air samples have also been collected onboard cargo ships during regular roundtrip cruises to North America and New Zealand/Australia since December 2001 and to Northeast Asia since September 2007. Concentration data derived from these samples showed clear seasonal cycles, secular trends, and spatial variations. In this presentation, we focus on spatial differences in the average seasonal cycles of atmospheric potential oxygen (APO = $1.1\times CO_2 + O_2$). First, we binned APO data from cargo ships into distinct 10°×10° cells. Then, we calculated average APO seasonal cycles at the three fixed sites (HAT, COI, and MNM) and in the 42 10°×10° cells. Observed peak-to-peak seasonal cycle amplitudes increased poleward in both hemispheres, from their lowest value near the Equator, and decreased eastward in the North Pacific. Observed seasonal cycles were subsequently compared with simulations using climatological ocean O_2 fluxes, prepared from monthly heat flux anomalies by Garcia and Keeling (2001), and an atmospheric transport model (NIES-TM). Although the observed seasonal cycles were generally well reconstructed by the simulation, there were slight discrepancies: the simulated peak-to-peak amplitudes were approximately 5% larger than the observation, and the simulated seasonal cycles consistently exhibited a few weeks phase lead. In addition, consistent APO enhancements observed in the fall and winter were not well reproduced by the model simulation. Assuming that atmospheric mixing was correctly expressed in the model, the observed fall-winter enhancements suggest additional O_2 emissions that are not included in the climatological O_2 fluxes of Garcia and Keeling (2001). The magnitude of the fall-winter enhancements was less than 15 per meg in the 10°×10° bins between 40°S and 20°N, but exceeded 15 per meg between 20°N and 50°N. We attribute these fall-winter APO enhancements to oceanic O_2 emissions likely associated with autumn blooming in the northern North Pacific and, partially, with the disappearance of the subsurface shallow oxygen maximum (SOM).

Diverging trends in the seasonal cycle in APO at 3 northern high latitude sites in the SIO Network

Cynthia Nevison

Atmospheric oxygen has been measured by the Scripps Institution of Oceanography (SIO) Network since the 1990s at a range of surface monitoring sites in both hemispheres, including 3 at northern high latitudes: Alert, Canada (ALT), Barrow, Alaska (BRW), and Cold Bay, Alaska (CBA). Oxygen measurements are reported in terms of deviations in the O_2/N_2 ratio and can be combined with co-measured atmospheric CO_2 to define atmospheric potential oxygen (APO ~ $O_2/N_2 + \alpha\ CO_2$), where the coefficient α is not precisely known but thought to be about 1.1. The $\alpha\ CO_2$ term is designed to largely remove the influence of terrestrial photosynthesis and respiration on atmospheric oxygen in order to isolate the influence of oceanic air-sea O_2 fluxes. APO data show both a long-term decreasing secular trend, the result of fossil fuel combustion, and small, annually repeating seasonal cycles, which are driven mainly by spring/summer outgassing of oxygen due to photosynthetic production in the surface ocean, followed by in-gassing due to fall/winter ventilation of O_2-depleted subsurface waters. Over the last 30 years, the APO seasonal cycle amplitude (SCA) has increased at CBA, declined at BRW and not changed significantly at ALT. Disparate trends in the shape of the seasonal cycle, as defined by the date of positive and negative zero crossing, also are observed among the 3 sites. This talk will examine the possible causes of these diverging trends in the APO SCA across the 3 sites as well as their sensitivity to uncertainties in the $\alpha\ CO_2$ term.

Changes in the Seasonal Cycle of APO at Cold Bay, Alaska

E. Morgan[1], M. Manizza[1], C. Nevison[2], R. Keeling[1]

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The Scripps O2 program has operated a flask sampling station at Cold Bay, Alaska (CBA) since 1995, as part of its global flask network. The CBA record is notable for the large number of positive outliers which can be seen during spring and summer in atmospheric potential oxygen (APO) . The amplitude of the APO seasonal cycle has also been increasing since 2006, with large interannual variations. The variability in the amplitude is due to both to the prevalence of enhancements of APO during spring/summer and variations in the depth of the winter minima. In order to investigate the changing seasonal cycle at CBA, use a combination of atmospheric transport modeling, in situ and satellite observations, and ocean biogeochemical models. Trends in the APO amplitude are correlated with the amplitude of Ar/N2, suggesting that the drivers of variations in seasonal exchange have a strong solubility component. This is also supported by increase in the seasonal amplitude of sea surface temperature (SST) in the Bering Sea and subpolar North Pacific, and by the observed seasonal amplitude of surface chlorophyll, which has been decreasing over the last 10-15 years. Most of the models examined fail to reproduce some or all of these features, suggesting deficiencies in the representation of mixed layer physics and biogeochemistry.

Decadal variability and long-term trend in the northern APO deficit.

Ralph Keeling (SIO), Yuming Jin (SIO)

The tracer atmospheric oxygen (APO ~ O_2 + 1.1 CO_2) varies on a wide range of space and time scales, including exhibiting an interhemispheric gradient with lower APO in the Northern Hemisphere. This northern deficit has been detected in flask data from surface stations (Stephens et al., 1998, Keeling et al., 2010), from ships (Tohjima et al., 2005), and in airborne measurements (Resplandy et al., 2016). This northern APO deficit has contributions from fossil-fuel (FF) burning, oceanic uptake of anthropogenic CO_2 (C_{anth}) as well as from imbalances in the natural exchanges of O_2, CO_2, and N_2 in the two hemispheres. This natural component, which can be resolved by correcting the observed deficit for the FF and C_{anth} components, have been provides a constraint on interhemispheric heat transport by the oceans (Resplandy et al., 2016) connected in part to the Atlantic meridional overturning circulation (AMOC). As shown in Keeling et al (2010) the northern deficit also exhibits considerable interannual and decadal variability.

Here we update the time series for the northern deficit, and discuss its variability over the full 30+ year time frame of the APO measurements. The deficit, as calculated based on a three-station set (ALT, LJO, CGO), has varied between a high of ~11 per meg (achieved twice in the early 1990s and ~2007) and a low of ~zero (achieved 3 times in 2000, 2016, and 2022), with considerable decadal variability but also with persistence on shorter time scales. Based on the long-term increases in the FF and C_{anth} contributions, the deficit is expected to have increased over time. Instead, the deficit has decreased over the 30 years. The decadal variability and long-term trend appear robust against systematic errors from drifting reference gases and from sampling artifacts. Reference gas drift can be discounted because it must influence stations in both hemispheres equally, and errors from sampling artifacts can be bounded using different station sets and by correcting the data for fractionation artifacts using Ar/N_2 measurements (available since 2003).

So why is the deficit so variable, and why is it trending in the wrong direction? Changes in AMOC? Anti-correlated variations in ventilation in the northern and southern hemispheres? This talk will offer a few speculations.

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Seasonal Air-sea Atmospheric Potential Oxygen Flux Inferred from Global Airborne Observations

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We present an analysis of the seasonal air-sea APO flux cycles, resolved using airborne APO observations from HIPPO, ORCAS, and ATom campaigns. We organize the APO data to resolve the season cycles within airmasses aligned with a mass-index isentropic coordinate, and we invert the data using a box model aligned with the same coordinate to resolve the flux cycles on two spatial scales: (1) hemispheric scale; (2) coarse latitude bands over the Southern Ocean (SO). The fluxes are broadly consistent with earlier inverse modeling based on surface APO data, and with the Garcia and Keeling (2001) climatology, but also resolve distinct differences.

On the hemispheric scale, we resolve clear seasonal cycles in both hemispheres, with the ocean releasing APO in the spring and summer and taking up APO in the fall and winter. We find a larger seasonal net outgassing of APO in the Southern Hemisphere (518±52.6 Tmol) than in the Northern Hemisphere (342±52.1 Tmol). We also find clear differences in APO phasing and amplitude between the two hemispheres, implying distinct physical and biogeochemical mechanisms driving the air-sea O_2 fluxes. In the Northern Hemisphere, we resolve a period of weak APO outgassing in the northern late summer and fall. This signal is likely related to the development of the subsurface oxygen maximum zone over the subtropical Pacific, which stores springtime photosynthetically produced O_2 below the mixed layer, and delays the O_2 outgassing until the fall, when the mixed layer deepens. This feature is noted by ship-based APO observations (Ishidoya et al. 2016) and is also confirmed by Argo float measurements over the western subtropical North Pacific, which show clear oxygen supersaturation beneath the mixed layer from May to November.

In the mid-latitudes of the Southern Hemisphere, we resolve two seasonal APO outgassing peaks. One of these occurs as expected in spring-summer, and the other in the fall. We interpret the second feature as arising from a fall bloom, which is also resolved in satellite chlorophyll data. We also show that the Jena inverse model configuration, which relied exclusively on station data from the Scripps network, has discrepancies with the airborne data at lower latitudes in the Southern Hemisphere where there is a major gap in the Scripps network. This discrepancy is reduced in configurations that combine the Scripps station data with western Pacific shipboard samples from the National Institute for Environmental Sciences (NIES).

Our estimates of seasonal SO APO flux cycles have implications for better understanding the SO carbon uptake. Comparing APO flux cycles with CO_2 flux cycles derived using the same airborne data, we find a distinct anti-correlation in the high-latitudes (south of 43°S), implying a biological-dominated air-sea CO_2 flux cycle. In the mid-latitudes (43°S to 33°S), however, the two cycles have a complex relationship, suggesting important influences from both temperature-driven solubility changes and biological production/mixing processes. In addition, the airborne APO and CO_2 separately provide constraints on atmospheric diabatic mixing rates (mixing across isentropes) in the Southern Hemisphere, suggesting that most atmospheric transport models (ATMs) used in inversion products overestimate diabatic mixing in this region.

Interannual variations in δ(APO) and δ(Ar/N_2) at the surface and gravitational separation in the stratosphere

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We have conducted the tropospheric and the stratospheric observations of major atmospheric components using air monitoring networks of Japanese research institutes (https://www.jsps.go.jp/file/storage/grants/j-grantsinaid/12_kiban/ichiran_r04/e-data/r_4_en_22h05006.pdf). In this talk, we present observational results of δ(APO) (APO=O_2+1.1xCO_2) and δ(Ar/N_2) at the surface since 2012 (updated from Ishidoya et al., 2021), and gravitational separation (GS) in the lower-to-middle stratosphere since 1989, evaluated by using δ(Ar/N_2) and stable isotopic ratios of N_2, O_2 and Ar (updated from Ishidoya et al., 2013). It has been reported by past studies that seasonal and interannual variations in δ(APO) are driven mainly by the air-sea O_2 and N_2 fluxes, while atmospheric Ar/N_2 ratio (δ(Ar/N_2)) varies due only to air-sea Ar and N_2 fluxes. As to the air-sea exchange, Ar and N_2 fluxes are driven by solubility change, and O_2 flux is driven by both solubility and biospheric changes. Therefore, it is expected that we can separate an interannual variation in δ(APO) due to the solubility change ($\delta(APO)_{therm}$) from that due to the net marine biological activities ($\delta(APO)_{netbio}$) by a combined analysis of δ(APO) and δ(Ar/N_2). The annual change rate of the average $\delta(APO)_{therm}$ at four sites of which data periods are longer than 10 years (Tsukuba (36°N, 140°E), Hateruma Island (24°N, 124°E), Cape Ochiishi (43°N, 146°E) and Takayama (36°N, 137°E), Japan) was found to vary in phase with the Southern Oscillation Index (SOI) and the annual change rate of the global ocean heat content (OHC). On the other hand, the corresponding annual change rate of the average $\delta(APO)_{netbio}$ varied in opposite phase with SOI. Ishidoya et al. (2021) also suggested secular trend in the surface δ(Ar/N_2) is modified by GS changes in the stratosphere. Recently, we analyzed archived air samples collected in the lower-to-middle stratosphere over Japan since 1989 to clarify long-term variations in GS. It was found that the vertical gradients of GS vary roughly in opposite phase with the middle stratospheric mean age of air (AoA). If we follow the 2-D model simulation by Ishidoya et al. (2013), then secular enhancement of the Brewer-Dobson circulation is suggested from the relationships between the observed long-term changes in GS and AoA. The average OHC increase rates estimated based on the secular trends in the surface δ(Ar/N_2) and the stratospheric GS, assuming a one-box ocean, was consistent with that reported by ocean temperature measurements. However, there are many issues left unsolved for GS such as fluctuations found in each observed vertical profile which have not been reproduced by the 2-D and 3-D model. Moreover, interannual variation in the surface δ(Ar/N_2) is much larger than that expected from the global average air-sea heat flux from the OHC by ocean temperature measurements. Therefore, more studies are needed both for observations and simulations to understand detail mechanisms of the spatiotemporal variations in δ(Ar/N_2) and GS.

Short-term and long-term variations of atmospheric CO_2 and O_2 observed at Ny-Ålesund, Svalbard

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In this presentation, we will present the following two topics.

1) Continuous measurements of the atmospheric CO_2, $\delta(O_2/N_2)$ were started in 2012–2013 at Ny-Ålesund (78º55'N, 11º56'E), Svalbard. In this study, we analyzed short-term CO_2 increasing events by using continuous CO_2, $\delta(O_2/N_2)$ and CO (Myhre et al., 2020) data and footprints calculated by Lagrangian particle diffusion model (FLEXCPP, Zeng, et al., 2013). Correlation analysis of the continuous CO_2, $\delta(O_2/N_2)$ and CO data identified a total of 868 short-term CO_2 increase events which were attributable to fossil fuel combustion between 2012 and 2019. We calculated the amount of CO_2 increase by the fossil fuel combustion at Ny-Ålesund by using the footprint of air parcels and the statistics of the fossil fuel CO_2 emission (ODIAC). The estimated values for the CO_2 events originating from Europe area are in good agreement with the observed CO_2 increase. The distribution of the oxidative ratios (OR) of fossil fuel burning in Europe were also examined using continuous CO_2 and O_2 data and footprints. The OR values calculated from observations were generally consistent with those estimated from statistical data, but partly lower than those estimated in the previous study (Steinbach et al., 2011).

2) To elucidate contributions of the terrestrial biosphere and the ocean to the CO_2 cycle on the earth's surface, we have conducted systematic observations of the CO_2 mole fraction, carbon isotopic ratio of CO_2 ($\delta^{13}C$) and $\delta(O_2/N_2)$ in the atmosphere at Ny-Ålesund, Svalbard since 1991, 1996, 2001, respectively. The CO_2 mole fraction shows clear seasonal cycles superimposed on the secular increase with an average rate of 2.0 ppm yr^{-1} for the period 1996–2020. On the other hand, $\delta^{13}C$ and $\delta(O_2/N_2)$ decrease secularly at an average rate of −0.024 ‰ yr^{-1} for 1996–2020, and −22.6 per meg yr^{-1} for 2001–2020, respectively. Based on the observed secular trends of the CO_2 mole fraction and $\delta(O_2/N_2)$ (O_2-method), the average terrestrial biospheric and oceanic CO_2 uptakes during 2001–2020 were estimated to be 1.5 ± 0.8 and 2.5 ± 0.6 GtC yr^{-1}, respectively. By using the observed CO_2 and $\delta^{13}C$ ($\delta^{13}C$-method), the corresponding CO_2 uptake of 1.2 ± 0.8 and 2.8 ± 0.6 GtC yr^{-1} were obtained for the same period. The terrestrial biospheric CO_2 uptake derived by the $\delta^{13}C$-method showed large inter-annual variability in association with El Niño events. On the other hand, the oceanic uptake increased secularly with less inter-annual variability during 1996–2020. The oceanic CO_2 uptake of the decadal periods (2001–2010, 2004–2013, 2008–2017, and 2011–2020) estimated by the O_2-method also showed an increasing trend. These uptake rates and the increasing trends estimated in this study agree with those reported by the Global Carbon Project (GCP) within the estimation uncertainty.

Continuous measurements of atmospheric oxygen in the United Kingdom

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We present continuous atmospheric measurements of O_2 and CO_2 from two locations in the United Kingdom: a 12-year time series from a coastal site at the Weybourne Atmospheric Observatory (WAO; 52.95°N, 1.12°E; recently published in ESSDD: doi.org/10.5194/essd-2023-129), consisting of 1.5 million O_2 and 1.9 million CO_2 two-minute measurements made between May 2010 and December 2021; and a more recent record from the Heathfield tall tower, established in 2021 (HFD; 50.98°N, 0.23°E; an inland station south of London). Air is sampled at HFD from a height of 100 m a.g.l and at WAO from a height of 10 m a.g.l.

For both stations, we describe details of our measurement system and present the main features of the datasets, including long-term trends (for WAO), seasonal cycle amplitudes, diurnal cycles and O_2:CO_2 ratios. We assess synoptic variability from both stations and discuss the level of (dis)agreement between the stations, which are approximately 230 km apart. For the WAO datasets we also show results from using curve fitting software to investigate trends and interannual variability in the long-term trends and seasonal cycle amplitudes of O_2, CO_2 and APO.

Evaluation of the diurnal cycle of O_2 and CO_2 above the canopy of a forest and its application to further constrain the forest carbon balance

Kim Faassen

We measured O_2 and CO_2 at two heights above a boreal forest, in Hyytiala Finland, to get a better understanding of the diurnal variability of both O_2 and CO_2 and their O_2:CO_2 ratios, called the Exchange Ratio (ER). O_2 was measured with a fuel cell instrument (Oxzilla) and CO_2 with an NDIR instrument (Uras). We evaluate two methods to calculate the ER of the boreal forest: 1) based on a single measurement height, where the slope of the linear regression of the mole fractions of O_2 and CO_2 is the ER of the atmosphere (ER_{atmos}) and 2) based on the vertical gradient of O_2 and CO_2 where the ratio of the resulting surface fluxes is the ER of the forest (ER_{forest}). We found that the fluxes-based approach (ER_{forest}) gives a more accurate representation of the processes driving the forest exchange compared to ER_{atmos}. We found ER_{forest} values between 0.84 ± 0.26 and 1.03 ± 0.05 (for the 24h period and night time respectively) and an estimation for the ER of assimilation (ER_a) of 0.96 ± 0.12. We analysed the diurnal cycle of the ER_{atmos} signal in more detailed as the data shows some unexpected values larger than 2. For this analysis we used a one-box model. The model results show that the high influence of entrainment of air from the free troposphere which causing the signal to be highly influenced by non-local processes, and therefore not equal to ER_{forest}. The combination of non-local and local processes with their own ER signals can result in an unexpected ER_{atmos} signal that cannot be related to a single process. We show the potential to use the O_2/CO_2 ratio to not only disentangle the processes in the carbon balance of the forest, but also to use this ratio and the difference between ER_{atmos} and ER_{forest} to get more insight into the contributions from non-local processes to the diurnal CO_2 cycle above a forest.

What can ecosystem-scale oxygen measurements tell us about the terrestrial carbon cycle?

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This presentation showcases an ongoing collaboration between the terrestrial ecosystem community and the high-precision atmospheric oxygen measurement community, initiated through a European Research Council (ERC) project, "OXYFLUX". We discuss the specific technical challenges of measuring O_2 with high precision in terrestrial ecosystems, and present some insights that can be gained about ecosystem processes from observed O_2:CO_2 exchange ratios (ER). Partitioning photosynthetic and respiratory fluxes in the terrestrial biosphere is something of a "holy grail" for ecologists and it is our hope that O_2 measurements will help with this.

We discuss three activities from our OXYFLUX project: 1) stem (tree trunk) chamber and branch chamber measurements from a beech forest site in Germany; 2) preliminary results using a flux gradient approach to quantify O_2 fluxes from an agricultural field site, also in Germany; and 3) a newly adapted biophysical multi-layer canopy model, "CANVEG", for examining contributions of various ecosystem components to the overall ecosystem O_2 exchange (https://doi.org/10.5194/bg-2023-30).

OXYFLUX results have already revealed important insights into ecosystem functioning. At our forest site, we used the stem chamber measurements to examine ARQ (apparent respiratory quotient, defined as the ratio of CO_2 efflux to O_2 influx), finding values of ~1.0 mol mol^{-1}, significantly different from previously published results, where ARQ values were sometimes reported to be as low as 0.6 mol mol^{-1}. Our branch chamber results show that ERs at leaf-level vary significantly between daytime and night-time, and are affected by the flux magnitude, PAR (photosynthetically active radiation) and VPD (vapour pressure deficit). Leaf-level ERs were usually found to be between 0.9 to 1.0 mol mol^{-1}. At our agricultural site, we successfully developed and tested the flux gradient approach for O_2 and CO_2 flux measurements, via sampling sequentially from three vertical intakes at 0.5, 1 and 3 m height above ground. CO_2 fluxes compared well to those derived from eddy covariance measurements. O_2 and CO_2 fluxes were anticorrelated with an O_2:CO_2 flux ratio of 1.18 ± 0.1 mol mol^{-1}, and also showing seasonal changes with crop development. Our CANVEG simulations showed similar patterns and diel variations of leaf-level ERs as our branch chamber measurements. Furthermore, CANVEG provided the opportunity to test the application of the flux gradient approach to estimate ecosystem O_2 fluxes, and provided a source partitioning method to estimate CO_2 flux components.

A New Inverse Modeling Tool for Understanding Plant Drought Stress using Atmospheric 13C of CO2 Measurements

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Feedbacks related to exchanges of water and carbon between the atmosphere and the terrestrial biosphere are key uncertainties in our understanding of Earth's climate. Of particular importance for climate projections is the response of diverse biomes to moisture stress due to increasing vapor pressure deficit and changing precipitation regimes, as well as responses to increasing atmospheric CO_2. The ^{13}C:^{12}C ratio of CO_2 (denoted as $\delta^{13}C$) is a proxy for plant water stress, since most plants favor the assimilation of $^{12}CO_2$ during photosynthesis by about 2%, and this "discrimination" is reduced under periods of moisture stress. While discrimination has been observed at the leaf and ecosystem scales for decades, recent studies have shown that atmospheric $\delta^{13}C$ is sensitive to changes in plant response to water stress at regional to global scales. However, few studies have tried to formally assimilate $\delta^{13}C$ within the context of an atmospheric inverse model to constrain regional-scale plant water stress. Here, we first examine the fundamental requirements that allow $\delta^{13}C$ to constrain discrimination using a simple physical model that links observed changes in $d^{13}C$ to net ecosystem exchange, discrimination, and atmospheric mixing. We then present a novel and rigorous regional data assimilation system and test it using synthetic measurements from a network of highly calibrated CO_2 and $\delta^{13}C$atm measurements. The model simultaneously solves for net ecosystem exchange of CO_2 and discrimination fluxes that are optimally consistent with pseudo-measurements. We find that the model can resolve signals that are considerably smaller than the limits of the simple physical model. However, this improvement is contingent on the analytical uncertainty of measurements. We find that a dense network of highly calibrated measurements of $\delta^{13}C$atm can constrain regional-scale linkages between carbon and water fluxes between terrestrial ecosystems and the atmosphere.

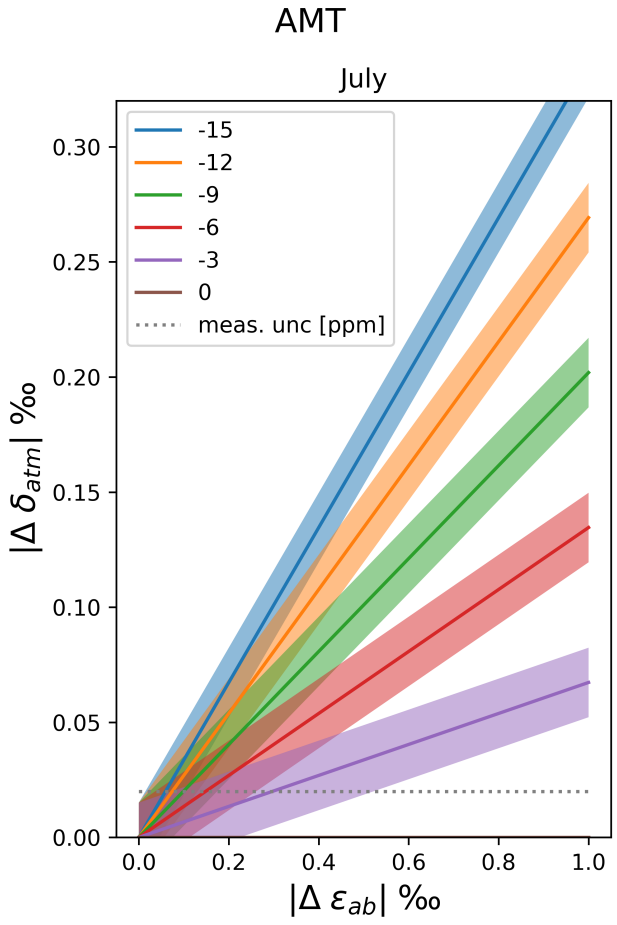

Figure 1. A simple physical model showing the sensitivity of atmopsheric $\delta^{13}C$ measurements to changing photosynthetic discrimination at a tall tower site in Maine. Here, different colors indicate different values of Net ecosytem exchange of CO_2 (NEE), and the shading represents variability in sensitivity to total surface flux (i.e., "footprints"). The model shows that the the sensitivity of atmopsheric $\delta^{13}C$ to photosynthetic discrimination is additionally contingent on the mgnitude of NEE. Finally the dotted horizontal line shows a typical value of analytical uncertainty for the measurements.

‘Urban Respiration’: Insights from Urban O_2 Measurements

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Cities occupy a mere 0.37% of the Earth’s land area but are home to 56% of the global population and account for over 70% of the energy consumption. In this presentation, we introduce the concept of ‘urban respiration’ - a phenomenon where cities inhale O_2 and exhale CO_2 and pollutants, akin to biological respiration. This process is driven by anthropogenic activities, including fossil fuel combustion and resident respiration. However, the relative contributions and spatial origins of these two processes remain poorly quantified.

In this work, we utilize atmospheric O_2/N_2 and pollutants measurements to monitor the ‘urban respiration’ in Lanzhou in the semi-arid region of northwestern China. The unique topography of Lanzhou, with its mountainous surroundings and constrained urban expansion, amplifies the trapping of pollutants and concentrates human settlements along the valley. With a population density of over 50,000/km^2, Lanzhou offers a unique opportunity to investigate how resident respiration (ΔO_{2RES}) and fossil fuel combustion (ΔO_{2FF}) shape O_2 variations in urban atmosphere (ΔO_{2URB}).

Emissions of atmospheric pollutants are closely related to ΔO_{2FF}, while they are decoupled from ΔO_{2RES}. This discrepancy enables us to disentangle the contributions of ΔO_{2FF} and ΔO_{2RES} using a robust statistical model. We found increased ΔO_{2FF} contribution (from 66.92% to 72.50%) and decreased ΔO_{2RES} contribution (from 33.08 to 27.50%) as O_2 declines and pollutants accumulate. Furthermore, utilizing a Lagrangian atmospheric transport model (STILT), we trace the origin of ΔO_{2FF} to atmospheric pollutants emitted by industrial sectors, with transportation sectors emerging as the primary O_2 sink in downtown Lanzhou.

By shedding light on the intricate relationships between O_2 levels, energy consumption patterns, pollutant emissions, and atmospheric transport processes, we gain insights into the dynamics of urban respiration. Our findings have important implications for policymakers, urban planners, and environmental scientists working towards sustainable and livable cities.