Thomas S. Barningham[1*], Andrew C. Manning[1], Gordon W. Brailsford[2] and Britton B. Stephens[3]

[1] Centre for Ocean and Atmospheric Sciences, School of Environmental Sciences, University of East Anglia, Norwich, UK.
[2] National Institute of Water and Atmospheric Research, Wellington, New Zealand.
[3] National Center for Atmospheric Research, Boulder, Colorado, USA.

[*]Corresponding author: stbarningham@gmail.com

A preliminary investigation into the detection and attribution of carbon cycle processes from APO observations at Baring Head, New Zealand

We investigate the variability of continuous atmospheric O_2 and CO_2 observations, collected by NIWA, at Baring Head , New Zealand (41.4°S, 174.9°E), for the period 1999-2012, to make deductions on the temporal and spatial variability of the Southern Ocean carbon cycle. Specifically, we identify marine net primary productivity (NPP) "events" and events indicative of ventilation of CO_2-rich, O_2-deficient deep water masses, from analyses of the derived Atmospheric Potential Oxygen (APO) tracer. Each APO event within the atmospheric record (typically lasting a few hours to days) was traced to a likely source region using simple air mass back trajectory analyses. The origin of each event was further confirmed by comparison to either satellite NPP estimates for productivity events, or sea surface temperature anomalies for upwelling and ventilation events. The magnitude, timing and seasonality of the events identified are quantified and used to build up a picture of oceanic carbon cycle processes within the region. The ΔAPO for each event was converted into either a flux of carbon (for NPP, in mg C m^{-2} day^{-1}) or a dissolved O_2 concentration (for ventilation events, in mL L^{-1}). For the identified source regions, these calculated values were compared to either satellite-based productivity estimates, or mixed layer depth estimates with concurrent dissolved O_2 profiles.

Mark Battle[1], Jacob Forsyth[1], Sara Mikaloff-Fletcher[2] and Michael Bender[3] Pieter Tans[4]

[1] Dept. of Physics, Bowdoin College, mbattle@bowdoin.edu

[2]NIWA sara-mikaloff-fletcher@niwa.co.nz

[3]Department of Geosciences, Princeton University bender@princeton.edu

[4]NOAA ESRL, GMD. pieter.tans@esrl.noaa.gov

Title: Zonal APO Gradients in the Equatorial Pacific

Abstract: Spatial gradients in APO across the Pacific have been used extensively in the past to test models of air sea fluxes of CO2 and O2 as well as atmospheric transport. This past work has focused primarily on climatological north-south (meridional) gradients, which tend to be relatively pronounced on account of generally zonal air flow.

In this study, we focus instead on zonal gradients, using a set of APO measurements taken from flask samples collected by the research ship Ka'imimo'ana and analyzed and Princeton University and NOAA/ESRL/GMD. The samples were collected in the equatorial Pacific between 165E and 95W, in the band between 10N and 8S, during the time period between early 2001 and late 2007. Because the data are irregularly located in space and time, we use a model of APO fluxes and atmospheric transport to develop a protocol for relating our sparse dataset to the full atmospheric concentration field. Preliminary results indicate modest gradients, with APO varying by 5-10 per meg across the region of study with lower values in the east. In general, the model predicts similar gradients. If we divide the dataset into el Nino and la Nina periods, we see little difference in the atmospheric structure, although these conclusions are less robust due to fewer data during la Nina periods. Implications of these results for fluxes and transport will be considered.

Jonathan D. Bent[1,2], Britton B. Stephens[1], Ralph F. Keeling[2], Sara E. Mikaloff-Fletcher[3], Prabir Patra[4], Andrew S. Watt[1], Stephen R. Shertz[1], Keith B. Rodgers[5], Olivier Aumont[6], Matthew C. Long[1], Scott C. Doney[7], Ivan D. Lima[7], Corinne Le Quéré[8], John P. Dunne[9]

[1]National Center for Atmospheric Research, Boulder, CO, USA
[2]Scripps Institution of Oceanography, La Jolla, CA, USA
[3]National Institute for Water and Atmospheric Research, Wellington, New Zealand
[4]Research Institute for Global Change, Japan Agency for Marine Science and Technology, Yokohama, Japan
[5]AOS Program, Princeton University, Princeton, NJ, USA
[6]IRD, Plouzané, France
[7]Woods Hole Oceanographic Institution, Woods Hole, MA, USA
[8]Tyndall˚ Center for Climate Change Research, University of East Anglia, Norwich, UK
[9]Geophysical Fluid Dynamics Laboratory, NOAA, Princeton, NJ, USA
Corresponding author: J. D. Bent, National Center for Atmospheric Research, Boulder, CO, 80304, USA. (jbent@ucsd.edu)

Assessing ocean biogeochemical models with high-resolution airborne observations of atmospheric oxygen over the Southern Ocean

We present measurements of vertical and meridional atmospheric oxygen distributions at five points in the seasonal cycle near the dateline over the Southern Ocean. From these we calculate a weighted average of atmospheric potential oxygen (APO $\approx O_2 + CO_2$) from the surface to the tropopause, between 65° and 45°S. These "curtain averages" have seasonal amplitudes approximately 70% of the amplitude observed at nearby surface stations and much less sensitivity to atmospheric transport uncertainty in models. We compare the seasonal cycle of APO from our observations with those from six global ocean biogeochemistry models and an additional set of climatological semi-empirical flux estimates run through two atmospheric transport models. We assess each model's performance by its agreement with observations on amplitude and phase, and estimate uncertainties in these parameters using a Monte Carlo technique. The first harmonic (i.e. fundamental) of the observed seasonal APO cycle has a peak-to-peak amplitude of 43.8 ±5.3 per meg, with a peak at year day 67. Ocean models underestimate or overestimate this amplitude by up to -21%/+29%, respectively, with most predicting seasonal maxima later in the year than observed. Analysis of heat fluxes suggests both physical and biological forces are behind differences between observed and modeled seasonal phasing and amplitude. We also find that Garcia and Keeling [2001] semi-empirical climatological O_2 fluxes using the Wanninkhof [1992] parameterization lead the observations by 2 weeks, and should be adjusted using a more recent global gas exchange scaling parameter, a_q, of 0.32, rather than the original value of 0.39. Our observations suggest that TM3 captures the mixing of APO signals slightly better than ACTM over the Southern Ocean, capturing the ratio of column (curtain) average seasonal cycle to surface station seasonal cycle more closely.

Jean-Louis Bonne[1,2], Marc Delmotte[1*], Laurent Bopp[1], Andrew C. Manning[3†], Laure Resplandy[1,4], Timothée Bourgeois[1], Gilles Reverdin[5], Jost V. Lavric[6]

[1] Laboratoire des Sciences du Climat et de l'Environnement, CEA-CNRS-UVSQ, IPSL, Gif sur Yvette, France

[2] now at Alfred Wegener Institute, Bremerhaven, Germany

[3] Centre for Ocean and Atmospheric Sciences, University of East Anglia, Norwich, UK

[4] Geosciences Research Division, Scripps Institution of Oceanography, University of California, San Diego, USA

[5] LOCEAN-IPSL, Paris, France

[6] Max Planck Institute for Biogeochemistry, Jena, Germany

[*]Corresponding author: marc.delmotte@lsce.ipsl.fr

[†]presenting author

Seven years of atmospheric oxygen and APO records at Ivittuut, South Greenland: data and model simulations results and comparison.

Between September 2007 and September 2014, continuous atmospheric monitoring of CO_2 and O_2/N_2 have been conducted at Ivittuut, on the south western coast of Greenland, using high precision analyzers (based on NDIR and CRDS techniques for CO_2 and paramagnetic technique for O_2/N_2).

The combination of both data sets enabled us to calculate APO (Atmospheric Potential Oxygen). All these measurements conducted to unique data series that have been analyzed in terms of multi-annual, seasonal, diurnal and synoptic variability for our monitoring site.

As depicted by Lagrangian back-trajectory simulations, this station is prevalently influenced by the Labrador and Irminger Seas as well as Baffin Bay, with frequent influences from North Atlantic and Northern Canada.

We will present our observational dataset and its comparison with simulated APO simulated in two steps: O_2, CO_2 and N_2 air-sea fluxes were first simulated by an ocean model (NEMO-PISCES) driven by atmospheric reanalysis; the fluxes were then transported to Ivittuut using an atmospheric transport model (TM3 model) and APO simulated at the station site, allowing direct comparison with the observations.

Our modeling framework simulates good amplitude of seasonal APO variability at Ivittuut. Significant inter-annual variability is simulated at multi-year and at monthly time scales. Sensitivity tests allow attributing about 3/4 of the fastest monthly variability to atmospheric transport. This comparison challenges the ability of models to capture the processes driving the inter-annual variability of APO.

Gordon W. Brailsford[1]*, Andrew C. Manning[2], Britton B. Stephens[3], Sara E. Mikaloff Fletcher[1]

[1] National Institute of Water & Atmospheric Research (NIWA), Wellington, New Zealand.

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

[3] National Center for Atmospheric Research, Boulder, Colorado, USA

Corresponding author: Gordon.Brailsford@niwa.co.nz

TITLE: Atmospheric oxygen observations from New Zealand.

ABSTRACT: Observations of atmospheric oxygen have been undertaken in situ at Baring Head, New Zealand, since 1999 to the present, representing the world's longest in situ time series of atmospheric oxygen. These observations have been made using a paramagnetic oxygen analyser (Paramax 101, Columbus Instruments), fitted with a Servomex PM1155B oxygen sensor through which sample air and a reference gas (called 'working tank') are alternately switched. The calibration is maintained with two span gases and a suite of at least four long-term standards with a lineage back to the Scripps O_2 scale. These oxygen measurements are supported by concurrent in situ CO_2 observations made using a non-dispersive infrared analyser (Ultramat 3, Siemens Corp.). We examine the seasonality and inter-annual variability of the observations, including for APO, and calibration issues relating to pressure and time dependent drift in the calibrations gases.

Alison Craggs, Andrew C. Manning*, Penelope A. Pickers, Philip A. Wilson,
Sander van der Laan, Thomas S. Barningham†, Alex J. Etchells and David Blomfield

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

*corresponding author: andrew.uea@gmail.com

†presenting author

Investigating short-term ocean events using continuous measurements of atmospheric O_2, CO_2 and APO from Mace Head Atmospheric Research Station, Ireland

Continuous atmospheric O_2, CO_2 and APO measurements have been made from Mace Head Atmospheric Research Station, situated on the west coast of Ireland, since February 2014. The seasonal cycle amplitudes of the CO_2, O_2 and APO data are 17.8 ± 2.3 ppm, 149.0 ± 10.1 per meg and 76.6 ± 7.0 per meg, respectively. These values compare well to O_2, CO_2 and APO seasonal cycle amplitudes from other continuous European measurement stations, and to flask sample measurements made at Mace Head by the University of Groningen.

Atmospheric O_2, CO_2 and APO data from coastal stations can be used to identify short-term ocean 'events' such as those caused by primary productivity and ocean ventilation. We investigate eleven APO events from Mace Head during 2014, six of which we assume to be ocean productivity events and five that we assume to be ocean ventilation events. We find seasonality in the magnitude of the events, with greater magnitude APO productivity events occurring in the spring and summer, and greater magnitude APO ventilation events occurring in autumn and winter. The O_2:CO_2 ratios for almost all events are negative, indicating anti-correlation of O_2 and CO_2 fluxes. Two events display positive O_2:CO_2 ratios, however, suggestive of thermally driven fluxes.

We also calculate ocean O_2 fluxes from the atmospheric measurements and compare these to modelled ocean O_2 and heat fluxes from the Plankton Types Ocean Model (PlankTOM) embedded within the Nucleus for European Modelling of the Ocean (NEMO) framework, using Hysplit backward trajectories, NAME (Numerical Atmospheric-dispersion Modelling Environment) model footprints, satellite ocean colour data, and Argo float dissolved O_2 data. For most of the ocean productivity events, there is good agreement between the modelled and the calculated O_2 fluxes. For ocean ventilation events, however, the modelled O_2 fluxes are consistently greater in magnitude than the calculated O_2 fluxes.

Yassir Eddebbar[1*], Ralph Keeling[1], Manfredi Manizza[1], Matthew Long[2], Laure Resplandy[1]

[1]Scripps Institution of Oceanography, UC San Diego, La Jolla, CA

[2] National Center for Atmospheric Research, Boulder, CO

*yeddebba@ucsd.edu

TITLE: ENSO-driven variability of air-sea fluxes of oxygen: Observations and mechanisms

ABSTRACT: The oceanic oxygen (O_2) inventory is expected to decline as anthropogenic warming reduces gas solubility and ventilation of the ocean's interior. Natural variability, however, can mask or modulate this decline, challenging the detection and attribution of ocean deoxygenation. Here, we combine the high precision measurements of atmospheric O_2/N_2 and CO_2 from the Scripps Flask Network using the Atmospheric Potential Oxygen ($APO \sim O_2/N_2 + 1.1 * CO_2$) to investigate the influence of El Niño Southern Oscillations (ENSO) on air-sea O_2 exchange. To explore the mechanistic nature of this relation, we employ hindcast and unforced coupled simulations of the NCAR Community Earth System Model (CESM). We find anomalous outgassing of O_2 during El Niño and drawdown during La Niña in the tropical Pacific dominate the global APO flux response to ENSO. This response, shared by other CMIP5 models, reflects combined influences of dynamic, biological, and thermal processes, and is dominated by ENSO-modulated changes in upwelling of low-O_2 waters. A sensitivity analysis using an atmospheric transport model shows that ENSO-induced anomalies in air-sea fluxes of O_2 contribute significantly to the variability of the atmospheric APO budget. This variability however, is mainly confined to the tropical Pacific and displays a zonally complex structure, calling for enhanced observational coverage in the tropics. The impact of ENSO dynamics on the oceanic oxygen cycle suggests a complex relation between heat and oxygen exchange in the tropics, and further informs the observed decadal trends in APO and dissolved O_2.

Daisuke Goto*, Shinji Morimoto, Shuji Aoki, Takakiyo Nakazawa and Prabir K. Patra

*National Institute of Polar Research, Tokyo, goto.daisuke@nipr.ac.jp

TITLE: Continuous measurements of APO at Ny-Ålesund, Svalbard

ABSTRACT:

To elucidate the variations of the atmospheric $\delta(O_2/N_2)$ and APO and to understand role of the Arctic region on regional and global carbon cycle, we developed a continuous measurement system using differential fuel-cell O_2 analyzer, and initiated continuous observation of the atmospheric $\delta(O_2/N_2)$ and CO_2 at Ny-Ålesund (78˚55'N, 11˚56'E), Svalbard in November 2012, which is the first such observational system operated from the Arctic region. We will report results based on the first two years of measurement.

APO observed at Ny-Ålesund shows a clear seasonal cycle with peak-to-trough amplitude of about 50 per meg, which reaches a minimum in late March to early April and a maximum in July. Short-term variations on time scales of several hours to several days are also clearly observed. In spring to summer, irregular fluctuations of APO reaches 30–50 per meg. Simulation of APO using atmospheric chemistry transport model (ACTM) reproduces such short-term variations. Tagged tracer simulation using ACTM indicates that the Greenland Sea, Norwegian Sea and/or Barents Sea are the main contributor to the short-term fluctuations of APO in spring–summer. The comparison of backward trajectories of air parcels with the distributions of marine biotic net primary production (NPP) also suggests that such fluctuations of APO are closely related to O_2 emission due to marine biological activity near Norwegian Sea. O_2 flux was estimated using observed APO variation. Using the estimated O_2 flux, the production of marine biological activities was also estimated. The estimation was comparable with the NPP derived from satellite data. This suggests that our data could be useful for the validation of NPP derived from satellite data.

Roberta C. Hamme[1], Ralph Keeling[2], and Bill Paplawsky[2]

[1]School of Earth and Ocean Sciences, University of Victoria, rhamme@uvic.ca

[2]Scripps Institution of Oceanography, UC San Diego, rkeeling@ucsd.edu, wpaplawsky@ucsd.edu

TITLE: Semi-continuous measurements of Ar/N_2, O_2/N_2, and CO_2 at the Scripps pier

ABSTRACT: Since early 2004, hourly measurements of Ar/N_2, O_2/N_2, and CO_2 have been made during weekends on air pumped from the Scripps pier directly through an inlet system to a mass spectrometer. In 2008, a second mass spectrometer began making continuous hourly measurements from a separate pumped air line and inlet system. These continuous flow measurements show reduced variability over flask-collected samples, clear seasonal cycles, and unusual high Ar/N_2 events. Standard gases in the early part of the record showed use-related drift in Ar/N_2, possibly due to temperature gradients even within our thermally-insulated, horizontally-orientated standard enclosure. Dip tubes within the gas cylinders, allowing gas to be removed from the exact center of the cylinder, reduced the drift effect. Additionally, linearly averaging calibration results over the life of working standards reduced week-to-week variability in the resultant record. The seasonal cycle in Ar/N_2 is almost exactly in-phase with Atmospheric Potential Oxygen (APO) at this location. We find an APO to Ar/N_2 ratio of 3.9 on seasonal timescales, from which we estimate that solubility-driven fluxes in O_2 and N_2 account for ~20% of the seasonal cycle in APO at La Jolla. Overlapping records from the two separate systems show that the anomalously high Ar/N_2 events are likely to be real atmospheric changes and not analytical biases. The largest of these variations are peaks in Ar/N_2 that extend to 30 per meg above the background seasonal cycle and can last for several days, usually occurring between late spring and early fall. Most of these large events are positively correlated with APO variations, but with variable APO to Ar/N_2 ratios from 1.5 to 5.0. The events are anecdotally related to coastal fog and strong inversion layers, suggesting that a stratified boundary layer is necessary allow ocean flux signals to be concentrated rather than mixed away.

Shigeyuki Ishidoya[1]*, Kazuhiro Tsuboi[2], Shoichi Taguchi[1], Yosuke Niwa[2], Hidekazu Matsueda[2], Shohei Murayama[1], Shinya Takatsuji[3], Tomoki Okuda[3], Kohshiro Dehara[3], Yoki Mori[3] and Shuichi Hosokawa[3]

[1]National Institute of Advanced Industrial Science and Technology (AIST), AIST Tsukuba West, 16-1 Onogawa, Tsukuba, Ibaraki 305-8569, Japan (s-ishidoya@aist.go.jp)

[2]Meteorological Research Institute, 1-1 Nagamine, Tsukuba, Ibaraki 305-0052, Japan

[3]Japan Meteorological Agency, 1-3-4 Otemachi, Chiyoda-ku, Tokyo 100-8122, Japan

TITLE: Time and space variations of Atmospheric Potential Oxygen over the Western North Pacific observed by using a cargo aircraft C-130H

ABSTRACT: Air samples collected in the middle troposphere (~6 km altitude) over the western North Pacific using a cargo aircraft C-130H since May 2012, have been analyzed for O_2/N_2 and Ar/N_2 ratios, as well as stable isotopic ratios of N_2, O_2 and Ar. The analysis indicated a significant artificial fractionation due to thermal diffusion during the air sample collection, and the effects of the fractionation on the observed O_2/N_2 ratio were corrected using the observed Ar/N_2 ratio (Ishidoya et al., 2014). The corrected O_2/N_2 ratio and the Atmospheric Potential Oxygen ($APO=O_2+1.1xCO_2$) showed prominent seasonal cycles superimposed on clear secular downward trends. The amplitude of the mid-tropospheric seasonal APO cycle at 33.5°N was found to be twice as large as that observed at 25.5°N, whereas the corresponding latitudinal difference in the seasonal CO_2 amplitude was less than 10%. Similar decreases in the seasonal amplitudes toward the lower latitudes were also detected in the seasonal APO cycles simulated by two atmospheric transport models (Taguchi et al., 2002; Niwa et al., 2011) forced with monthly air-sea O_2 (N_2) flux climatology (Garcia and Keeling, 2001). On the other hand, a much smaller latitudinal difference was found in the amplitudes of the seasonal APO cycles simulated by the same models but forced only with the northern hemispheric monthly air-sea O_2 (N_2) flux. These results suggest that the mid-tropospheric seasonal APO cycle in the northern low latitudes is reduced by the anti-phase seasonal APO cycles in the northern and southern hemispheres. Therefore, the seasonal APO cycles observed in the troposphere over the subtropical region can be used to evaluate the interhemispheric air mixing.

Ralph F. Keeling*

*Scripps Institution of Oceanography, UC San Diego, rkeeling@ucsd.edu

TITLE: Grand challenges for atmospheric O_2/N_2 and Ar/N_2 measurements

ABSTRACT: High precision measurements of atmospheric O_2/N_2 ratio have now been made for several decades, and have provided great insight into ocean and land biogeochemistry and carbon cycling, particularly via the tracer atmospheric potential oxygen (APO). High precision measurements of Ar/N_2 have now been made for roughly 15 years, which have shown variations related to solubility-driven exchanges with the ocean and homogenous thermal and gravimetric settling in the stratosphere and near the ground. While progress has been significant, there is are important milestones which these measurement could still attain with further developments.

One such milestone is to incorporate O_2/N_2 (or APO) measurements into carbon data assimilation systems, such as NOAA's Carbon Tracker. These assimilation systems now provide only limited insight into land fluxes on decadal time scales and provide limited insight into air-sea fluxes on all time scales, owing to the overwhelming impact of short-term land exchanges. In principle, O_2/N_2 measurements could help overcome this limitation, but to fully exploit O_2/N_2 data will require shifting the focus from optimizing surface fluxes to optimizing processes internal to the ocean using joint ocean/atmospheric transport modelling. Another objective is to resolve secular changes in Ar/N_2 ratio (or other inert gas ratios) caused by long-term warming of the ocean, which could provide an important complement to measuring ocean heat content changes using in situ ocean temperature measurements.

Methodologically, all O_2/N_2 measurements depend on specialized apparatus and copious supply of calibration gas, or both. These requirements hamper the application by a broader community, but in principle could be overcome. Also, measurement are almost always limited in part by the difficulty of delivering constant ratios from air stored in high pressure cylinders. Air delivered from tanks is understood to vary as result from thermal diffusion and/or gravimetric settling. These influences appear very difficult to fully eliminate, and other factors not yet understood may also be at work.

***M. C. Leuenberger, M. F. Schibig, T. Berhanu, P. Nyfeler and H. Moret**

Climate and Environmental Physics, Physics Institute and Oeschger Centre for Climate Change Research, University of Bern, Switzerland

Correspondence to:
M. Leuenberger
Sidlerstrasse 5
3012 Bern, Switzerland
Ph: +41316314470
leuenberger@climate.unibe.ch

APO variations in Central Europe obtained at the Jungfraujoch Research Station, Switzerland in comparison to a combined record of Scripps La Jolla and Alert values

Abstract

The main purpose of the present work is the investigation of residuals from linear trends – that show an excellent agreement between Jungfraujoch and the mean of the Scripps stations La Jolla and Alert for CO_2, O_2 and APO – in order to have a better insight into potential causes of these yearly or half-yearly deviations. The slope of the residuals for the full Scripps dataset corresponds to -1.89 ± 0.12 mole O_2 / mole CO_2, this is similar to the slope of the whole data with -2.20 ± 0.01 mole O_2 / mole CO_2. However, the APO residuals have a slope of -0.79 ± 0.12 ppm APO / ppm CO_2 in contrast to the data -1.10 ± 0.01 ppm APO / ppm CO_2. This is different for the period 2005 to 2013, for which the residuals for the Scripps dataset corresponds to -1.42 ± 0.12 mole O_2 / mole CO_2 but the slope of the data itself is -2.30 ± 0.02 mole O_2 / mole CO_2. The correspondent APO residuals have a slope of -0.32 ± 0.11 ppm APO / ppm CO_2 quite different to the data -1.20 ± 0.02 ppm APO / ppm CO_2.

In contrast to the Scripps dataset the correlations of the residuals of the Jungfraujoch dataset for 2005 to 2013 are slightly less robust for the data and much less robust for the residuals of the linear trends mentioned above – most probably due to larger local and/or regional imprints.

In summary, both measurement records document highly comparable linear CO_2 increase and linear decrease rates for O_2 as well as APO for correspondent time periods. Investigations on residuals from these linear trends document a dominance of short-term variations in the terrestrial biosphere over the ocean outgassing or solubility effect.

Valerie Livina*, Teresa Vaz[+], and Alistair Forbes*

*National Physical Laboratory, Teddington, United Kingdom, valerie.livina@npl.co.uk

[+]John Innes Centre, Norwich, United Kingdom

TITLE: Tipping point analysis of atmospheric oxygen concentration

ABSTRACT: We apply tipping point analysis to nine observational oxygen concentration records around the globe, analyse their dynamics and perform projections under possible future scenarios leading to oxygen deficiency in the atmosphere. The analysis is based on statistical physics framework with stochastic modelling, where we represent the observed data as a composition of deterministic and stochastic components estimated from the observed data using Bayesian and wavelet techniques.

[1] Livina et al, Chaos 2015

Manfredi Manizza[1,*], Laure Resplandy[1], Ralph F. Keeling[1], C. D. Nevison[2], Sara Mikaloff-Fletcher[3], and the ocean modelers

[1]Scripps Institution of Oceanography, UC San Diego, La Jolla, CA.

[2]University of Colorado, Boulder, CO.

[3]NIWA, Wellington, NZ

*email: mmanizza@ucsd.edu

TITLE: Testing ocean biogeochemical models with atmospheric potential oxygen (APO) and Ar/N_2 ratio

ABSTRACT: Ocean general circulation models coupled to biogeochemical components are useful tools to study how climate variability controls biogeochemical processes in the oceans, including air-sea gas fluxes. In order to be credible these models need to be evaluated in their performance at reproducing observed natural phenomena such as for instance the air-sea exchange of both inert gases, like Argon and nitrogen (that mostly track the heat exchange between the ocean and the atmosphere) and the air-sea fluxes of oxygen and carbon dioxide that are influenced by both physical and biogeochemical processes occurring in the water column.

Oxygen and Argon have the same solubility in seawater but oxygen abundance only in seawater can be modified by biogeochemical processes therefore, based on this principle, the difference in the seasonal amplitude of air-sea fluxes of these two gases can give us a measure of the importance of biogeochemical processes and can be used to test the performance of these models, both for ocean physics and biogeochemistry separately. For this study we rely on the use of atmospheric observations of APO and Ar/N_2 in stations in extra-tropical locations of both hemispheres. The ratio of their seasonal amplitude of APO and Ar/N_2 gives typical values of 3-4 (no units) providing a key metric to test our models. To test our hypothesis and this new metric we collected the output of different ocean physical-biogeochemical models, we transported their fluxes in an atmospheric transport model (ATM, TM3), and we then compared our results to available observations from four stations. The new metric based on amplitude ratio allows us not only to rank the performance of models but also to pinpoint where the model has major deficiencies when APO and Ar/N_2 amplitudes are considered separately. In this study we also demonstrate that our results are insensitive to the ATM chosen for this study.

Furthermore, in order to further verify the validity of our method we try to combine this novel metric together with another older metric based on the ratio between air-sea O_2 and heat fluxes based on the work of Garcia & Keeling (2001). We demonstrate that these two independent metrics nicely agree and converge towards the same conclusion on the performance of different models tested for this study.

A. C. Manning[1*], R. F. Keeling[2], A. J. Etchells[1], M. Hewitt[1], M. L. Bender[3], K. Bracchi[2], G. W. Brailsford[4], W. A. Brand[5], N. Cassar[3,6], A. C. Cox[2], M. Leuenberger[7], H. A. J. Meijer[8], S. Morimoto[9], T. Nakazawa[9], R. E. M. Neubert[8], W. J. Paplawsky[2], J. M. Richter[5], B. B. Stephens[10,4], Y. Tohjima[11], S. van der Laan[7,1], I. T. van der Laan-Luijkx[7,12], A. Watt[10] and P. A. Wilson[1]

[1] Centre for Ocean and Atmospheric Sciences, School of Environmental Sciences, University of East Anglia, United Kingdom
[2] Scripps Institution of Oceanography, University of California San Diego, USA
[3] Department of Geosciences, Princeton University, USA
[4] National Institute of Water and Atmospheric Research, New Zealand
[5] Max Planck Institute for Biogeochemistry, Germany
[6] Division of Earth and Ocean Sciences, Nicholas School of the Environment, Duke University, USA
[7] Physics Institute and Oeschger Centre for Climate Change Research, University of Bern, Switzerland
[8] Centre for Isotope Research, University of Groningen, The Netherlands
[9] Center for Atmospheric and Oceanic Studies, Tohoku University, Japan
[10] National Center for Atmospheric Research, USA
[11] National Institute for Environmental Studies, Japan
[12] Meteorology and Air Quality Group, Wageningen University, The Netherlands

[*]corresponding author: andrew.uea@gmail.com

The "GOLLUM" O_2 intercomparison programme: Latest results and next steps

No international calibration scale exists for atmospheric O_2/N_2 measurements, making it difficult if not impossible 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 as an interim measure to help address these deficiencies, by quantifying laboratory offsets in O_2/N_2 calibration scales. We now have an eleven year time series record documenting these offsets for all ten of the O_2/N_2 laboratories throughout the world.

The primary component of the GOLLUM programme involves the circulation of six high pressure cylinders of air, in two sets of three, 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, and also include results from CO_2 and Ar/N_2 analyses, where available. We also present a small number of results from a flask analysis intercomparison component of GOLLUM. Finally, we discuss possible next steps that the community might like to consider, including soliciting advice from the modelling community*. We will outline a suggestion that the community support submission of an "International Opportunities Fund" proposal to the UK Natural Environment Research Council, in order to further progress atmospheric O_2/N_2 intercomparisons, calibration scales, and quality control of data sets.

* See also the abstract by Rödenbeck *et al.*

Sara Mikaloff Fletcher[1], Kay Steinkamp[1], Nicolas Gruber[2], and Yasunori Tohjima[3]

1. National Institute for Water and Atmospheric Research (NIWA), Wellington, New Zealand, Sara.Mikaloff-Fletcher@niwa.co.nz
2. Environmental Physics, Institute of Biogeochemistry and Pollutant Dynamics, ETH Zurich, Switzerland
3. National Institute for Environmental Studies, Center for Global Environmental Research, Tsukuba, Japan

TITLE: Oxygen gradients across the Pacific Ocean: Resolving an apparent discrepancy between atmospheric and ocean observations and models

ABSTRACT: We use oceanic and atmospheric model simulations to investigate and resolve a disagreement between observations of APO and air-sea fluxes estimated from ocean data. A recent study identified a deep APO minimum in the Northwest Pacific from measurements collected on a repeat transect between New Zealand and Japan. This minimum could not be reproduced in atmospheric model simulations forced with air-sea fluxes estimated from ocean data, suggesting that oxygen uptake in the Northwest Pacific must be under-estimated by a factor of two.

We present an updated ocean inverse method to estimate new air-sea fluxes from the ocean interior measurements at a higher spatial resolution than previous work using a suite of ten ocean general circulation models (OGCMs). These new air-sea flux estimates are able to match the atmospheric APO data when used as boundary conditions for an atmospheric transport model. Analysis of ocean interior observations of oxygen and nutrient data along transects in the Pacific confirms vigorous oxygen uptake in this region, and the relative roles of heat fluxes and biological productivity in controlling these fluxes are investigated.

Shinji Morimoto*[1], Daisuke Goto[2], Shigeyuki Ishidoya[3], Prabir K. Patra[4], Shuji Aoki[1], Takakiyo Nakazawa[1]

*[1]Center for Atmospheric and Oceanic Studies, Graduate School of Science, Tohoku University, Sendai, Japan. mon@m.tohoku.ac.jp

[2]National Institute of Polar Research, Tokyo, Japan.

[3]National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan.

[4]Japan Agency for Marine-Science and Technology, Yokohama, Japan.

TITLE: Temporal variations of $\delta(O_2/N_2)$ and Atmospheric Potential Oxygen (APO) observed at Syowa Station, Antarctica.

ABSTRACT: For a better understanding of the global carbon cycle and oxygen exchange between atmosphere and ocean, we have conducted systematic and continuous observations of the CO_2 concentration and $\delta(O_2/N_2)$ at Syowa Station, Antarctica (69.0°S, 39.6°E) since 1984 and 2008, respectively. The CO_2 concentration and $\delta(O_2/N_2)$ were measured by using a non-dispersive infrared analyzer (NDIR) and a differential fuel-cell analyzer, the analytical reproducibility being 0.01 ppm and 2.5 per meg (one standard deviation), respectively. The CO_2 concentration, $\delta(O_2/N_2)$ and APO observed at Syowa Station showed clear seasonal cycles with the respective average peak-to-peak amplitudes of 1.2 ppm, 71 per meg and 65 per meg. The amplitudes of $\delta(O_2/N_2)$ and APO are similar to those obtained from our bi-weekly flask samples which were previously reported. Short-term variations of APO on the synoptic time scale (hours to several days) were observed throughout a year, however, they were most prominent in the austral summer season (December to January), showing abrupt APO increases of 20-30 per meg within 1-3 days. Forward simulations by an atmospheric transport mode with prescribed climatological O_2, N_2 and CO_2 fluxes showed that O_2 outgassing from the Southern Ocean on the west side of Syowa Station (150°W – 30°E) were responsible for such summertime APO variations.

C.D. Nevison[1], M. Manizza[2], J. Bent, R.F. Keeling[2], Britt Stephens[3], Mati Kahru[2], B.G. Mitchell[2]

[1] University of Colorado, Boulder, Institute for Arctic and Alpine Research, Cynthia.Nevison@colorado.edu
[2]Scripps Institution of Oceanography, UC San Diego
[3]National Center for Atmospheric Research, Boulder, CO

Evaluating CMIP5 ocean biogeochemistry and Southern Ocean carbon uptake using APO: Present day performance and future prediction

ABSTRACT: The observed seasonal cycles in atmospheric potential oxygen (APO) are used to evaluate the output of 8 ocean biogeochemistry models participating in the Coupled Model Intercomparison Project (CMIP5). APO data from 3 southern hemisphere surface monitoring sites and from a new 300-1000 mb column average over the Southern Ocean are used in the evaluation. The CMIP5 air-sea O_2, N_2, and CO_2 fluxes are translated into APO seasonal cycles using the GEOS-Chem atmospheric transport model (ATM). The column average APO constraint helps reduce the ATM uncertainty that has weakened previous ocean model evaluations based on observed surface-level APO. Of the tested ocean biogeochemistry models, half capture the observed APO seasonal cycle relatively well while the other half do not. The future APO cycle under RCP8.5 predicted by the 8 CMIP5 models is also examined. With the exception of changes in the oceanic CO_2 component associated with ocean acidification, few of the models predict substantial changes in APO over the Southern Ocean at the end of the 21st Century, despite large changes in ocean productivity and CO_2 uptake predicted in this region. The models that perform best on present-day APO tend to predict a more conservative Southern Ocean carbon sink, both today and in 2100.

Prabir K. Patra*, Rona Thompson, Tazu Saeki and APO colleagues

*DEGCP/IACE JAMSTEC, Yokohama Japan, prabir@jamstec.go.jp

TITLE: Can O_2/N_2 measurements help to constrain global total fossil fuel emission?

ABSTRACT: Estimations of global and regional fluxes of carbon dioxide (CO_2) are being done over the past three decades. But scientists are yet to come up with desirable solution to estimating regional or global fluxes of CO_2, at lower uncertainty and bias. In inverse modeling of CO_2 fluxes, the emissions from fossil fuel (FF) consumptions and cement production are assumed known, and residual terrestrial source and sinks are estimated. Thus high (or low) bias in FF CO_2 emission inventory leads to over- (or under-) estimation of terrestrial CO_2 sink by inversions. Since the reduction of O_2/N_2 ratio in the atmosphere is linked with FF CO_2 emissions, we are seeking help from the APO community to constrain global total FF CO_2 emission. Some preliminary ideas will be shown in the presentation.

Penelope A. Pickers*, Andrew C. Manning, Philip A. Wilson, Alex J. Etchells and David Blomfield

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

*correspondence address: p.pickers@uea.ac.uk

First continuous shipboard measurements of atmospheric O_2, CO_2 and APO from meridional Atlantic Ocean transects

Continuous APO data, derived from continuous measurements of atmospheric O_2 and CO_2, can be used to identify short-term ocean 'events' such as those caused by primary productivity, or upwelling of deep water. We present the first ongoing, continuous atmospheric O_2, CO_2 and APO measurements traversing the Atlantic Ocean, collected onboard a Hamburg Süd commercial container ship, the *Cap San Lorenzo*, which travels continuously between Europe and South America. The measurements, which began in September 2014, cover a latitudinal range of 54°N to 35°S, with a complete Europe-South America-Europe cycle taking 8 weeks to complete, allowing up to 13 meridional transects per year.

We present latitudinal and seasonal variability in atmospheric O_2, CO_2 and APO in the Atlantic Ocean sector, and compare our measurements to those from the Pacific Ocean sector, to nearby coastal stations, and, for CO_2, to the National Oceanic and Atmospheric Administration (NOAA) marine boundary layer reference product. Measurements made when the ship is travelling in the English Channel, North Sea, and along the South American coastline show clear land biosphere and fossil fuel influences. Measurements made in the equatorial Atlantic show CO_2 outgassing, a clear step change at the inter-tropical convergence zone (ITCZ), as well as a clear seasonal migration of the ITCZ. As measurements continue, we will obtain times series of O_2, CO_2 and APO binned into nine 10° latitudinal bands, illustrating seasonal cycles, long-term trends, short-term events, and interannual variability.

Penelope A. Pickers[1*], Andrew C. Manning[1], Grant L. Forster[1,2], Sander van der Laan[1], Phil A. Wilson[1], Angelina Wenger[3], David E. Oram[1] and William T. Sturges[1]

[1] Centre for Ocean and Atmospheric Sciences, School of Environmental Sciences, University of East Anglia, Norwich, UK.

[2] National Centre for Atmospheric Science (NCAS), Natural Environment Research Council, UK.

[3] School of Chemistry, University of Bristol, Bristol, UK.

[*]corresponding author: p.pickers@uea.ac.uk

Quantifying fossil fuel CO_2 from continuous measurements of APO: a novel approach

Using atmospheric greenhouse gas measurements to accurately quantify CO_2 emissions from fossil fuel sources ($ffCO_2$) requires the separation of biospheric and anthropogenic CO_2 fluxes. The ability to quantify $ffCO_2$ from atmospheric measurements will enable more accurate 'top-down' verification of CO_2 emissions inventories, which have large uncertainty. Typically, $ffCO_2$ is quantified from discrete atmospheric measurements of $\Delta^{14}CO_2$, which are combined with higher resolution atmospheric CO measurements. In the UK, however, measurements of $\Delta^{14}CO_2$ are often significantly biased by nuclear power plant influences, which limit the use of this approach. In addition, the $\Delta^{14}CO_2$ and CO method is not able to distinguish between CO_2 from fossil fuels and biofuels, of which the latter is expected to become more prevalent in the future.

We present a novel approach for quantifying $ffCO_2$ using measurements of APO from two measurement sites in Norfolk, UK. Our approach is similar to that used for quantifying $ffCO_2$ from CO measurements ($ffCO_2(CO)$), whereby $ffCO_2(APO) = (APO - APO_{bg})/R_{APO}$, where $(APO - APO_{bg})$ is the APO deviation from the background, and R_{APO} is the APO:CO_2 combustion ratio for fossil fuel. Time varying values of R_{APO} are calculated from the COFFEE dataset (Steinbach *et al.*, 2011) combined with NAME (Numerical Atmospheric-dispersion Modelling Environment) model footprints. We compare our $ffCO_2(APO)$ method to $ffCO_2(CO)$, using CO:CO_2 fossil fuel emission ratios (R_{CO}) from the UK National Atmospheric Emissions Inventory and EDGAR (Emission Database for Global Atmospheric Research). We also compare our $ffCO_2(APO)$ results to $ffCO_2$ derived from $\Delta^{14}CO_2$ measurements from Norfolk during periods of high and low nuclear power plant influences, in order to determine the accuracy of our method, and to assess the benefits of using APO to quantify $ffCO_2$ in the UK.

Reference:
Steinbach, J., et al. (2011), The CO_2 release and Oxygen uptake from Fossil Fuel Emission Estimate (COFFEE) dataset: effects from varying oxidative ratios, Atmos. Chem. Phys., 11(14), 6855-6870.

L. Resplandy*, R. Keeling*, B. B. Stephens[1], J. D. Bent[1], A. . Jacobson[2], C. Rödenbeck[3], S. Khatiwala[4]

* Scripps Institution of Oceanography, UCSD, La Jolla USA, lresplandy@ucsd.edu
[1] National Center for Atmospheric Research, Boulder, Colorado, USA
[2] NOAA, Boulder USA
[3] Max Planck Institute for Biogeochemistry, Jena Germany
[4] Lamont-Doherty Earth Observatory of Columbia University, Palisades USA

TITLE: Constraints on oceanic meridional heat transport from combined measurements of atmospheric potential oxygen

ABSTRACT: Despite its importance to the climate system, the ocean meridional heat transport is still poorly quantified. We identify a strong link between the northern hemisphere deficit in atmospheric potential oxygen ($APO = O_2 + 1.1 * CO_2$) and the ocean heat transport asymmetry between hemispheres, using atmospheric data and ocean interior inversions. Recent aircraft observations from the HIPPO campaign reveal a northern APO deficit in the tropospheric column of -10.4 +/- 1.0 per meg, double the value at the surface and more representative of large-scale air-sea fluxes. The global northward ocean heat transport asymmetry necessary to explain the observed APO deficit is about 0.6-1 PW, which corresponds to the upper range of estimates from hydrographic sections and atmospheric reanalyses.

Rodgers, K.B.[1], Aumont, O.[2], Mikaloff Fletcher, S.E. [3], Plancherel, Y.[4], Bopp, L.[5], de Boyer Montégut, C.[6], Iudicone, D.[7], Keeling, R.F.[8], Madec, G.[2,9], and Wanninkhof, R.[10]

1. AOS Program, Princeton University, Princeton, NJ, krodgers@princeton.edu

2. LOCEAN, CNRS IRD, UPMC, MHNH IPSL, Paris, France, olivier.aumont@ird.fr

3. NIWA, Wellington New Zealand, sara.mikaloff-fletcher@niwa.co.nz

4. Department of Earth Sciences, University of Oxford, Oxford, UK, yvesp@earth.ox.ac.uk

5. LSCE, IPSL, CNRS, CEA, UVSQ, Gif-sur-Yvette, France, laurent.bopp@lsce.ipsl.fr

6. IFREMER, Centre de Brest, Plouzané, France, deboyer@ifremer.fr

7. Stazione Zoologica Anton Dohrn, Naples, Italy, iudicone@szn.it

8. Scripps Institution of Oceanography, UC San Diego, rkeeling@ucsd.edu

9. National Oceanography Centre, Southampton, UK, gurvan.madec@noc.ac.uk

10. NOAA-AOML, Miami, FL, rik.wanninkhof@noaa.gov

TITLE: Sensitivity of the seasonal and intraseasonal variations of APO over the Southern Ocean to wind stirring

ABSTRACT:

Here we test the hypothesis that wind stirring over the Southern Ocean can impact the seasonal cycle in both O_2 and CO_2 fluxes, thereby impacting the seasonal cycle in atmospheric potential oxygen (APO). This is tested with a sensitivity study using an ad hoc parameterization of wind stirring in a widely used ocean carbon cycle model (NEMO-PISCES), in conjunction with an atmospheric transport model. Our main finding is that wind stirring exerts a strong control on the phasing of the seasonal cycle of APO, primarily through its impact on the seasonality of air-sea O_2 fluxes, with the sensitivity being stronger to the south of the ACC than to the north of the ACC. The model sensitivity is evaluated against station measurements from both Palmer Station and Cape Grim.

We also identified significant intra-seasonal variations in APO for Palmer Station. Although the intra-seasonal variations are expected to reflect the response timescales of APO to synoptic-scale storms, the relative contributions of oceanic and/or atmospheric processes remain unkown. Here we give preliminary consideration to data constraints that point to ocean mechanisms that may contribute to intra-seasonal APO variability.

Christian Rödenbeck*, Nicolas Cassar, Yasunori Tohjima, Martin Heimann, and Ralph Keeling

*Max Planck Institute for Biogeochemistry Jena, Christian.Roedenbeck@bgc-jena.mpg.de

TITLE: Using atmospheric O2/N2 data to estimate the variability of ocean biogeochemistry

ABSTRACT:

Variability in the oceanic biogeochemical processes that affect carbon fluxes (biological conversion, physical transport and mixing) also causes variability in sea-air O2 exchange and thus –through atmospheric transport– variability in atmospheric O2. Thus, measurements of atmospheric O2 can be used as inverse constraints on ocean carbon biogeochemistry. We first demonstrate this potential of atmospheric O2/N2 data by a comparison of variability estimated from atmospheric O2/N2 data and independently from pCO2 (surface-ocean CO2 partial pressure) data on interannual and seasonal time-scales.

However, use of this potential is currently limited not only by yet open questions how to quantitatively link carbon and oxygen sources/sinks in the ocean (in development), but also by yet open questions how to combine O2 data from the various atmospheric observation networks into a fully mutually consistent data set. As a contribution to this, we secondly illustrate the information gain that would be possible with such a unified global O2 data set. As a particular example, we demonstrate the added information from the temporally and latitudinally extensive data set collected by NIES along ship tracks in the Western Pacific.

Britton Stephens[1], Jonathan Bent[1], Ralph Keeling[2], Andrew Watt[1], Steve Shertz[1], Colm Sweeney[3], Sara Mikaloff-Fletcher[4], Prabir Patra[5], Matt Long[1]

[1]National Center for Atmospheric Research, Boulder, CO, USA, stephens@ucar.edu
[2]Scripps Institution of Oceanography, La Jolla, CA, USA
[3]University of Colorado, Boulder, CO, USA
[4]National Institute for Water and Atmospheric Research, Wellington, NZ
[5] Japan Agency for Marine-Earth Science and Technology, Yokohama, Japan

TITLE: Global scale airborne and ship based observations of atmospheric potential oxygen

ABSTRACT: The HIAPER Pole-to-Pole Observations (HIPPO) campaign, which flew on the NSF/NCAR Gulfstream V research aircraft from 2009-2011, measured the vertical, latitudinal, and seasonal distribution of APO with unprecedented vertical extent and latitudinal coverage. Subsequently, since 2012 we have been conducting continuous measurements of APO from the NSF ship ARSV Laurence M. Gould, operating in all seasons between Punta Arenas, Chile and Palmer Station Antarctica, and resolving the seasonal and latitudinal APO variations over the Southern Ocean with even greater clarity. We will present these measurements and their comparison to a set of combined ocean and atmosphere model predictions. We find that the column average airborne measurements are very effective at eliminating atmospheric transport uncertainty in model-data comparisons, thus enabling rigid tests of ocean models. The HIPPO measurements show that: 1) the equatorial mid-Pacific APO bulge is vertically homogeneous, smaller than some early estimates at approximately 5 per meg, and shifted south of the Equator, 2) the north to south interhemispheric APO gradient is approximately 12 per meg, consistent with strong northward heat transport (see Resplandy et al. abstract), and 3) the seasonal APO amplitude in the mid Pacific is very similar between the two hemispheres, despite the disparity in ocean area. Several models which perform well predicting seasonal APO amplitudes over the Southern Ocean (see Bent et al., abstract) do poorly over the North Pacific, and vice versa. From our shipboard measurements we find that the seasonal APO cycle in Drake Passage is larger than at adjacent station observations and over the mid Pacific at 75-80 per meg, and that the latitudinal peak in amplitude is sharper than represented in coarse resolution models. At Palmer Station, annual mean agreement between ship based in situ and station flask measurements is very good, but with opposing seasonal differences reflecting significant wind direction effects.

Yasunori Tohjima*, Hitoshi Mukai, Toshinobu Machida, Yukio Terao, Shamil Maksyutov, Yukihiro Nojiri

*National Institute for Environmental Studies, Tsukuba 305-8506, Japan, tohjima@nies.go.jp

TITLE: Spatiotemporal variability in APO in the western Pacific region observed from the NIES's observing network

ABSTRACT: We present spatiotemporal variability in atmospheric potential oxygen (APO) based on the systematic observation of the atmospheric CO_2 and O_2 concentrations in the western Pacific region. Air samples were collected into glass flasks at fixed sites including HAT (24°03′N, 123°48′E) and COI (43°10′N, 145°30′E) and onboard volunteer observation ships (VOSs) sailing between Japan and Australia/New Zealand, between Japan and United States, and between Japan and Southeast Asia. In-situ observations were also carried out at HAT and COI and onboard between Japan and Australia/New Zealand.

The distributions of the seasonality and the annual mean values of the observed APO clearly show geographical characteristics. The seasonal amplitude increases with latitude in both hemisphere, reflecting the fact that the seasonal air-sea gas exchanges occur in the mid- and high-latitude. The latitudinal distribution of the annual mean APO shows an equatorial elevation, which is mainly caused by the latitudinal differences in the net air-sea gas exchanges while atmospheric transport also significantly contribute the distributions. We found that the amplitude of the equatorial elevation varied with the ENSO cycle: suppressed and enhanced elevation during El Niño and La Niña periods, respectively. The comparison between the observation and model simulation suggests that the ENSO related variations are mainly attributed to the temporal variation in the atmospheric transport while there is slight possibility that the air-sea gas exchange enhance the observed variations. Finally, we examine the global carbon budgets based on the APO trends. Assuming that net ocean O_2 outgassing flux remained unchanged temporally, the ocean sinks are almost same between the periods of 1999-2006 and 2006-2013 despite increase in the fossil CO_2 emission by 1.7Pg-C yr^{-1}, suggesting significant increase in the land biotic sink for the recent period.

Sander van der Laan[1]*, Andrew C. Manning[1], Laurent Bopp[2], Laure Resplandy[3], Penelope A. Pickers[1], Ingrid T van der Laan-Luijkx[4] and Ralph F. Keeling[3]

[1] Centre for Ocean and Atmospheric Sciences, School of Environmental Sciences, University of East Anglia, Norwich, United Kingdom.
[2] Laboratoire des Sciences du Climat et de l'Environnement, Institut Pierre-Simon Laplace, CEA-CNRS-UVSQ, Gif sur Yvette, France.
[3] Scripps Institution of Oceanography, University of California San Diego, La Jolla, USA.
[4] Meteorology and Air Quality Group, Wageningen University, Wageningen, the Netherlands.

Corresponding author: svanderlaan1978@gmail.com

Is climate change affecting the biotic pump of the Pacific Ocean?

We analyse APO data from the Scripps atmospheric O_2 network to investigate the potential role of climate change on the Pacific Ocean's biotic pump. In an oceanic analogy to the terrestrial biosphere study of Piao et al. (2008), we examine the 'zero-crossings' of detrended APO time series to check for potential anomalies and trends in the timing of oceanic O_2 uptake and release. Our provisional results suggest consistent negative trends in the APO downward (winter) zero-crossing across the Scripps network, implying a trend towards an earlier oceanic O_2 uptake season. Such trends may indicate long-term changes in ocean processes, such as marine productivity, or vertical mixing and ventilation, in response to climate change. In an attempt to explain our results and identify driving mechanisms, we investigate APO zero-crossing correlations with potential driving parameters such as sea surface temperature, ocean colour and the Pacific Decadal Oscillation (PDO). The latter suggests a Pacific surface water cooling anomaly for most of our observation period (1999-2014), which might explain our findings. In addition, we perform the same zero-crossing analysis on modelled APO data derived from the ocean biogeochemical model, Nucleus for European Modelling of the Ocean Pelagic Interactions Scheme for Carbon and Ecosystem Studies (NEMO-PISCES). If consistency is found between the observations and modelled results, we will extend our analysis of the modelled results back to 1950 to further investigate the role of climate change on oceanic seasonality.

Reference:
Piao, S. L., et al. (2008), Net carbon dioxide losses of northern ecosystems in response to autumn warming, *Nature*, *451*(7174), 49-U43.

Charlotte van Leeuwen and Harro A.J. Meijer
Centre for Isotope Research (CIO), Energy and Sustainability Research Institute Groningen (ESRIG), University of Groningen, Groningen, the Netherlands

Detection of CO_2 leaks from Carbon Capture and Storage (CCS) sites with combined atmospheric CO_2 and O_2 measurements*

ABSTRACT:

CO_2 and O_2 are coupled in most processes on earth (e.g. photosynthesis, respiration and fossil fuel burning), but not in the case of a leak from a CCS site. Whereas a natural increase of the CO_2 concentration is accompanied by a drop in the O_2 concentration, an increase in the CO_2 concentration caused by a leak from a CCS site does not have any effect on the O_2 concentration. Aiming to aid in the detection of CO_2 leaks from CCS sites, we have constructed a transportable instrument that simultaneously measures the CO_2 and (relative) O_2 concentration of the atmosphere The instrument consists of an ABB Uras26 NDIR instrument for CO_2, a modified Oxzilla II dual fuel cell instrument for O_2, and an extensive air inlet control system.The instrument shows an excellent precision for the CO_2 measurements; for O_2 the transportable and flexible design of our system compromised the precision somewhat. The precision in both CO_2 and O_2 determines the detection limit of the system for leaks of CO_2.
The principle of CO_2 leak detection is illustrated by several CO_2 release experiments in which CO_2 was released at a small distance from the air inlet of the measurement system. We present two strategies that can be used to analyze a dataset to find a leak of CO_2. The detection limit of our instrument is estimated to be around 6 ppm. If a transportable design would not be necessary, the precision for the O_2 measurements can be improved such that the ultimate detection limit of this method is estimated to be around 3 ppm, which would correspond to distances up to 500 meters for a leak of 1000 ton CO_2 $year^{-1}$ (32 g s^{-1}) provided favorable atmospheric conditions (wind direction and atmospheric stability) exist. This implies that monitoring time should be long enough to ensure that these conditions occur.

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Charlotte van Leeuwen, Bert Scheeren, Ingrid T. van der Laan-Luijkx, Harro A.J. Meijer, Huilin Chen and Bert A.M. Kers

Centre for Isotope Research (CIO), Energy and Sustainability Research Institute Groningen (ESRIG), University of Groningen, the Netherlands

TITLE: Continuous and flask observations of atmospheric $\delta O_2/N_2$ and CO_2 at Lutjewad station, the Netherlands, and Mace Head station, Ireland

ABSTRACT:

We present an update of the flask-based observations of atmospheric $\delta O_2/N_2$ and CO_2 at the atmospheric monitoring stations Lutjewad, the Netherlands (53°24'N, 6°21'E), and Mace Head, Ireland (53°20'N, 9°54'W), as well as the first continuous $\delta O_2/N_2$ observations from Lutjewad. The flask observations now cover a period of 15 years or more for both stations, running from 1998 to 2014 for Mace Head and 2000 – 2015 for Lutjewad. The $\delta O_2/N_2$ ratio of all flasks is determined in our laboratory, on a Micromass Optima dual inlet isotope ratio mass spectrometer (DI-IRMS) with an estimated precision of 4 per meg for replicate measurements. The accuracy on the internal scale of the laboratory is better than 2 per meg, but the conversion to the international scale is still unsatisfactory due to difficulties with measuring high-pressure gas cylinders, on which the establishment of the international scale is based. Trends and (peak-trough) amplitudes for CO_2, $\delta O_2/N_2$ and the related tracer APO (Atmospheric Potential Oxygen) were determined for the flask measurements of the two stations, using only samples collected at baseline conditions (not influenced by local sources and sinks), for both the complete dataset as well as the most recent data running from 2009 to 2014 / 2015. The data record of Mace Head appeared to be very robust, with almost no need to remove data points from the dataset due to non-background measurements and almost no variation in the seasonal cycle throughout time. Lutjewad station included more locally influenced samples, with as a consequence a higher need for background condition filtering and more variation in the calculated seasonal cycles and trends. The time series from the new, continuous $\delta O_2/N_2$ measurement system running at Lutjewad since 2007 unfortunately still contains many gaps.

Gen Zhang* and Lingxi Zhou*

*Chinese Academy of Meteorological Sciences (CAMS), China Meteorological Administration (CMA), Beijing 100081, China, zhoulx@cams.cma.gov.cn; zhangg@cams.cma.gov.cn

TITLE: Determination of the changes in atmospheric Ar/O_2 and O_2/N_2 by using GC-TCD

ABSTRACT: An improved method for measuring changes in atmospheric Ar/N_2 and O_2/N_2 ratio by GC-TCD was described by using a capillary column with the aid of Dr. Tohjima from NIES. Preliminary results indicated Ar, O_2, and N_2 were successfully separated, however, precisions are far from the recommended targets (Table 1). One of the attempts to improve the precisions was carefully minimize fluctuations of pressure and temperature. For example, differential pressure gauges (Model 239) and pressure control units (PCU-2100) were added to both input and output of the GC. Further suggestion and help are expected and appreciated to optimize the system.

Table 1. Preliminary test results of the cylinder natural gas by this method

Time(min)	RT（min）			Peak Area			Ar/N_2	O2/N2
0	Ar	O2	N2	Ar	O2	N2		
10	2.764	2.809	5.054	312.5756	6529.872	26040.6	0.012003	0.250757
20	2.764	2.809	5.054	311.1126	6561.598	26025.5	0.011954	0.252122
30	2.764	2.810	5.055	311.8908	6525.167	26018.5	0.011987	0.250789
40	2.765	2.810	5.055	**311.7377**	**6522.99**	**26005.4**	0.011987	0.250832
50	2.765	2.810	5.055	**311.7261**	**6588.239**	**26002.4**	0.011988	0.253370
60	2.764	2.810	5.055	312.1133	6589.31	26035	0.011988	0.253094
70	2.764	2.809	5.054	312.2048	6595.405	26048.8	0.011985	0.253194
80	2.765	2.810	5.055	313.331	6539.109	26078.9	0.012015	0.250743
90	2.764	2.809	5.054	312.3455	6604.219	26050.9	0.011990	0.253512
100	2.765	2.810	5.055	311.5289	6577.831	26054.7	0.011957	0.252462
110	2.764	2.809	5.054	312.3776	6587.303	26045.2	0.011994	0.252918
120	2.764	2.810	5.055	311.6351	6550.114	26037	0.011969	0.251569
130	2.765	2.810	5.055	312.2865	6598.628	26018.4	0.012003	0.253614
140	2.766	2.811	5.056	310.5711	6589.925	26028.1	0.011932	0.253185
150	2.764	2.808	5.054	312.7065	6592.308	26074.1	0.011993	0.252830