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UNIVERSITY OF CALIFORNIA, SAN DIEGO

**Continuous Measurements of Atmospheric Ar/N₂ as a Tracer of
Air-Sea Heat Flux: Models, Methods, and Data**

A dissertation submitted in partial satisfaction of the
requirements for the degree Doctor of Philosophy in
Oceanography

by

Tegan Woodward Blaine

Committee in charge:

Professor Ralph F. Keeling, Chair
Professor Paul Robbins
Professor Jeff Severinghaus
Professor Richard Somerville
Professor Mark Thiemens
Professor Ray Weiss

2005

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PUBLICATIONS

- Keeling, R. F., T. Blaine, W. Paplawsky, L. Katz, C. Atwood, and T. Brockwell. 2004. Measurement of changes in atmospheric Ar/N₂ ratio using a rapid-switching, single capillary mass spectrometer system. *Tellus* 56B: 322-338.
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ABSTRACT OF THE DISSERTATION

Continuous Measurements of Ar/N₂ as a Tracer of

Air-Sea Heat Flux: Models, Methods, and Data

by

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Doctor of Philosophy in Oceanography
University of California, San Diego, 2005
Professor Ralph F. Keeling, Chair

This work primarily concentrates on establishing a long-term, continuous measurement program of atmospheric Ar/N₂. The atmospheric argon and nitrogen cycles should be dominated by ocean ingassing and degassing due to air-sea heat exchange, which links the heat and chemistry cycles through changes in solubility. Atmospheric Ar/N₂ can thus serve as a tracer of air-sea heat flux and ocean heat storage on both seasonal and interannual time scales, providing an independent estimate of the long-term warming of the earth's oceans due to global warming.

In this dissertation, I use simple box models to develop the argument that Ar/N₂ measurements should yield useful information on air-sea heat flux. I also employ predictions from a comparative project testing atmospheric transport models to create global maps of the expected seasonal cycle in atmospheric Ar/N₂.

I then describe the development of a continuous air intake system that is coupled with an existing mass spectrometer. I discuss the technical issues associated with calibration, especially the recognition of thermal fractionation at the sampling

inlet. This result has already led to changes in the way atmospheric flask sampling is performed at stations as well as allowing continuous measurements with a precision of 2-3 per meg over an hour.

Lastly, I present the first 17 months of semi-continuous data measured at the Scripps Pier, La Jolla, CA, showing a seasonal cycle of 9 per meg. Parallel measurements of O_2/N_2 and Ar/N_2 allow the seasonal cycle in air-sea O_2/N_2 flux to be partitioned into components due to heat flux and changes in ocean biology and stratification. The annual cycle is overlaid with significant synoptic variability, which has been observed at this level for the first time. The correlation between the deviations in Ar/N_2 and O_2/N_2 suggest that these changes may be due to changes in air-sea heat flux or atmospheric transport, however the anomalies are not clearly driven by regional or local changes in air-sea heat flux. It is possible that instrumental issues remain to be worked out, but the anomalies may also hint at unexpected complexities in the atmospheric Ar/N_2 cycle.

Chapter 1

Introduction

1.1 Background

The international community has become increasingly aware of evidence for the rise in average global temperature due the anthropogenic buildup of greenhouse gases in the atmosphere. The resultant climate changes, ranging from ecosystem effects and changes in rainfall patterns and increased extreme weather events to the rise in the sea surface height (Houghton et al. 2001), have wide-ranging implications for human populations: food, water, and energy security, political conflict and refugee crises due to changing and degrading resources, and human health concerns are all linked to these climatic changes.

Atmospheric carbon dioxide is presently the most important anthropogenic greenhouse gas. Its concentration is increasing due to anthropogenic emissions, of which about 75% come from fossil fuel burning. Only about half of this carbon

dioxide has contributed to atmospheric increases; the rest is being taken up by dissolution in the ocean and photosynthesis in terrestrial ecosystems (Houghton et al. 2001). Understanding the mechanisms behind this uptake and its geographic variability is critical to predicting how the CO₂ system will change in the future due to increased emissions and resultant climate change. The division of the uptake by oceans and land also varies interannually as such processes as the El Niño-Southern Oscillation result in changes in sea surface temperature and land uptake (McKinley et al. 2003).

The partitioning between the ocean and land reservoirs can be determined on interannual time scales by combined measurements of atmospheric CO₂ and O₂ (Keeling et al. 1996). The two gases are tightly coupled through photosynthesis, respiration, and fossil fuel combustion. On subannual time scales, however, they have very different patterns of air-sea exchange. O₂ and most other gases equilibrate within a few weeks. In contrast, CO₂ exchange is buffered by conversion into other, non-gaseous forms in the ocean; the gaseous form of CO₂ is only about 1% of the total amount of oceanic CO₂. Chemical equilibrium takes on the order of a year or longer to reach (Broecker and Peng 1974). This difference from the O₂ cycle is exploited in order to calculate the magnitude of two different components of the seasonal cycle: that due to exchange with the terrestrial biosphere and that due to air-sea fluxes.

It is useful to understand the seasonality in the air-sea O₂ exchange in order to better understand potential sources of variability in the O₂ signal. The large O₂ fluxes across the interface are driven both by ocean photosynthesis and by air-sea heat flux (Garcia and Keeling 2001). Ocean uptake of most gases depends on the temperature

of the surface ocean through changes in solubility, linking heat and chemistry cycles. In general, as the temperature of the ocean surface rises, the solubility of a gas in the ocean drops, and gas is naturally released to the atmosphere. The reverse happens with cold water, where the solubility is higher (Weiss 1970). Biologically mediated air-sea O₂ exchange tends to have the same direction as O₂ exchange due to air-sea heat flux (Garcia and Keeling 2001). However, atmospheric O₂ measurements alone cannot distinguish between gas exchange due to air-sea heat flux or due to ocean biology. Research into the biogeochemistry of O₂ and CO₂ has led to a pressing need to better understand air-sea heat flux and its controls on cycles of important atmospheric gases.

The ocean has the potential to exert enormous influence on global climate through its role in storage and transport of carbon and other gases. It also has more direct roles in climate change: as a source of water for evaporation in the hydrological cycle; and in exchanging heat across the air-sea interface and transporting it around the globe, as well as serving as a large heat reservoir (Ganachaud and Wunsch 2000). The concentration of important greenhouse gases in the atmosphere has increased since the beginning of the industrial era (Houghton et al. 2001). The earth is presently thought to be out of radiative balance due to the buildup of these gases, receiving more solar radiation than that which is being emitted back to space and leading to a gradual warming of the earth's temperature (Hansen et al. 2005). Because the ocean delays the global response to this forcing, the amount by which the earth is out of balance can be independently estimated as the rate of the observed ocean heat storage (Pielke

2003). Using data on ocean heat storage from Levitus et al. (2000), Hansen et al. (2005) estimate that the earth is receiving an excess 0.85 W m^{-2} of radiation.

Both the ocean and the atmosphere transport heat from equatorial to polar regions (Peixoto and Oort 1992). The partitioning of poleward heat transport between ocean and atmosphere is not well known and is likely to change in the future.

Timmerman et al. (1999) suggest that the interactions between air and water in equatorial areas may be stronger in a warmer climate, increasing the amount of interannual variability and more strongly skewing it, with strong cold events relative to a mean warm state becoming more frequent. Understanding the important mechanisms in different latitudes and how poleward heat transport is distributed between air and sea is an active region of debate (Keith 1995; Cohen-Solal and Le Truet 1997; Trenberth and Caron 2001; Trenberth et al. 2001; Held 2001; Jayne and Marotzke 2001; Ganachaud and Wunsch 2003; Talley 2003; Hazeleger et al. 2004; Kelly 2004). Estimates of mean ocean heat transport still have large associated errors, and so it is difficult to even begin looking at temporal variability (Hazeleger et al. 2004). However, future changes in the mechanisms involved and possible ocean feedbacks to the atmospheric and cryogenic systems will be important to understand (Willis et al. 2004).

At the moment, the best estimate of ocean warming during the last five decades comes from over seven million historical data points from profiles, buoy data, and floats compiled into the World Ocean Database (Conkright et al. 2002; Levitus et al. 2005; Levitus et al. 2000). The strength of the dataset lies in the large number of measurements and the regional and temporal information that is available (Levitus et

al. 2005). However, the data are still sparse in many areas, especially in the Southern Hemisphere and at depths lower than 360 m. The method used to fill in places where data is lacking may bias some of the results (Gregory et al. 2004). Although comparisons with atmosphere and ocean coupled general circulation models suggest that the trend in the data over the last 30 years is real and attributable to anthropogenic forcing (Barnett et al. 2005; Levitus et al. 2001; Reichert et al. 2002), Gregory et al. (2004) and Pielke (2003) question the estimated interannual variability in the Levitus estimates because the subsurface temperature variability is so large in comparison to that estimated by models.

An independent estimate of the warming of the oceans and interannual variability in air-sea heat flux and oceanic heat storage is needed. Inferring such variables from oceanographic data would require frequent measurements of ocean temperature at many depths and locations. This is extremely difficult given the poor sampling of ocean temperature over much of the ocean (Willis et al. 2003). However, because the time scale for atmospheric mixing is on the order of a few weeks within a latitude band and on the order of a year for interhemispheric exchange (Bowman and Cohen 1997; Geller et al. 1997), an abiotic atmospheric tracer of air-sea heat flux could serve as an “integrator,” where a few measurements could quantify oceanic changes on a global scale. This potential is the driving idea behind research into the atmospheric cycle of argon. As the most abundant noble gas, the atmospheric argon concentration should be dominated by ocean ingassing and degassing due to air-sea heat exchange (Battle et al. 2003). Although latitudinal gradients due to ocean heat transport and synoptic variability related to regional effects may be exhibited in the

argon measurements at a suite of stations just as they are in CO₂ or O₂/N₂ measurements (Manning et al. 2001), the long-term pattern at any station will reveal global changes.

Argon is an inert gas. Its concentration in the ocean is controlled by both solubility and kinetic controls. However, the kinetic controls, such as bubble injection and surfactants, have only a small effect, further minimized by rapid gas equilibration. The primary control on the ocean concentration is solubility, which is strongly dependent on water temperature. Changes in the atmospheric argon concentration thus are proportionally related to changes in the integrated temperature of the ocean ventilated layer, or heat content.

A long-term measurement program of such a noble gas atmospheric tracer would have the power to address ocean warming questions, as well as many other aspects of ocean heat transport and air-sea heat flux. It would provide one consistent, atmospherically integrated measurement record with high temporal resolution that has the potential to be as scientifically important as the long-term CO₂ record from Mauna Loa. Any trend in the annual mean concentration due to warming of the global oceans would probably be visible within five years for a continuous record and closer to 10 years in a flask record due to present measurement precision. (The relevant techniques, measurement precision, and expected size of such fluxes will be discussed in later chapters.)

Such a measurement program could provide important information not only on long-term time scales but on seasonal ones as well. It has proven difficult to close the global climatological ocean heat budget; errors of 30 W m⁻² are typical, whereas

estimates need to be closed to within $2\text{--}3 \text{ W m}^{-2}$ to be comparable with hydrographic temperature data (Josey et al. 1999). The air-sea heat flux has been estimated using several techniques: shipboard or buoy measurements (Graber et al. 2000); residual calculations from satellite measurements of radiation based on atmospheric circulation models (Trenberth and Caron 2001); bulk formulas based both on hydrographic and satellite information (Josey et al. 1999; Hasse and Smith 1997; Jo et al. 2004); and inverse methods based on hydrographic information and ocean circulation models (Gloor et al. 2001). All of these methods have both strengths and problems.

Measurements of an atmospheric noble gas tracer at an array of stations with a zonal distribution have the potential to give information about regional air-sea fluxes of heat and how these fluxes change on seasonal, interannual, and long-term scales as the ocean warms. Estimates of the climatological cycle in ocean heat content will be important for verifying atmosphere-ocean general circulation models (Antonov et al. 2004). Air-sea gas exchange rates can also be estimated regionally and may yield more insight into questions dealing with variations in exchange rates and possible parameterizations (Nightingale et al. 2000; Wanninkhof 1992; Liss and Merlivat 1986).

Assessed concurrently with O_2 and CO_2 , a noble gas tracer may also be used to address the partitioning of the seasonal O_2 flux between ocean biology and gas exchange associated with air-sea heat flux. As the ocean warms due to climate change, O_2 is being degassed to the atmosphere; present estimates of the amount are based through indirect methods on the heat storage change estimated by Levitus et al. (2000) and may have significant interannual variability (Keeling and Garcia 2002;

Table 1.1. Effect of ocean warming at different temperatures on global atmospheric composition of the noble gases. N₂ is include for comparison. Adapted from Keeling et al. (2004).

Species	Mole fraction in dry air	Relative change of atmospheric concentration for a 100×10^{21} J ocean warming		
		0°C	10°C	20°C
He	5.24×10^{-6}	0.23×10^{-6}	0.14×10^{-6}	0.1×10^{-6}
Ne	18.2×10^{-6}	0.54×10^{-6}	0.4×10^{-6}	0.33×10^{-6}
Ar	0.00934	6.56×10^{-6}	4.31×10^{-6}	2.99×10^{-6}
Kr	1.14×10^{-6}	16.4×10^{-6}	10.43×10^{-6}	6.95×10^{-6}
Xe	0.087×10^{-6}	40.27×10^{-6}	23.73×10^{-6}	14.8×10^{-6}
N ₂	0.0781	2.66×10^{-6}	1.75×10^{-6}	1.22×10^{-6}

Plattner et al. 2002). Natural changes such as ENSO and wintertime convection in the north Atlantic are already known to be important for understanding interannual variability in air-sea O₂ flux (McKinley et al. 2003). Model results suggest that ocean warming will also lead to changes in stratification, impacting ventilation and biological productivity (Sarmiento et al. 1998; Bopp et al. 2002). Correcting the partitioning of contributions of land and ocean production in the overall O₂ and CO₂ budgets requires more information on the size of physical and biological processes on O₂ air-sea fluxes. This information may also help to constrain the interannual changes in air-sea CO₂ flux, which are presently poorly known (Le Quéré et al. 2000), although the variability of the ocean CO₂ sink is likely much smaller than that on land (Le Quéré et al. 2003).

Table 1.1 shows the relative changes in atmospheric abundances for the noble gases and N₂ given a heat flux of 100×10^{21} J into the ocean, assuming solubility equilibrium. The calculation of gas fluxes and the dependence on temperature will be

discussed more thoroughly in Chapter 3. For now, it is useful to note that the ratios using heavier noble gases, such as Kr/N₂ or Xe/N₂, should be more sensitive to air-sea heat flux. However, because their atmospheric concentrations are so small, it would be necessary to concentrate samples before analysis.

This dissertation primarily concentrates on establishing a long-term measurement program of atmospheric Ar/N₂, balancing the size of the expected change due to air-sea heat flux with the complexity of the measurement technique. Although many of the scientific issues discussed above are beyond the scope of this work, they give an idea of the range of questions that an atmospheric tracer of air-sea heat flux could help address and their scientific significance. This work instead focuses on the development of a new measurement technique and what can be learned from seasonal patterns of tracers of air-sea heat exchange and the impact on atmospheric gas cycles. Such initial steps will lay the groundwork for interpretation of a long-term record.

1.2 Atmospheric geochemistry

Dry air is primarily made up of three elements: nitrogen (~78%), oxygen (~21%), and argon (~1%) with many other trace gases, of which CO₂ is the most common (~0.03%). Although the mean concentrations of the major gases were determined more than 50 years ago (summarized in Glueckauf (1951)), and the seasonal cycle in CO₂ concentration and other trace gases has been monitored for several decades, the seasonal cycle in O₂ concentration has only been measured for the

last 15 years (Keeling et al. 1992; Keeling et al. 1998). The major challenges in measuring the seasonal cycle in the relative abundance of the most plentiful atmospheric gases are due to the small size of the seasonal changes relative to the total amount in the atmosphere. The CO₂ and O₂ concentrations vary on the order of 15-20 parts per million on seasonal timescales. Whereas that change is equivalent to a 4-5% change in net CO₂ concentration, it is equivalent to a 0.0060 – 0.010% change in O₂, creating unique challenges in both instrumentation and in development of reference gases.

The interest in CO₂ and its close coupling with O₂ spurred the initial innovations needed to measure the O₂/N₂ ratio, using an interferometric method (Keeling 1988). Subsequent research resulted in three other methods for measuring the O₂/N₂ ratio, including using mass spectrometry (Bender et al. 1994), a vacuum ultraviolet oxygen analyzer (Stephens 1999), and a paramagnetic analyzer (Manning et al. 1999). At the same time, these techniques began to be used for continuous measurements, both at stations such as Baring Head, New Zealand (Manning 2001) and for measurements at sea (Stephens 1999). Flask measurements provided large geographic coverage; continuous measurements provided high resolution time series at specific stations. The joint measurement programs have allowed new questions to be addressed, such as the interannual partitioning between land and ocean sinks of CO₂ (Keeling et al. 1996; Manning 2001) and the size of air-sea CO₂ fluxes due to coastal upwelling and plankton bloom events (Lueker 2004).

At this point, the atmospheric cycles in O_2 and CO_2 are comparatively well-understood. In contrast, almost nothing is known about atmospheric cycles in Ar abundance, although it is the third most abundant component of the atmosphere.

The amount of Ar in the ocean/atmosphere system is thought to be extremely constant. On geologic time scales, radioactive potassium (^{40}K) in the earth's crust decays into radiogenic argon (^{40}Ar) with a half-life of 1250 million years (Turner 1989). About 11.5% of the decay product is ^{40}Ar , and the balance is ^{40}Ca . Because Ar is an inert gas, this radiogenic component is very important in the global Ar budget, accounting for 99.6% of atmospheric ^{40}Ar (Dickin 1995). Allegre et al. (1996) estimate a yearly maximum flux to the atmosphere of 5×10^7 moles of argon from potassium decay and subsequent degassing in the mantle. Considering that the atmosphere has about 1.7×10^{20} moles of air, this yearly flux still only accounts for annual increases in argon concentration of 1 part in 3.5×10^{12} , an extremely small annual growth rate. For comparison, our instrument precision is on the order of 1 part in 10^6 . The other two stable isotopes of argon in the atmosphere are ^{36}Ar and ^{38}Ar , comprising 0.34% and 0.063% respectively (CRC Handbook (Lide 1995)).

As will be discussed in a later chapter, measurements of Ar concentration rely on comparison to an atmospheric species whose concentration has even smaller seasonal changes, in this case N_2 . Because the atmosphere is 0.934% argon and 78.084% nitrogen (Glueckauf 1951), the Ar/ N_2 molar ratio is about 0.0120. Atmospheric N_2 is derived from primitive outgassing from volcanic activity and mantle outgassing, with a present-day net flux of 2.2×10^9 mol N_2 yr⁻¹ (Marty 1995). For many applications, it can be considered as an inert gas. The largest available pool

of N_2 is located in the atmosphere, with 3.9×10^{21} g. In comparison, only ~ 100 - 145×10^{15} g is contained in soils and land biota (Schlesinger 1997), with another 570×10^{15} g contained in the oceans (Pilson 1998). With a flux of about 460×10^{12} g N yr^{-1} due to biological fixation and denitrification both on land and in the ocean (Schlesinger 1997), the net effect on the atmospheric N_2 concentration due to a seasonal biological cycle is negligible. However, the assumption that biological activity does not influence the seasonal cycle of atmospheric N_2 may be inaccurate in coastal areas, where biological pulses can release $0.2 \times 10^{12} \pm >70\%$ g N_2O-N yr^{-1} (Nevison et al. 2004) and potentially much larger pulses of N_2 . On short time scales, these pulses could change the local atmospheric concentration of N_2 .

Even if not for the critical role that Ar/ N_2 measurements could play in understanding questions of heat, research into its atmospheric cycle would be of interest to the field of geochemistry.

1.3 Overview of research

In Chapter 2, I start by examining the seasonal cycles of a tracer called atmospheric potential oxygen (APO), generated when the oxygen record is adjusted for changes in CO_2 concentration due to land photosynthesis and decomposition. The seasonal cycles in APO largely reflect air-sea fluxes of O_2 , since air-sea fluxes of CO_2 are known to be small on seasonal time scales. In collaboration with the Transport Comparison Project (TransCom), I submitted monthly seasonal air-sea oxygen and nitrogen flux fields to TransCom members, which they ran as a boundary condition in

off-line atmospheric transport models. They returned high temporal resolution output on atmospheric concentrations from 120 stations and global monthly maps from nine altitudes. I compare the high resolution station data to APO data from the Scripps station network in order to assess how well the models perform based on such a tracer. I then compare global maps and transects of the models to develop ideas about where more measurements need to be taken in order to better distinguish between the performance of different models.

The seasonal variations in APO are tied both to air-sea heat flux (through changes in solubility) and ocean biology. In the rest of my thesis, I shift my focus to the Ar/N₂ ratio as the abiotic analog to APO. I use simple box models in Chapter 3 to help explain the relationship between air-sea heat flux and atmospheric Ar/N₂ and to develop the argument that Ar/N₂ measurements may yield useful information on air-sea heat flux. I also employ the model results used in Chapter 2 to give predictive maps of atmospheric concentrations of the Ar/N₂ ratio near the surface, which would be directly comparable to station measurements.

Chapter 4 describes laboratory work involving developing techniques to measure the atmospheric Ar/N₂ ratio. Although recent advances in elemental mass spectrometry have permitted measurements of the Ar/N₂ ratio in flasks in the last five years, both Battle et al. (2003) and Keeling et al. (2004) find that the measurement precision is significantly limited due to problems in collecting and extracting flask air samples, and the error is of the same order of the seasonal cycle in Ar/N₂. I thus developed a continuous air intake system that is coupled with the existing mass spectrometer, bringing air directly from the Scripps Pier to the laboratory and

bypassing some of the problems inherent in flask measurements. I describe this new system, as well as some of the technical issues associated with calibration. I also show that the 17 months of data successfully measures a seasonal cycle of ~ 9 per meg in atmospheric Ar/N₂ in La Jolla during the period from February 2004 to June 2005.

Chapter 5 provides an in-depth look at the first 17 months of semi-continuous data. The measured seasonal cycle is compared to regional air-sea heat flux estimates from the National Center for Environmental Prediction (NCEP) reanalysis output for the same time period and found to be within expectations. Parallel measurements of O₂/N₂, CO₂, and Ar/N₂ allow the seasonal cycle in O₂/N₂ to be partitioned into components due to land photosynthesis and respiration, air-sea heat flux, and changes in ocean biology and stratification.

The annual cycle is overlaid with significant synoptic variability on time scales from one week to a month and which has been observed at this level for the first time. The correlation between the synoptic variations in Ar/N₂ and APO suggest that these changes may be due to changes in air-sea heat flux or atmospheric transport. However, the anomalies are not clearly driven by regional or local changes in air-sea heat flux. It is possible that instrumental issues remain to be worked out, but the anomalies may also hint at unexpected complexities in the atmospheric Ar/N₂ cycle.

These results have significant implications for improving flask measurements of Ar/N₂. One of the important developments in this thesis is the recognition of thermal fractionation of up to 60 per meg at a sampling inlet (Chapter 4), which may be one of the reasons that flask measurements show so much variability. Commercial aspirators have already begun to be installed at the Scripps network of flask stations.

Also, if the synoptic variability in the Ar/N_2 concentration turns out to be real rather than an artifact of instrumental problems, such knowledge may be critical to analyzing and interpreting station flask measurements.

It is planned that the semi-continuous measurement system will continue to be maintained and improved at the La Jolla station. As the record of atmospheric Ar/N_2 grows longer, it will provide useful information on interannual changes in the size and timing of air-sea heat flux and ocean heat storage and new knowledge about the atmospheric geochemistry of argon.

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Chapter 2

Testing tracer transport models with combined measurements of atmospheric O₂ and CO₂

2.1 Background

Since the late 1800s, the atmospheric CO₂ concentration has been growing due to burning of fossil fuels and changes in land use and land cover. However, the actual concentration of CO₂ in the atmosphere is rising at a much smaller rate than expected from emissions, because CO₂ is taken up by the land biosphere and the ocean. Estimating the size of these sinks is not an easy calculation. One method uses atmospheric transport models to refine initial estimates of different sources and sinks through inverse modeling techniques and comparison with station CO₂ data (Gurney et al. 2003). Basically, the models use assumptions about how CO₂ is transported in the atmosphere (formalized in a model) to connect CO₂ fluxes from sources and sinks to final concentrations of atmospheric CO₂ as measured at stations and to refine the estimates of the initial fluxes.

The Atmospheric Tracer Transport Model Intercomparison Project TransCom) has its roots in the 4th International CO₂ conference in 1993. A collaboration between modeling groups, it was created to assess and analyze the behavior and transport algorithms of atmospheric tracer transport models (Denning et al. 1999). For a particular project, each participating research group uses the same shared datasets of gas fluxes from sources and sinks as input into their tracer transport model. The model predictions of atmospheric concentrations are then submitted in a standardized format to a central computer server, where any member of the group can access the output. The first two studies centered on forward simulations to compare model predictions with atmospheric measurements: Law et al. (1996) used estimates of CO₂ emissions from both fossil fuel and land biology; Denning et al. (1999) employed sulfur hexafluoride (SF₆), which has similar spatial patterns of anthropogenic emissions to CO₂ but no biological source. The third project concentrated on inverse calculations of carbon dioxide sources and sinks on annual mean, seasonal, and interannual time scales, as well as evaluating the sensitivity of the results to the choice of data used (Gurney et al. 2002, Gurney et al. 2003, Law et al. 2003, Gurney et al. 2004).

One of the weaknesses associated with transport models has to do with a lack of understanding of the “rectifier effect” – the relationship between seasonal changes in fluxes and transport. In general, both tracer concentrations and the time scale of atmospheric transport can be broken into seasonal and annual mean components for analysis. However, the interaction of seasonal fluxes and seasonal changes in

atmospheric transport can lead to a mean annual signal, known as the rectifier.

Likewise, the mean annual fluxes and transport can lead to a seasonal signal (Keeling et al. 1993). Models may not be accurately reflecting seasonal changes in transport and fluxes, which may lead to problems in both forward predictions and inverse analyses.

This study extends the earlier TransCom work by building an understanding of atmospheric transport of an oceanic tracer on seasonal time scales. The tracer chosen for this analysis is atmospheric potential oxygen (APO), as defined by Stephens et al. (1998). APO is effectively the amount of O_2 that would be present in an air parcel if land photosynthesis drew CO_2 down to zero. Based on the stoichiometric relationship between O_2 and CO_2 in terrestrial photosynthesis and respiration (Keeling 1988; Severinghaus 1995), APO is conservative to land biology but reflects the oceanic component in the atmospheric CO_2 and O_2/N_2 cycles. On seasonal time scales (the focus of this study), the oceanic O_2 exchange is much larger than the CO_2 exchange, because the equilibration time for oceanic CO_2 is 12-20 times longer than for most other gases. As carbon is stored primarily in carbonate and bicarbonate, the reactions between dissolved CO_2 and these species buffer the air-sea CO_2 flux (Keeling et al. 1993). Like the air-sea CO_2 exchange, the combustion of fossil fuels contributes very little in seasonality in APO in comparison to the size of air-sea fluxes of oxygen. The seasonal cycle in APO thus is effectively equivalent to the oceanic component of the O_2/N_2 cycle.

The seasonal air-sea oxygen flux contribution to the atmospheric O_2/N_2 cycle reflects both biological and physical processes across the air-sea interface. Biological processes include marine production and remineralization of organic matter. Physical processes include air-sea gas exchange, water ventilation, solubility changes driven by temperature changes, and near-surface turbulence and mixing (Garcia and Keeling 2001). The seasonal cycle is characterized by a net O_2 flux into the atmosphere during spring and summer, whereas the fall and winter are characterized by a net flux out of the atmosphere and into the ocean (Najjar and Keeling 2000). There is also a small thermal component in N_2 , which reduces the amplitude of the overall O_2/N_2 ratio by about 10%. These seasonally varying fluxes are small in equatorial areas and largest between $30-60^\circ$ in each hemisphere where the seasonal air-sea heat fluxes are largest (Garcia and Keeling 2001). On top of this seasonal flux is a mean zonal component, with tropical areas serving as a source of O_2 and high-latitude areas serving as a sink (Stephens et al. 1998).

Recent work has concentrated on developing global maps of seasonal air-sea O_2 fluxes based on the dissolved O_2 anomaly in the upper ocean and using these maps to calculate the air-sea gas exchange velocity. Najjar and Keeling (2000) first developed such maps, although they are known to have seasonal sparseness of data that leads to a summertime bias and a possible underestimate of seasonal variations and overestimate of the annual mean. These fluxes were used as a boundary condition into the atmospheric transport model TM2 to estimate the air-sea O_2 exchange velocity based on comparison of APO measured at stations (Keeling et al. 1998). The authors

concluded that the Wanninkhof (1992) formulation for air-sea gas exchange velocity performed better than alternative formulations. They further refined the air-sea O₂ exchange velocity by calculating regional scaling constants of 1.15 ± 0.05 and 1.23 ± 0.05 in the northern and southern hemispheres, respectively, poleward of 31°. Although any estimate of low latitudes is likely to have more error, they suggested a range of values between 0.07 and 0.53 for individual stations.

These results were revised by Garcia and Keeling (2001), who presented a refined estimate of air-sea O₂ fluxes. Using the same transport model, Garcia and Keeling concluded the Wanninkhof (1992) formulation for air-sea gas transfer velocities worked well with no scaling coefficient. The results of both of these papers depend on the accuracy of the atmospheric transport model used. This point will be relevant later in the discussion of this present work.

APO has previously been used to evaluate models of ocean transport. Stephens et al. (1998) employed ocean models to predict annual mean air-sea fluxes and then used the modeled fluxes as input to an atmospheric transport model in order to compare its predictions with the distribution of atmospheric APO observations. The study concluded that the oceanic models were underestimating the interhemispheric gradient in APO and the southward oceanic fluxes of oxygen and carbon dioxide. High atmospheric APO concentrations were predicted near the equator, where outgassing led to large air-sea O₂ fluxes in the ocean models. However, their conclusions were limited by lack of any monitoring stations in equatorial areas and by the ability of the atmospheric transport model to correctly represent transport. A

following study using a different atmospheric transport model (Gruber et al. 2001) suggested that the underestimates of oceanic flux found by Stephens et al. (1998) could be inaccurate due to problems in the atmospheric transport model used rather than to problems with the ocean models. More recent measurements of APO in equatorial areas, however, confirm the “equatorial bulge” and suggest that it is larger than expected from either of the two previous studies (Battle et al. 2005). These three papers highlight the importance of better understanding the limitations – and predictive abilities – of atmospheric transport models.

In the present study, TransCom participants were asked to run seasonal flux fields of oceanic O_2 and N_2 in their own atmospheric transport models. Each modeling group then submitted seasonal model predictions of atmospheric concentrations to the TransCom program archive, from which I could access the output. The resulting changes in O_2 and N_2 in the atmosphere can then be combined to estimate changes in the O_2/N_2 ratio, which in turn can be compared to observations.

In this chapter, I compare station-specific model predictions and observations of seasonal atmospheric APO cycles and the rectifier effect on APO in order to evaluate the transport models and the flux fields used. I then consider global maps and transects of APO to further study differences in predictions among the models. The annual mean component of the air-sea fluxes is not used in this study because the mean air-sea O_2 flux is not well-defined. Any resultant annual mean is thus limited solely to the interaction between seasonal atmospheric transport patterns and oceanic variability in sources and sinks. This study thus helps to resolve the size of these

cross-terms, or rectifier effects. Lastly, this work may help to pinpoint important areas where new observations could provide the most sensitive test of models.

2.2 Methods

2.2.1 Surface O₂ and N₂ fluxes

I submitted global monthly O₂ and N₂ air-sea flux maps to be used as boundary conditions for the TransCom model runs. Developed by Garcia and Keeling (2001), the oxygen flux fields consist of a monthly climatology based on a weighted least squares fit between historical ocean O₂ data and monthly heat flux anomalies. Garcia and Keeling (2001) use the Wanninkhof (1992) relationship to calculate the air-sea O₂ flux from the oceanic O₂ anomalies. This approach is based on the empirical finding that O₂ fluxes and heat fluxes are reasonably well correlated. Garcia and Keeling (2001) exploit the better time resolution in heat flux estimates in order to improve the space/time resolution in O₂ fluxes, improving on the data sparseness problem in the Najjar and Keeling (2000) oxygen flux fields. This approach assumes that the O₂ fluxes are exactly in phase with the heat fluxes. However, the O₂ fluxes should have a lag period associated both with the efficiency of gas equilibration in the mixed layer with the overlying atmosphere and with the response time of photosynthesis to seasonal stratification and nutrient availability (Garcia and Keeling 2001). For the thermal component, a lag of about three week is expected. For the biological component, it is less clear what to expect, since the biological O₂ fluxes and heat

fluxes do not have as strong a mechanistic link; however, the lag is likely to be similar to the thermal lag.

The nitrogen flux fields consist of a global monthly map of N_2 ocean fluxes developed by scaling climatological European Center for Medium-Range Weather Forecast (ECMWF) heat fluxes from Gibson et al. (1997). The annual mean N_2 flux at every grid point was subtracted from the monthly heat flux fields in order to leave only the seasonal cycle. Using a monthly sea surface temperature data set (Shea et al. 1992) masked for land and ice and assuming constant salinity, I calculated the derivative of the Weiss (1970) solubility relationship with respect to temperature at a given grid point and time. This value was then used with the ECMWF heat fluxes to compute gas fluxes following Keeling et al. (1993):

$$\text{Gas Flux} = - \left(\frac{dN}{dT} \right) \left(\frac{Q}{c_p} \right), \quad (2.1)$$

where (dN/dT) is the change in solubility with temperature for a particular gas (in this case, N_2) in $\mu\text{mol kg}^{-1} \text{ } ^\circ\text{C}^{-1}$, Q is the heat flux in $\text{J m}^{-2} \text{ month}^{-1}$, and c_p is the heat capacity with units of $\text{J kg}^{-1} \text{ } ^\circ\text{C}^{-1}$. This formulation assumes that air-sea heat flux is the only determinant of the ocean surface concentration of N_2 and that surface waters equilibrate rapidly and completely. Although the N_2 cycle does have small biological influences, they are negligible in this context. The N_2 flux fields assume that the saturation anomalies and thus tracer fluxes depend directly on air-sea heat flux and equilibrate instantly, although it takes about three weeks for the mixed layer to equilibrate (Keeling et al. 1993).

The O₂ and N₂ fluxes were originally calculated on an ECMWF grid of 1.125° x 1.125° latitude and longitude. I then regridded them to a 0.5°x0.5° grid for distribution to project participants, allowing individual modelers to aggregate data according to the particular model's resolution. The difference in horizontal resolution between the models may introduce small differences into the input sources used for each model (Law et al. 1996).

Following Gurney et al. (2004), the flux fields were run forward for one year and then turned off, while the model was subsequently run for two more years, at which time the fields had effectively decayed to zero. To compute the steady-state response – the quantity of interest here – I simply summed the fields for all three years. The approach is valid conceptually because the steady-state response can be represented as the sum of response to the fluxes from the present year, the past year, and two years previously; these components are given by the first, second, and third years of the model runs, respectively.

2.2.2 Submitted model output

Each model group supplied the following standardized output: monthly mean 3D fields on the following pressure levels: 100 mb, 200 mb, 300 mb, 400 mb, 500 mb, 700 mb, 850 mb, 925 mb, and 1000 mb; monthly mean 2-D global maps of surface layer, a combination of the two lowest layers; and 4- or 6-hour instantaneous single-point reporting at 228 stations. The oxygen and nitrogen fields are carried through as though they are trace gases, ignoring their impact on the total moles of air.

Thus, the output fields were supplied as mixing ratios in μmole per mole of dry air. I then combined the two fields to compute changes in the O_2/N_2 ratio in per meg units according to:

$$\delta(\text{O}_2/\text{N}_2) \cong \frac{O_2}{0.20946} - \frac{N_2}{0.78084}, \quad (2.2)$$

where “ O_2 ” and “ N_2 ” designate the equivalent trace gas mixing ratio anomaly computed by the model in $\mu\text{mole}/\text{mole}$ and 0.20946 and 0.78084 reflect the O_2 and N_2 mole fractions in dry air (Glueckauf 1951).

2.2.3 Model descriptions

The calculations were run with 9 different tracer transport models and model variants. A tenth (TM2-ECMWF86), which I ran, is included in certain figures early in this chapter for continuity with previous papers (Garcia and Keeling 2001; Keeling et al. 1998). The models were submitted by users, rather than developers, although these roles may overlap in some research groups. Every model used in this chapter is an off-line version, with winds input from external data sets or atmospheric general circulation model predictions driving the model rather than using an internal calculation of the winds. A few of the models have been extensively used and tested (GCTM, TM2) whereas others have been more recently developed and tested less extensively (NIES, JMA).

The submitted models can be broken down into related groups. TM2 and TM3 are different versions of a model originally developed by Heimann and Keeling (1989), which used the monthly vertical convection statistics of the Goddard Institute

Space Studies model (GISS) (Heimann 1995). TM2 updates the calculation of subgrid-scale vertical transport by clouds and turbulent diffusion, and TM3 has a higher spatial and vertical resolution. NIRE is also related to the GISS model, although it uses a different advection scheme. Two other models, NIES and JMA-CDTM, are both offshoots of the NIRE model.

MATCH and GCTM are more independent of the GISS history. MATCH shares components of the National Center for Atmospheric Research Community Climate Model (CCM, Rasch et al. 1997), which is not used in this study. GCTM was first developed at the National Oceanic and Atmospheric Administration Geophysical Fluid Dynamics Laboratory in the early 1970s (Mahlman and Moxim 1978).

All of these models vary in resolution and in their transport characteristics (see Table 2.1 for a summary of the model characteristics). Many share similar parameterizations, but not all have parameterizations for certain characteristics, such as horizontal diffusion or convection related to cloud formation. Some explicitly model a planetary boundary layer, others do not. These choices result from various priorities in each model's development and lead to some recognized differences in predictive ability. For example, JMA, first developed in the aftermath of the Chernobyl accident by the Japan Meteorological Agency, overestimates ground-level concentrations in the short term (less than 24 hours), probably because of weak vertical diffusion (Iwasaki et al. 1998). NIES is known to have a faster vertical transport than NIRE but slower than GISS (Maksyutov and Inoue 2000). GFDL has weak vertical mixing out of the surface layer, resulting in higher surface peak values

Table 2.1 Information on the submitted models and their transport characteristics.

Model	Submitted by	Horizontal Grid	Advection	Wind	References
GCTM	D. Baker	256 km x 256 km	2nd/4th order	ZODIAC GCM	Mahlman and Moxim (1978); Levy et al. (1982)
GISS	I. Fung	5° long x 4° lat	slope	GISS CGM II	Hansen et al. (1997)
JMA-CDTM	T. Maki	2.5° long x 2.5° lat	hor: semi-lagrangian, vert: box	JMA	Taguchi (1996); Iwasaki et al. (1998)
MATCH	R. Dargaville	2.8° long x 2.8° lat	spitfire	NCEP	Rasch et al. (1997)
MATCH	R. Law	5.6° long x 2.8° lat	semi-lagrangian	MACCM2	Rasch et al. (1997); Law and Rayner (1999)
NIES	S. Maksyutov	2.5° long x 2.5° lat	semi-lagrangian	ECMWF (97)	Maksyutov and Inoue (2000)
NIRE	S. Taguchi	2.5° long x 2.5° lat	semi-lagrangian	ECMWF (95)	Taguchi (1996)
TM2	T. Blaine	10° long x 7.5° lat	slope	ECMWF (86)	Heimann (1995)
TM2	T. Naegler	7.5° long x 7.2° lat	slope	ECMWF (90)	Heimann (1995); Bousquet et al. (1999)
TM3	M. Heimann	5° long x 4° lat	slope	ECMWF (90)	Heimann (1995)
Model	Horizontal Diffusion?	Vertical Diffusion?	Convection?	Explicit PBL?	
GCTM	Y	Y	N		
GISS		N	Y	N	
JMA-CDTM	N	Y		N	
MATCH	N	Y	Y	Y	
MATCH	N	Y	Y	Y	
NIES			Y	Y	
NIRE	N	N	N	Y	
TM2	N	Y	Y	N	
TM2	N	Y	Y	N	
TM3	N	Y	Y	N	

in the source distribution better. Likewise, TM2 is known to display a smaller rectifier effect above continent, probably due to its coarse resolution, whereas TM3 generally displays a larger rectifier (Bousquet et al. 1999; Law et al. 1996). All of these characteristics will contribute to the predictive abilities of particular models in dealing with APO. Previous TransCom results highlight the importance of subgrid-scale parameterized vertical transport, more than any other parameterization, for explaining the difference between models and accurately representing atmospheric concentrations of a tracer (Denning et al. 1999).

2.3 Results

2.3.1 Comparison of station measurements and model predictions

Measurements of APO in air samples from 12 stations in the Scripps Institution of Oceanography (SIO) flask measurement program, provided by R. F. Keeling, are used in comparisons with model output. The available data are summarized in Table 2. Nine of these stations are effectively located in the marine boundary layer, while three are located between 2800 and 3800 m. All stations were selected to allow sampling under “clean air” conditions. All the data, except that from Trinidad Head, are based on flask measurements. Flasks were analyzed using a nondispersive infrared analyzer for carbon dioxide and an interferometric method for oxygen (Keeling et al. 1998). Air at Trinidad Head was analyzed continuously at the site using a LiCor infrared analyzer for CO₂ and a paramagnetic oxygen analyzer (Lueker et al. 2003).

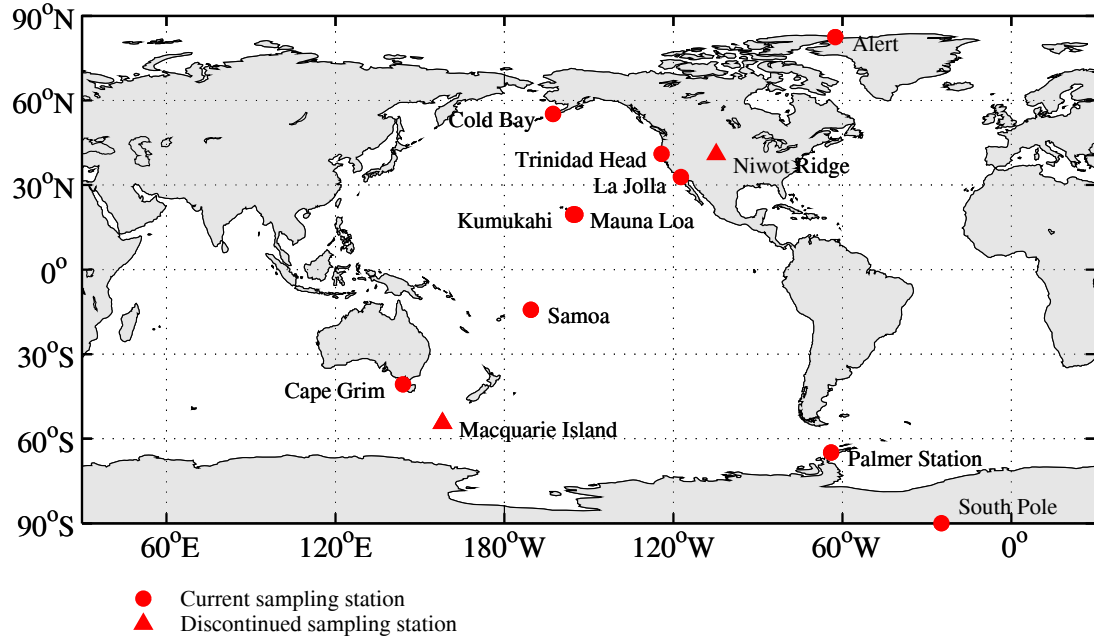


Figure 2.1. Map of the locations of stations with data used for comparison with models.

The O_2/N_2 ratios and CO_2 concentrations are combined to derive atmospheric potential oxygen, APO, using the following equation:

$$APO = \delta(O_2/N_2) + \frac{R_{O_2:C}}{0.2095} (X_{CO_2} - 350), \quad (2.3)$$

where $R_{O_2:C}$ represents the $O_2:C$ exchange ratio for land photosynthesis and respiration and is assumed to be 1.1 (see Severinghaus 1995).

The APO data are fit with the first four harmonic functions of the annual cycle and a slowly varying interannual function that consists of a stiff spline fit (Keeling et al. 1998). With the stiff spline fit removed, the detrended APO data for four representative stations are plotted along with a four-harmonic seasonal function of the high-resolution model predictions from all of the TransCom models in Figure 2.2.

Table 2.2. Sampling stations in the Scripps O₂/N₂ network.

Station Code	Site	Latitude	Longitude	Elevation	Time Period
ALT	Alert, Northwest Territories	82.45 N	62.52 W	210 m	Nov 1989 to Mar 2004
CBA	Cold Bay, Alaska	55.20 N	162.72 W	25 m	Aug 1995 to Apr 2004
TRH	Trinidad Head, California	41.05 N	124.15 W	109 m	Oct 1999 to Sep 2004
NWR	Niwot Ridge, Colorado	40.90 N	104.80 W	3000 m	Apr 1991 to Jan 1993
LJO	La Jolla, California	32.83 N	117.27 W	14 m	May 1989 to Mar 2004
MLO	Mauna Loa, Hawaii	19.53 N	155.58 W	3397 m	Jan 1991 to Apr 2004
KUM	Kumukahi, Kawaii	19.52 N	154.82 W	3 m	Jun 1993 to Feb 2004
SMO	Cape Matatula, American Samoa	14.25 S	170.57 W	42 m	Jun 1993 to Apr 2004
CGO	Cape Grim, Tasmania	40.68 S	144.68 E	94 m	Jan 1991 to Apr 2004
MCQ	Macquarie Island	54.48 S	158.97 E	12 m	Jan 1993 to Jan 1994
PSA	Palmer Station, Antarctica	64.92 S	64.00 W	10 m	Sep 1996 to Jan 2004
SPO	South Pole	89.98 S	24.80 W	2830 m	Nov 1991 to Feb 2004

Any annual mean concentration at a given location (the rectifier) caused by interaction of seasonal variations in transport with seasonal sources has been subtracted from the seasonal cycle. The station data are plotted as though taken all in one “climatological” year in order to emphasize the seasonal cycle.

In general, there is good agreement at most stations between models and observations in the structure of the seasonal cycle. The models tend to better predict the distribution of APO at a distance rather than in close proximity to sources and

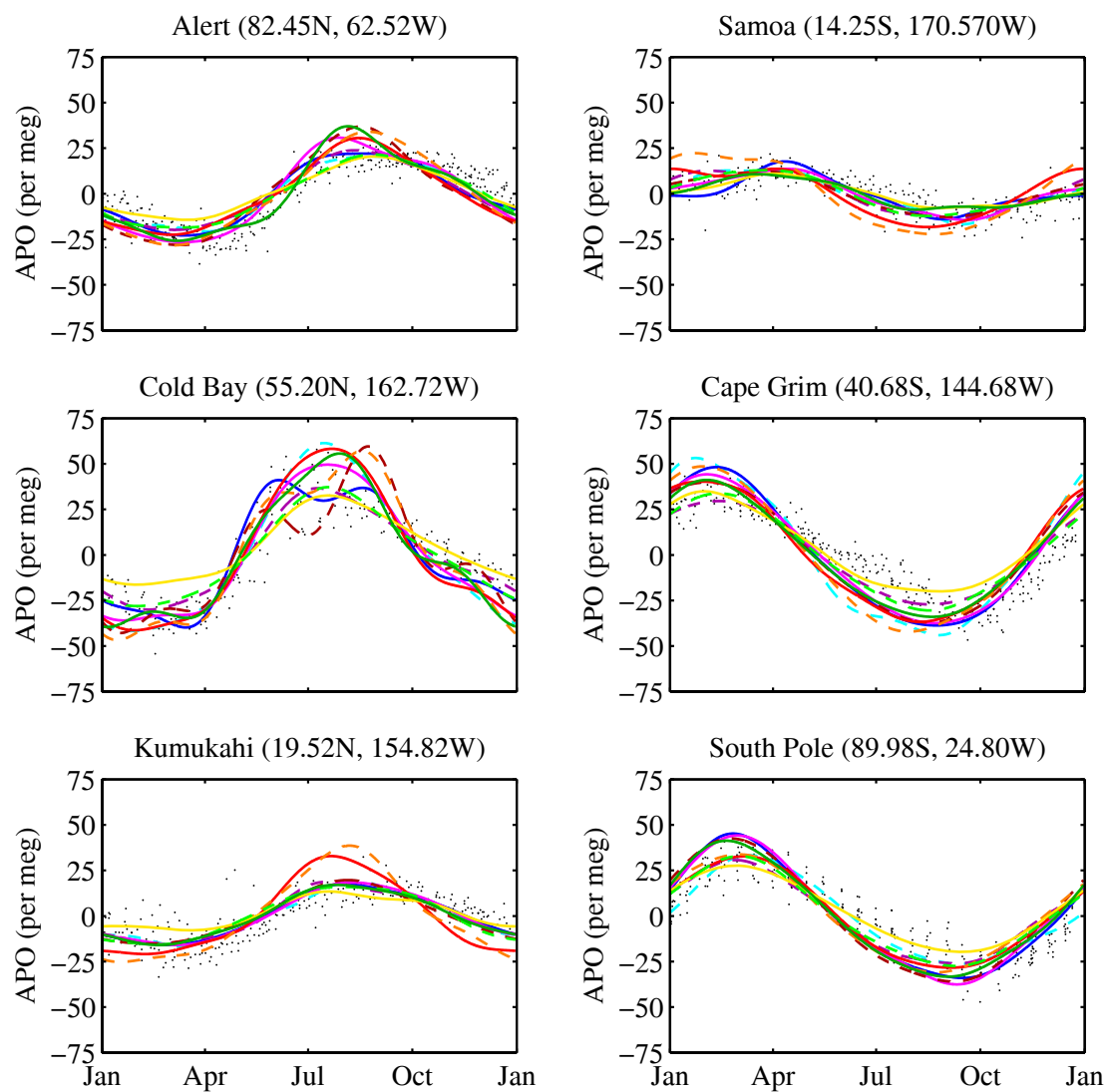
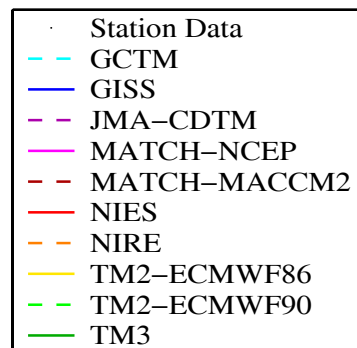
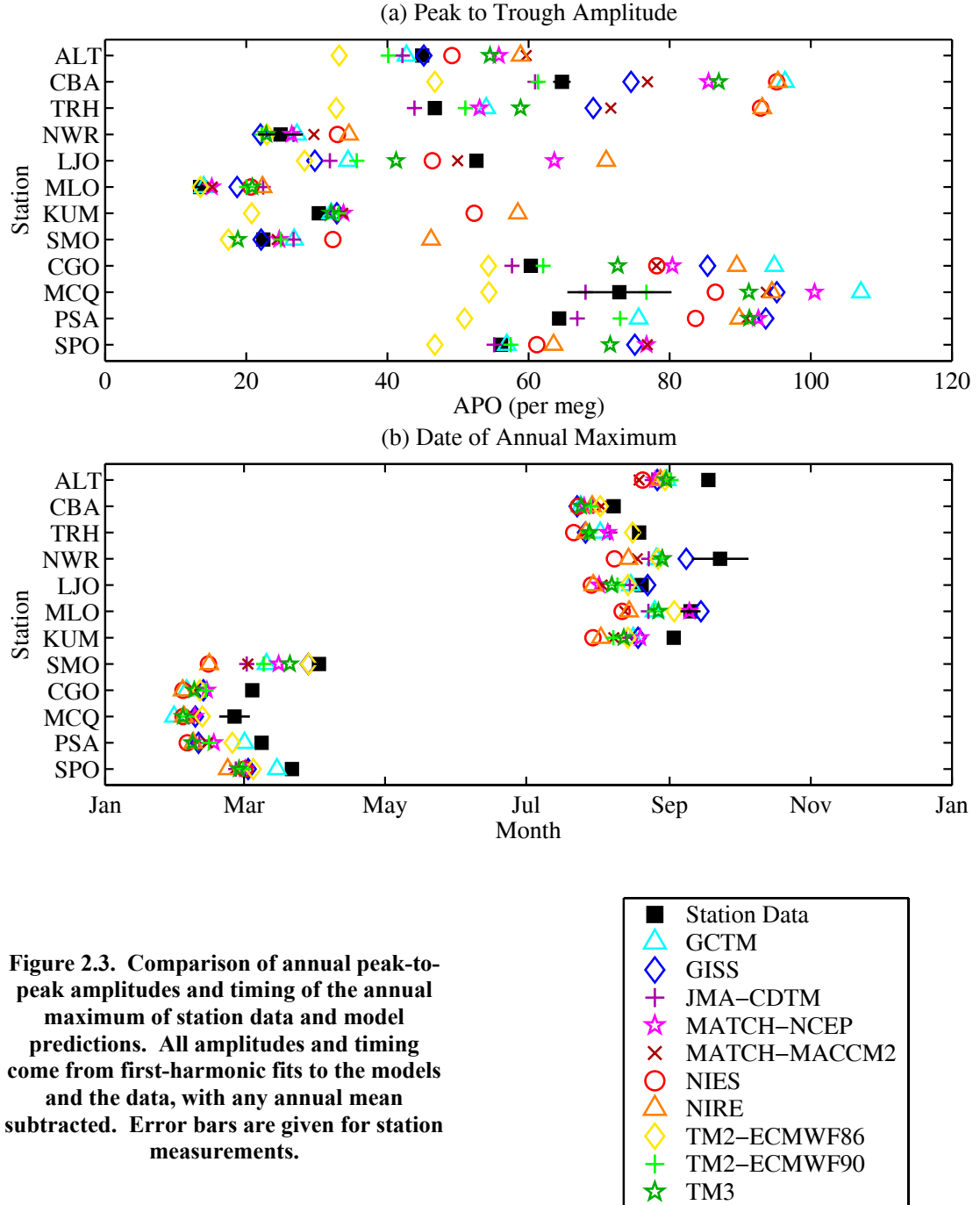


Figure 2.2. Annual cycles of model predictions and measurements at six stations. These model predictions are plotted as four-harmonic fits to 4- or 6-hour instantaneous station reporting, with any annual mean created by the seasonal fluxes subtracted. The detrended APO data are plotted as though taken all in one “climatological year” in order to emphasize the seasonal cycle.



sinks, a result also found by Law et al. (1996). In tropical areas, the model predictions of peak-to-peak amplitude generally cluster close to the measured values, whereas in mid to high latitudes the model results span a two-fold range in predictions. Some models show features that are not supported by the observations. For example, the models MATCH-MACCM2 and NIRE show both double maxima and double minima for Cold Bay, Alaska, and the model GISS shows a double peak. In contrast, the APO data show a smooth annual cycle, though with increased variability in June and July.

Located on the edge of the North Pacific, Cold Bay is one of the more challenging stations to fit because of its proximity to a large source/sink region in the northern Pacific Ocean. While the global surface concentration maps (Figure 2.6, discussed more in depth later) reveal broadly similar distributions with maximum peak-to-peak amplitudes in the North Pacific, there are large differences in the maximum and minimum concentrations and the horizontal extent of the peak. Although it is not possible to identify which subgrid scale process is specifically responsible, in some of the models APO mixes rapidly into the upper atmosphere, leading to smaller annual cycles at lower levels of the atmosphere and larger annual cycles at higher altitude, whereas reduced transport in other models results in large annual cycles only in the proximity of the source. Such variability among model predictions would likely occur for stations near the North Atlantic as well, but no station data for oxygen exist from that area. Alert, the only station near the North Atlantic, is too far north and most likely reflects a combination of North Pacific and North Atlantic sources.



Comparisons of the annual peak-to-peak amplitude of the APO cycle and the date of the annual maximum of each station are shown in Figure 2.3. For both the data and the model predictions, I use first harmonic fits with the annual means subtracted. Error bars for the fits to the station data are shown by black lines. Several of the models fit the amplitude of the data well; others perform better in low latitude or high latitude locations. Cape Grim and Macquarie Island have the largest spread in model predictions of the annual cycle. Many of the models consistently overestimate the annual cycle. This overestimation is also visible in the model cycles in Figure 2.2, where rapid changes in model predictions of concentration do not match the more gradual changes in the station data.

The model TM2-ECMWF86 underestimates the APO cycle at every station and is an outlier among all the models. This model was chosen by Garcia and Keeling (2001) to evaluate the estimates of the oxygen fluxes submitted as the input to this study. As mentioned in the discussion of the flux fields, Garcia and Keeling (2001) concluded that the Wanninkhof (1992) gas transfer velocity for O_2 did not need to be adjusted by a calibration factor.

At the Northern Hemisphere extratropical stations (Alert, Cold Bay, Trinidad Head, and Niwot Ridge), the modeled amplitude is generally larger than the observed amplitude. Weighing all stations and models equally, the models overestimate the amplitude by a factor of 1.17. A similar analysis of the Southern Hemisphere stations (Cape Grim, Macquarie Island, Palmer Station, and the South Pole) yields an overestimate by a factor of 1.12. This rough calculation has many caveats, among

which is the assumption that the average of the models accurately predicts transport. However, these results suggest that the initial Wanninkhof (1992) flux formulation should be scaled by about 0.85, in contrast to Garcia and Keeling (2001) and Keeling et al. (1998), who suggested a scaling constant of 1.15 in the Northern Hemisphere and 1.23 in the Southern Hemisphere.

Based on known limitations of the flux fields, mentioned earlier, we expect the model will predict cycles with phasing shifted early by about three weeks. As shown in both Figures 2.2 and 2.3, the phasing of the model cycles is consistently shifted early relative to observations on average by 20 days. This value is well-defined, as the models agree closely on phasing.

La Jolla is underestimated by eight of the models. In order to avoid contamination by local pollution sources, La Jolla is only sampled during steady west-wind conditions, which are scarce during the fall and winter months. The seasonal cycle estimated using the La Jolla station flask record may therefore be biased in comparison to model predictions, which reflect a seasonal cycle regardless of wind conditions (Keeling et al. 1998). However, another factor may be at play: the meteorology of the California coast is dominated by a north-south coastal jet, which may not be resolved in the coarse grids of the models (Burke and Thompson 1996; Rogers et al. 1998). In contrast to La Jolla, the annual cycle at Trinidad Head station, in northern California, tends to be overestimated by many of the models, similar to the model predictions for stations even further north.

Data from Mauna Loa and from the South Pole, both high altitude stations, are generally well-matched by model results, most likely because of the smaller annual APO cycle at high altitudes far from oceanic sources and sinks where the flask measurements are taken. Niwot Ridge, also a high latitude station, is the only temperate continental station from the SIO network. Although there are only a few O₂ and CO₂ flask measurements from Niwot Ridge, all models are in close agreement on the size of the annual cycle and agree well with the existing data. Although the cycle is small, the reasonable fits suggest that models may more accurately represent values over continents where the net flux is zero than those near sources and sinks of APO.

2.3.2 Station-station comparisons

As has been mentioned briefly in the previous section, stations near to oceanic APO sources may be more challenging to model than those located far away from the source regions. The stations for which APO data exist can generally be divided into two groups: those in the proximity of source regions, such as Cold Bay or Cape Grim, and those far away from source regions whether by altitude or horizontal distance, such as Samoa, Mauna Loa, Niwot Ridge, or the South Pole.

The relationship between the concentrations at a station close to oceanic sources and a distant station depends on the flux between them. Conceptually, their relationship can be characterized by a simple two-box model according to:

$$V_P \frac{dC_P}{dt} = Qe^{i\omega t} - F(C_P - C_D) \quad (2.4)$$

$$V_D \frac{dC_D}{dt} = F(C_P - C_D), \quad (2.5)$$

where C is the tracer concentration, subscripts P and D represent proximate and distant stations respectively, $Qe^{i\omega t}$ is a sinusoidal forcing term describing air-sea flux, F is the air flux between the two boxes, and V is the volume of each box. Both the air-sea flux and the flux out of the box due to atmospheric transport are important for the box close to sources; only the atmospheric transport is important for the box far away from sources. The solutions to these equations are the following:

$$C_P = \left(\frac{i\omega V_D + F}{i\omega V_D} \right) \left(\frac{Qe^{i\omega t}}{i\omega + F_{TOT}} \right) \text{ and} \quad (2.6)$$

$$C_D = \frac{F}{i\omega V_D} \left(\frac{Qe^{i\omega t}}{i\omega + F_{TOT}} \right), \quad (2.7)$$

$$\text{where } F_{TOT} = F \left(\frac{1}{V_P} + \frac{1}{V_D} \right).$$

Treating the volumes of the boxes in terms of a relative change, the amplitude ratio and phase difference between the boxes is thus dependent on a single, dimensionless parameter, F^* :

$$F^* = \frac{\omega V_D}{F}. \quad (2.8)$$

This model suggests a means of evaluating the station predictions from the TransCom models. As discussed in the previous section, problems in the assumptions about timing and the constants used to estimate air-sea oxygen fluxes may make direct

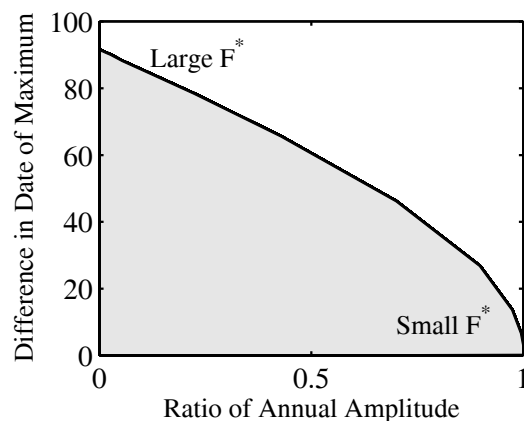


Figure 2.4. The ratio of the annual peak-to-peak amplitude versus the difference in the timing of the annual maximum for the two boxes in a simple two-box model. When the exchange between the boxes is fast, the peak-to-peak amplitudes in the two boxes are nearly identical and the distant box has slightly delayed timing. However, as the exchange between the boxes slows, the amplitude of the box closest to the source increases, while the amplitude in the distant box decreases. The timing of the maximum in the distant box also becomes significantly delayed and the two cycles fall out of phase by three months. The grayed area represents the relationship between two distant boxes that are related to the proximate box by different flux amounts.

comparison of model predictions and station data difficult. In contrast, one would expect the relative differences in amplitude and timing between stations to be a more reliable indicator of how well a particular model performs. Using the ratio of amplitudes between two stations takes out any errors in a multiplicative constant in the flux fields, while the difference in the date of the annual maximum at two stations largely take out errors in phasing of the air-sea oxygen fluxes.

In the simple box model described above, the ratio of the peak to peak amplitude of the distant to proximate stations and the difference in the date of maximum show a relationship that depends directly on the value of F^* , the transport efficiency. As shown in Figure 2.4 as the solid line, as F^* decreases, the ratio of the amplitude approaches one and the difference in the date of the maximum approaches zero. As F^* increases, the ratio of the two boxes approaches zero and the timing is out

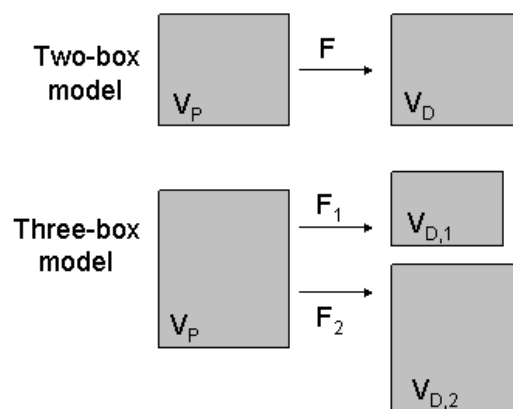


Figure 2.5. Diagram of the two-box and three-box models.

of phase by three months. This line is robust even when the relative size of the boxes is varied. When this model is expanded to include two “distant” boxes with different values of F as shown in Figure 2.5, then the relationship between the two distant boxes falls below the solid line (represented by the grey area in Figure 2.4). In order for the relationship between two stations to fall outside of this space, they most likely need to represent air coming from different sources rather than the same source.

Figure 2.6 shows panels from several station pairs combining stations located close and far from oceanic APO sources. Information on the peak to peak amplitude and date of maximum are the same as those used in Figure 2.3, and the line predicted from the two-box model, which frames the area in which the relationship between stations with the same sources should fall, is drawn on each plot. Deviations from the line can give insight into the origin and mixing of air masses and why some models may not correctly predict the seasonal cycles at particular stations.

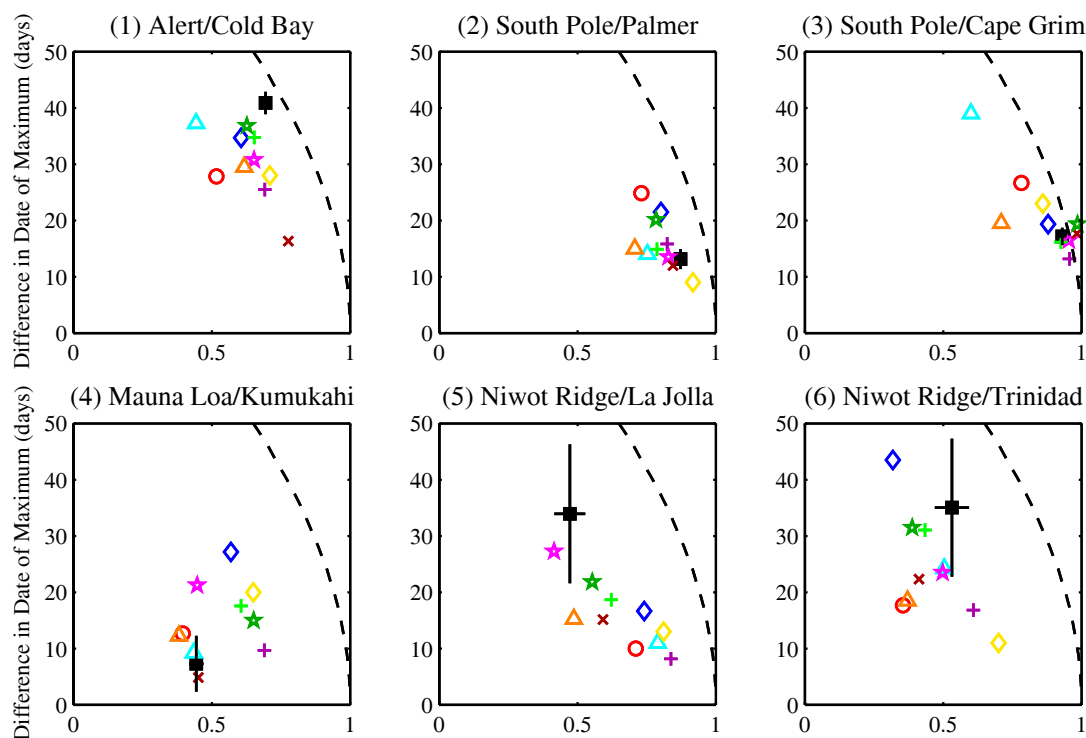
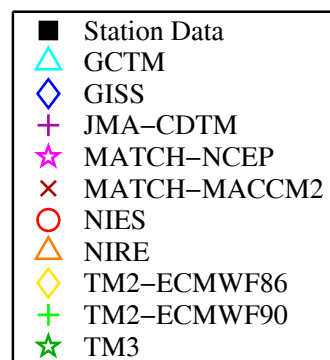


Figure 2.6. The ratio of the annual peak-to-peak amplitudes versus the difference in the timing of the annual maximum for several station pairs. (1) Alert vs. Cold Bay, (2) South Pole vs. Palmer, (3) South Pole vs. Cape Grim, (4) Mauna Loa vs. Kumukahi, (5) Niwot Ridge/La Jolla, (6) Niwot Ridge vs. Trinidad Head. The dotted line on each graph is the relationship between amplitude and timing from Figure 2.4.



Panels 1 and 2 in Figure 2.6 show Alert/Cold Bay and South Pole/Palmer, both high-latitude pairs. The model predictions show greater spread in the Northern Hemisphere than in the Southern Hemisphere, with a difference in the date of maximum varying almost thirty days between models in the Northern Hemisphere whereas the predictions scatter over less than twenty days in the Southern Hemisphere. The South Pole and Palmer station are more tightly correlated, with station data and model predictions falling closer to the area of the plot associated with a larger F value representing greater exchange.

The South Pole/Palmer comparison as well as the South Pole/Cape Grim comparison in Panel 3 suggests that mixing in models is more consistent in the Southern Hemisphere than in the northern one. Air masses from around Palmer Station and Cape Grim are exchanged more rapidly with air near the South Pole than air masses are exchanged between Alert and Cold Bay. The South Pole and Cape Grim in particular are closely linked as predictions and the station data tend to fall along the line derived in the box model. The model predictions do not fall as closely to the station results in Alert/Cold Bay, possibly reflecting the difference atmospheric transport and mixing in the two hemispheres, as well as the heterogeneity in the location of sources and sinks of APO in the Northern Hemisphere divided between the Atlantic and Pacific Oceans. In the Southern Hemisphere, where sources are much more evenly distributed, the model predictions fall relatively close to the station results. In the Northern Hemisphere, the models tend to predict a maximum at Alert that is earlier than the station data, whereas the models predict a slightly later

maximum at Cold Bay in comparison to data, as is confirmed by comparison with Figure 2.2.

Panel 4 shows a comparison of the Mauna Loa and Kumukahi stations, both on the big island of Hawaii. While Kumukahi is at sea level, the Mauna Loa station is at 3397 m. In the station flask data, the annual maximum at Kumukahi precedes that at Mauna Loa by about a week with amplitude ratio of about 0.5, which clearly put this pair off of the line expected from mixing just between the two boxes. Keeling et al. (1998) suggest that, while Mauna Loa may get part of its air from low latitude sources, it may represent a mix of air from other sources with different phases. The model predictions appear to fall in two different clusters: one which contains the actual station data, and another, parallel cluster that is offset in both date of maximum and the ratio. Keeling et al. (1998) suggest that the vertical gradient reflected in the measurements at these stations may reflect a trade wind inversion at intermediate altitudes that separates the air masses associated with the marine boundary layer from those in the tropospheric air connected to the sinking Hadley's circulation. This result may show which models are better at predicting the mixing of the atmosphere at high altitudes near the equator: GCTM, NIES, NIRE, and MATCH-MACCM2 all come closer to describing the relationship between these two stations, whereas the other model predictions fall on a different line.

Measurements at Niwot Ridge, as a mid-continental station, most likely characterize a plume of air which has had its APO concentration determined by air-sea exchange over the northeastern Pacific Ocean and which has mixed with other air masses as it moves over the continent. Pair comparisons of Niwot Ridge against La

Jolla and Trinidad Head (Panels 5 and 6) both show that the models tend to underpredict the timing difference between the coastal stations and Niwot Ridge and overpredict the amplitude at Niwot Ridge relative to the coastal stations, suggesting more effective transport in the models between the coasts and continental sites than is reflected in measurements. Although most models keep the same relative position between the two plots, the GISS model predictions have different relative positions; GISS estimates a higher rate of exchange between La Jolla and Niwot Ridge than between Trinidad and Niwot Ridge. This difference represents an idiosyncrasy of this particular model.

2.3.3 Global surface patterns

Global maps of the peak-to-peak amplitude maps are shown for every model at the surface level in Figure 2.7 and similar maps of the “rectifier” in Figure 2.8. Following Law et al. (1996), the peak-to-peak amplitude is calculated as the difference between the maximum and minimum monthly mean concentration at each grid point. The “surface” level was defined by individual modelers and submitted independently of the predictions at specific pressure levels. Similar patterns are visible across all the models: the cycles over land, further from the locations of APO sources and sinks, tend to be smaller with annual cycles of 60-70 per meg, whereas the cycles at the same between the maximum and minimum monthly mean concentration at each grid point. The “surface” level was defined by individual modelers and submitted independently

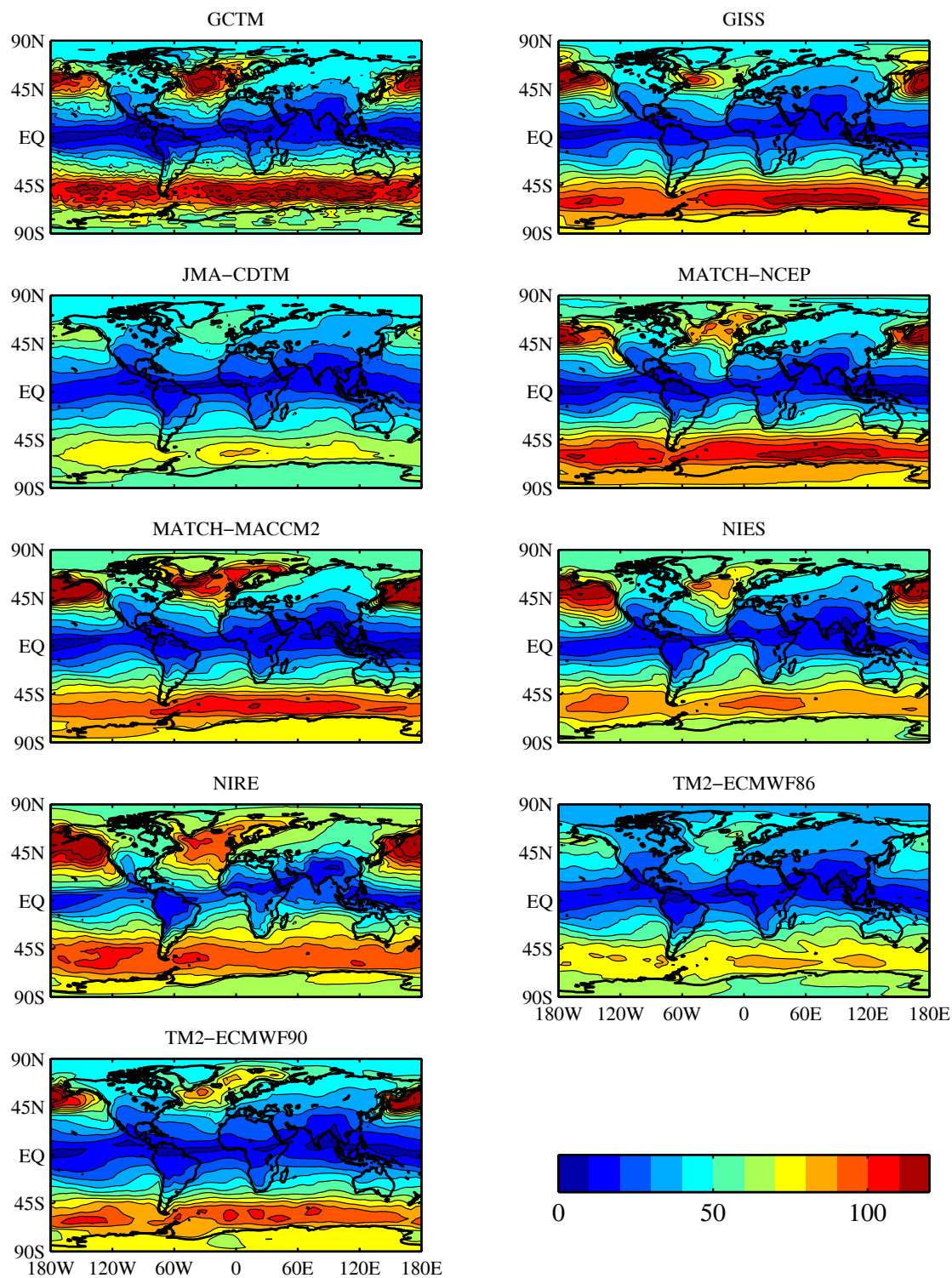


Figure 2.7. Surface maps of the annual peak-to-peak APO amplitude for each submitted model. Units of measurement are per meg.

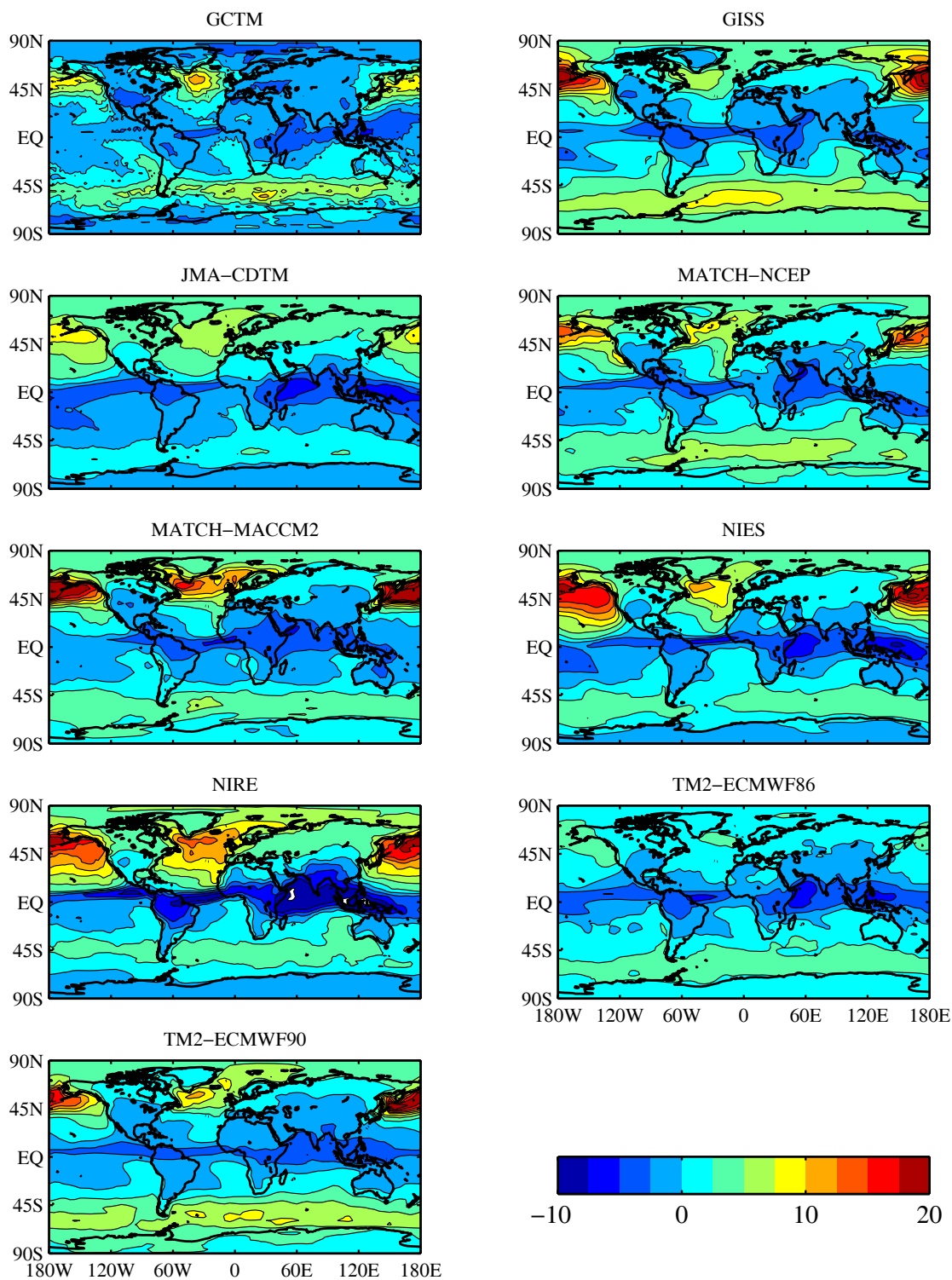


Figure 2.8. Surface maps of the rectifier, or annual mean, for each submitted model. As in Figure 2.7, units of measurement are per meg.

of the predictions at specific pressure levels. Similar patterns are visible across all the models: the cycles over land, further from the locations of APO sources and sinks, tend to be smaller with annual cycles of 60-70 per meg, whereas the cycles at the same latitudes over the ocean may be as high as 120 per meg in peak-to-peak amplitude. In temperate latitudes, where the prevailing winds are from west to east, most models show similar surface plots with small decreases in the size of the annual cycle across a continent's extent as an air mass gets more distant from the source area. Seasonal cycles in APO over the ocean take 2-3 months to move across continents, spreading out in both the north and south directions and getting damped over time. At the western continental edges, even in Australia, contour lines in the peak-to-peak amplitude go north (or dip south) in the Northern Hemisphere (or Southern Hemisphere), following local wind patterns and isolating the largest cycles above the oceans.

In general, the surface rectifier maps in Figure 2.8 look like the amplitude maps: where the seasonal cycle is high, the rectifier value is also high. All the models show a negative rectifier in equatorial areas, which can be 50% of the size of the annual amplitude cycle; in contrast, the regions in the north Pacific and north Atlantic located close to high source regions have a positive rectifier that is generally not larger than 20% of the total cycle, and the surface rectifier over most of the ocean is close to zero but slightly negative. In equatorial areas, the seasonality of the fluxes is small, resulting in a small seasonal cycle of the atmospheric concentrations. The rectifier is thus representing large changes in the seasonal transport in these areas, where deep convection occurs around the Intertropical Convergence Zone (ITCZ). These results

suggest that equatorial areas may be a particularly difficult area for analysis of atmospheric tracer measurements, as the signal is influenced by transport in both hemispheres that can change significantly in strength on a seasonal basis. Most general circulation models are also known to have problems representing the seasonal migration of the ITCZ precipitation (Gates et al. 1999; Hack et al. 1998; Wu et al. 2003); in CCM3, the ITCZ precipitation peak remains north of the equator throughout the year (Wu et al. 2003). The seasonal amplitude and rectifier predictions in this area of tracer transport models which rely on output of general circulation models for their winds may be particularly suspect.

2.3.4 Zonal patterns

Figures 2.9-2.12 compare model predictions of altitudinal zonal averages. The variables are first calculated for each grid point, then averaged using a given model's zonal resolution. All the models agree qualitatively in their large-scale patterns of the seasonal cycle: near the surface, the largest annual amplitudes in the latitudinal means are in the Southern Ocean at about 60°S and a smaller peak occurs at 45-60°N. The profiles in Figure 2.9 show a more tightly defined peak in the Southern Hemisphere than in the Northern Hemisphere during the summer months (February and August, respectively), reflecting the narrower zonal distribution of source regions in the Southern Hemisphere. Figure 2.10 presents zonal mean transects for every model rather than profiles, showing that the zonal mean amplitude at the surface increases

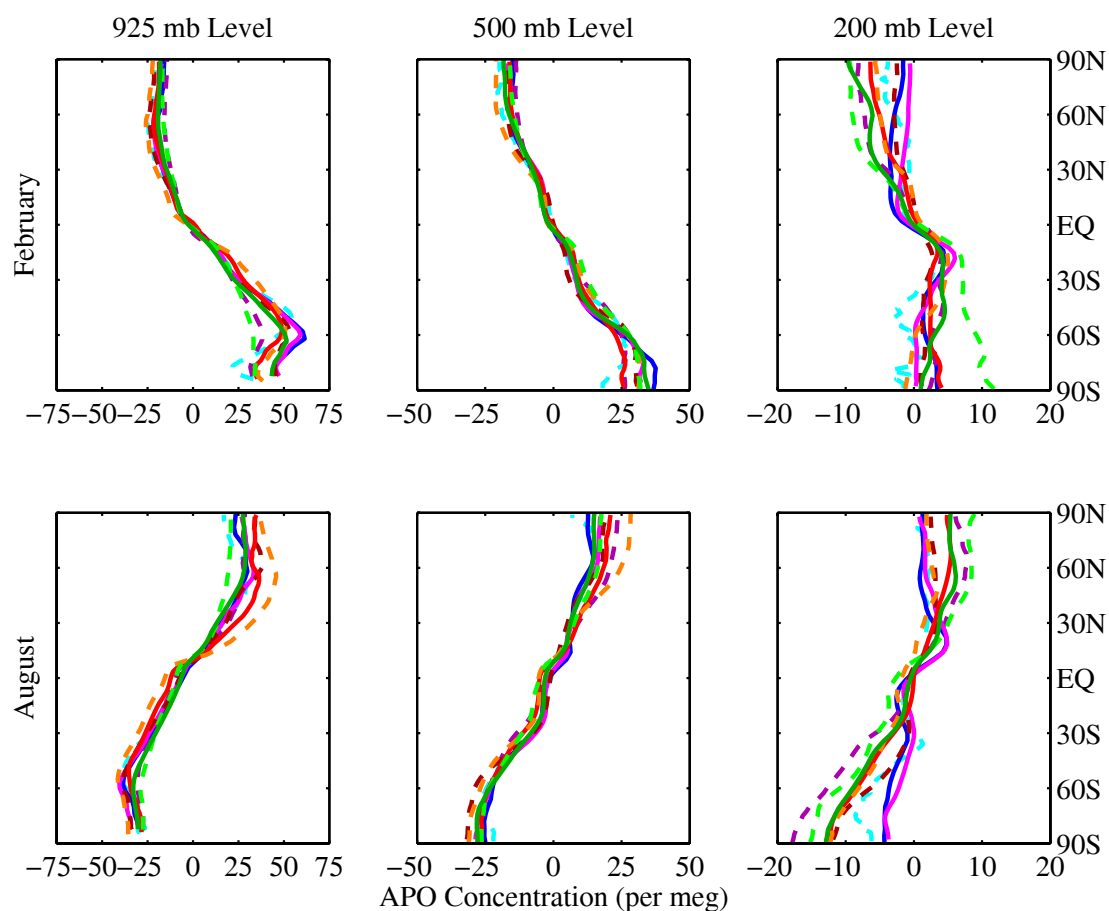
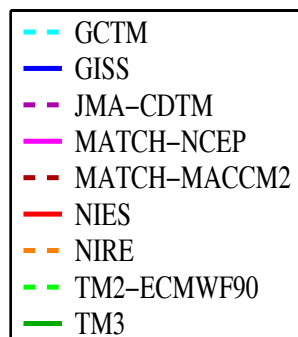


Figure 2.9. Zonal average concentration in February and August at three different altitudes. The greatest difference in model predictions occurs in the summer in each hemisphere closer to the surface of the earth. At altitude, the greatest differences occur during the winter.



from 5-20 per meg at the equator to 40-70 per meg at 45-60°N and 70-100 per meg at 60°S. Away from the source regions, the variation between models is smaller, a pattern which was found in studies of land sources of CO₂ (Law et al. 1996).

Many of the differences in annual amplitude between models are attenuated at 500 mb but emerge again at 200 mb, where the maximum in each hemisphere shifts slightly poleward at higher altitudes. Near the top of the atmosphere, the annual cycles are small, and the models show much more variability, agreeing closely at the equator where the amplitude is near zero but predicting very different annual amplitudes at the poles. This variability among models generally comes from differences between models during a particular season; for example, at 200 mb, the models agree quite closely in February in the Southern Hemisphere with the exception of one outlier (TM2-ECMWF90) (shown in Figure 2.9). However, the model predictions differ by almost 15 per meg for the month of August, and it is these differences that lead to differences between the models in the predicted amplitude. At the same altitude in the Northern Hemisphere, the greatest discrepancy in the model predictions occurs in February rather than August. It is thus the wintertime concentrations at high altitude (close to the tropopause) that show the most divergence between models, at the times that a polar vortex is strongest and atmospheric patterns may be more difficult to represent in a model. Some of the models do not have a stratosphere, and so any predictions near this level are suspect.

In contrast, at 500 mb and 925 mb, the largest discrepancy between models occurs in high latitudes during the summer, rather than during the winter. The zonal averages in Figure 2.9 obscure the relevant spatial patterns visible in the surface maps

of Figure 2.7; the largest cycles are actually correlated with the sources and sinks of APO in the northern Pacific and Atlantic Oceans, but the overall mean for that latitude in the Northern Hemisphere is smaller than in the Southern Ocean because the oceanic areas are interspersed with land masses. The differences between models representing large source regions helps explain the difference in summer peaks. However, vertical transport is also strongest in the summertime over continents as the land warms up faster than the overlying air, and differences in how vertical transport is modeled can cause discrepancies in the predictions.

Figure 2.11 shows mean zonal transects of the rectifier. At the surface, the rectifier patterns seem primarily driven by the size of the local seasonal air-sea flux. Away from the surface near the equator, where warm and moist air is rising in the upward branch of the Hadley cells, the values are negative at all but the highest altitudes. Several models also show positive values at middle and high altitudes in areas near the downward branches of the Hadley cell at about 30° in each hemisphere. This is as expected; where the atmosphere has significant uplift, the rectifier should be negative, and where the atmosphere is descending, the rectifier should be positive. Large rectifier values extend high into the atmosphere over the Northern Hemisphere, whereas they are more limited to the surface in the Southern Hemisphere. This observation is most likely due to the strength of summertime vertical transport over continents and the fact that the Northern Hemisphere has a much greater land mass.

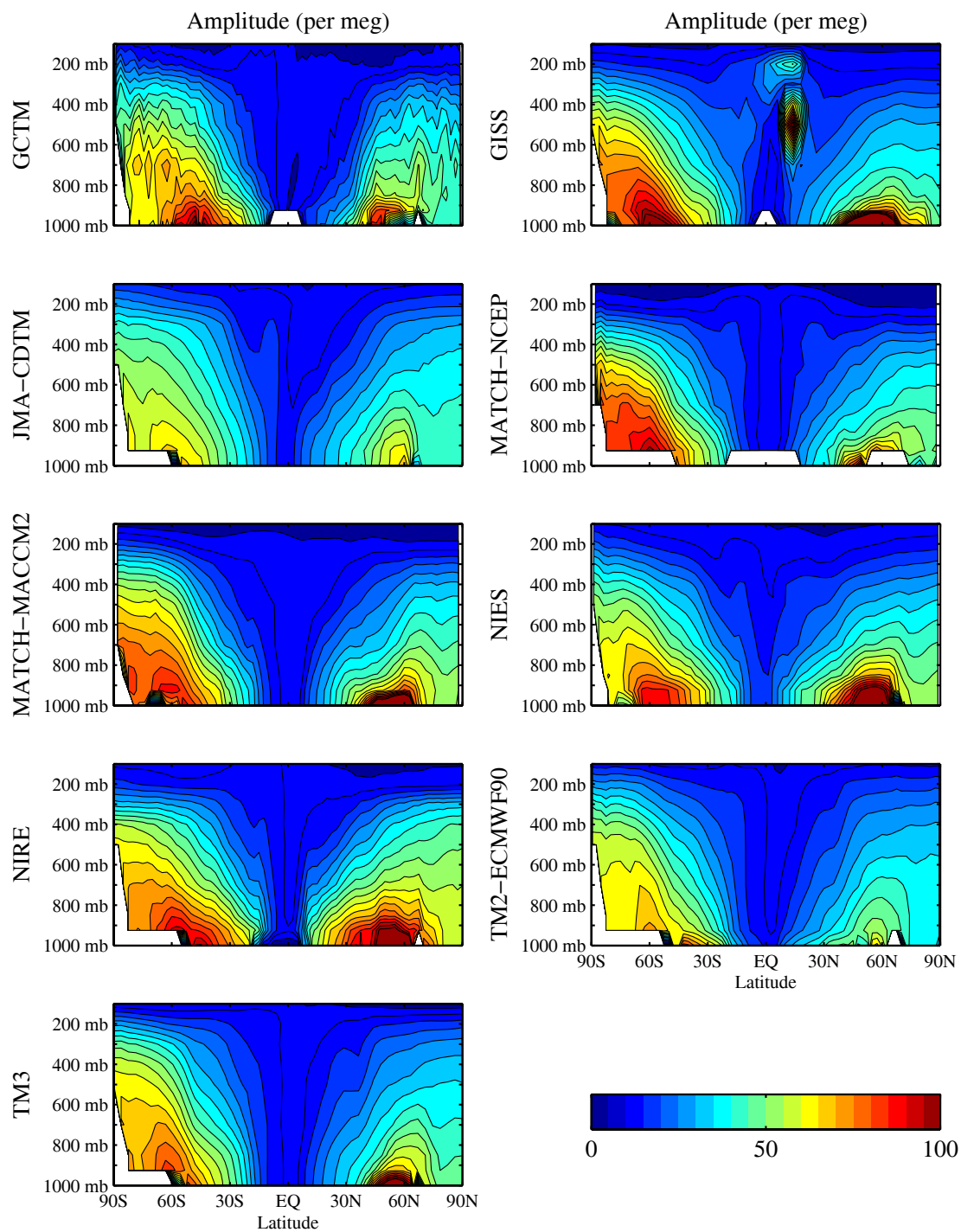


Figure 2.10. Zonal average peak-to-peak amplitude for all 9 models submitted to TransCom.

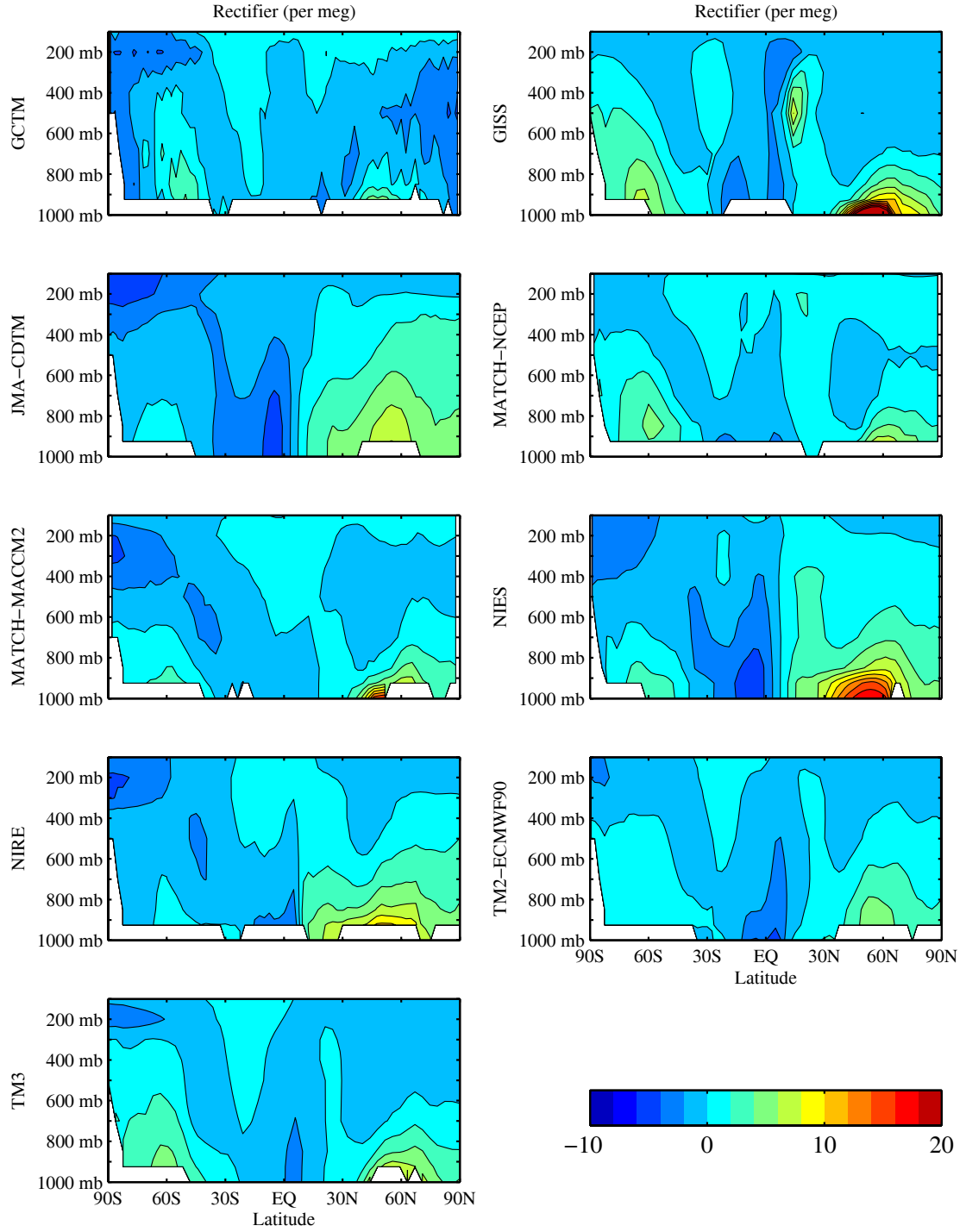


Figure 2.11. Zonal rectifier for all 9 models.

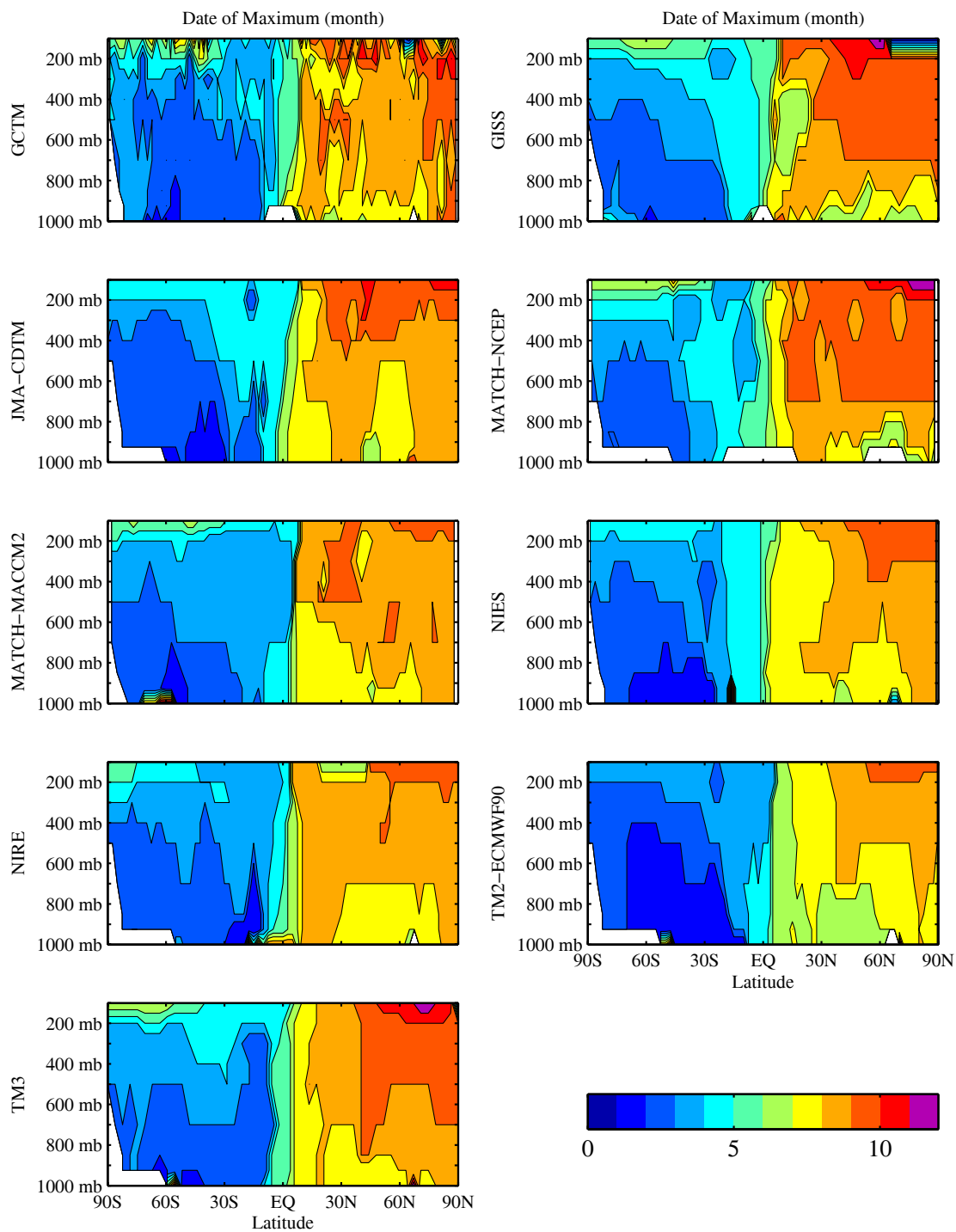


Figure 2.12. Month of the maximum in the zonal average seasonal cycle for all 9 models.

As noted by Gurney et al. (2002), areas with high rectifier values signal key areas where transport and mixing processes are thought to change throughout the year.

As seen in the timing of the maximum of the annual cycle (Figure 2.12), a lag of two to four months in the timing of the peak develops with altitude in both hemispheres. This lag is slightly shorter in the Northern Hemisphere. Measurement programs may have the ability to resolve the phasing of cycles within days (R. Keeling and S. Walker, pers. comm.). If so, new measurement programs concentrating on altitudinal profiles in different seasons could significantly contribute to evaluating the validity of seasonal changes in vertical transport in models and distinguishing between different parameterizations.

2.3.5 Transects of amplitude, rectifier, and phase along 60° North and South

Two models are chosen to demonstrate transects in the Northern Hemisphere and two in the Southern Hemisphere (Figures 2.13 and 2.14). Each of these pairs of models serves as a good example of the range of predictions among the nine models. Visible in transects across 60°N is the extent of the large annual cycles in the northern Pacific and Atlantic Oceans. The signal resulting from sources and sinks of oceanic APO extends into the atmosphere, showing the presence of mixing over land especially over Western Europe, as well as over northeastern Siberia, Alaska, and Canada.

In general, the land-ocean contrasts are smeared out by 600 mb; above this level, a given altitude tends to have the same value across the transect. The models with larger surface-level cycles (such as NIRE) tend to have much smaller cycles at

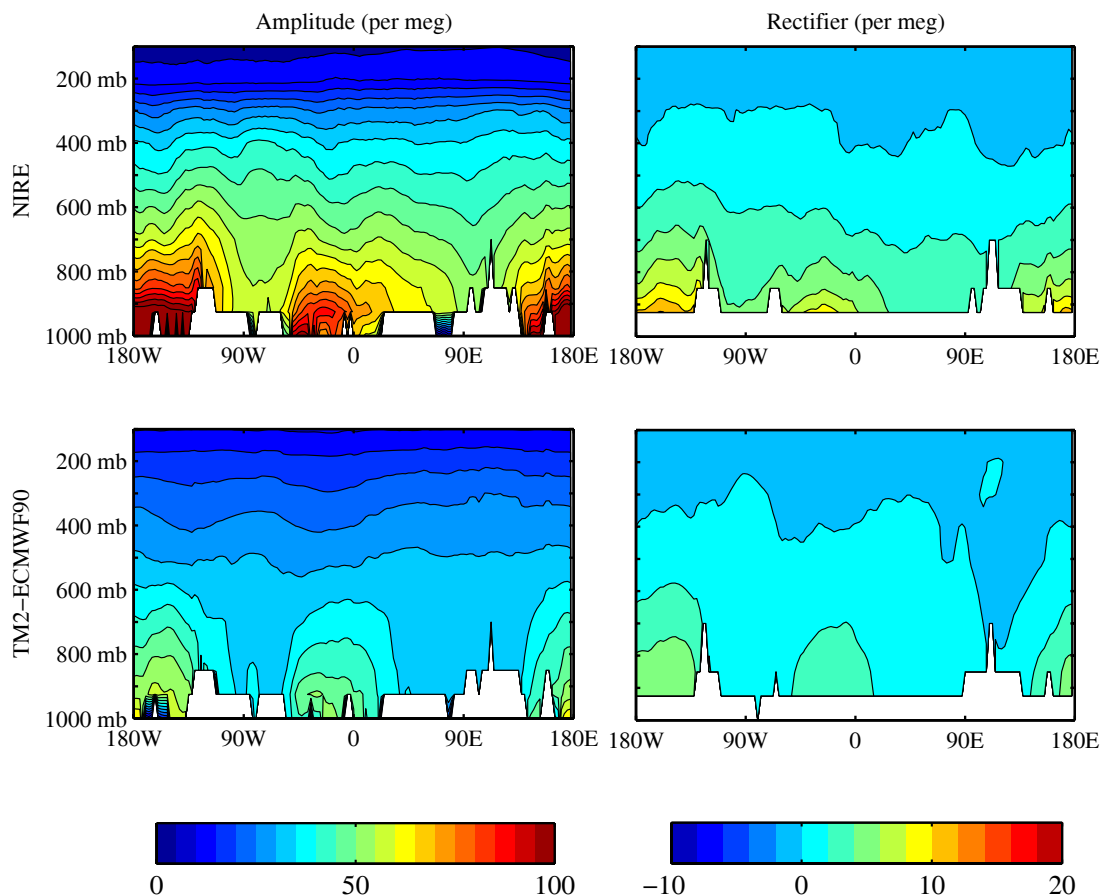


Figure 2.13. Representative transects of the annual peak-to-peak amplitude and rectifier at 60°N.

very high altitudes, showing that the vertical transport in that model is slower at mixing a tracer into the higher atmosphere. In contrast, those models where the APO flux is carried away from the surface faster (such as TM2-ECMWF90) do not show such large areas of surface maxima and have larger cycles at high altitudes.

In contrast to the Northern Hemisphere transects, the Southern Hemisphere transects shows less spatial variability near the surface. Because the integrated APO fluxes are larger in the Southern Hemisphere, the size of the cycles even at higher

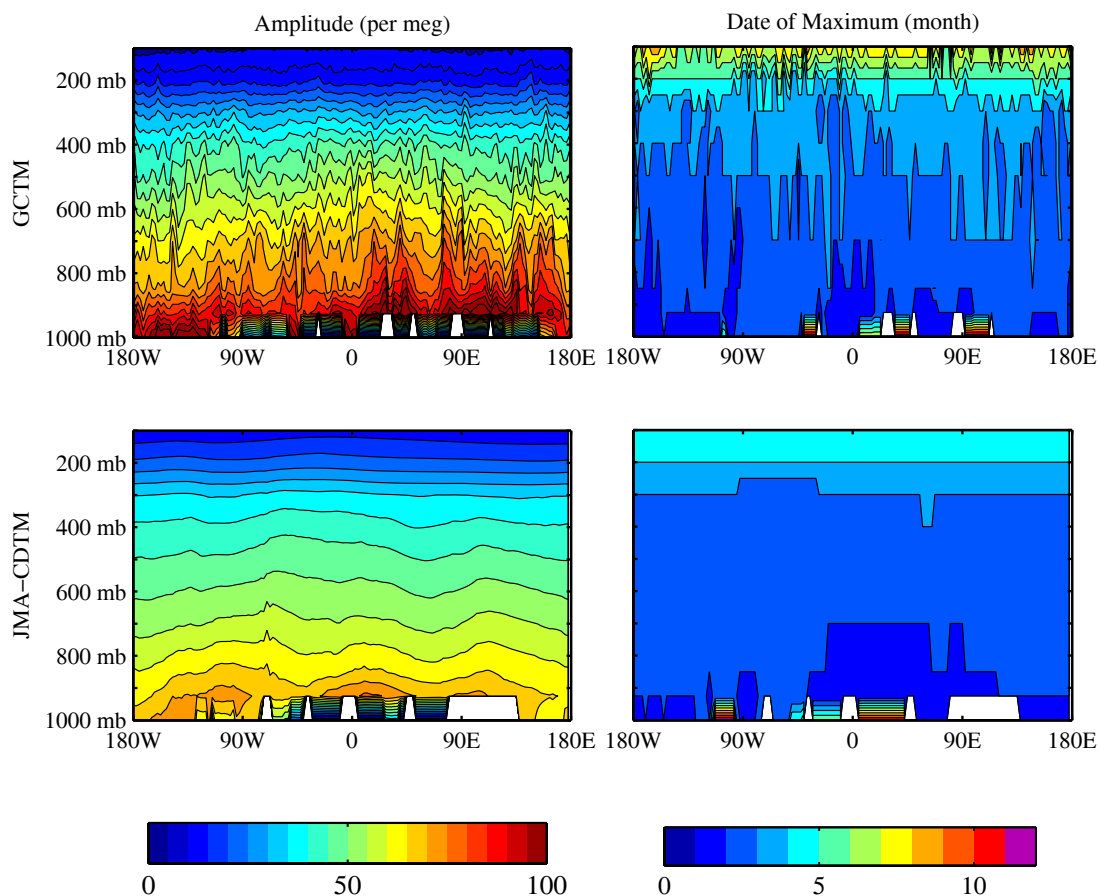


Figure 2.14. Representative transects of the annual peak-to-peak amplitude and phasing at 60°S.

altitudes is much larger than in the Northern Hemisphere. Whereas cycles of only about 25 per meg are common in the Northern Hemisphere at 500 mb, in the Southern Hemisphere the cycles are closer to 50 per meg at the same altitude. The Northern Hemisphere appears in general to have a higher vertical mixing at these latitudes; the lag in annual maximum between the lower and upper atmosphere is generally about 3-4 months between the 800 and 100 mb levels, whereas it is 4-6 months in the Southern Hemisphere transects.

2.4 Discussion

Plots of model transects can be used to classify the models into groups with stronger and weaker vertical transport, as found by Denning et al. (1999). The gradients in zonal mean peak-to-peak amplitude over source regions in the extratropics of the Southern Hemisphere, visible in Figure 2.10, are used to roughly group models with stronger or weaker vertical transport. Those with stronger vertical transport are JMA-CDTM, NIES, TM2-ECMWF90, and TM3. Those with weaker mixing and larger gradients include GCTM, MATCH-NCEP, MATCH-MACCM2, and to a lesser extent, GISS and NIRE. This grouping has TM3 and GISS classed differently than in Denning et al. (1999), possibly due to changes in the models used and/or differences in tracer characteristics that necessitate different classification schemes. Those with weaker mixing significantly overestimate the station amplitudes shown in Figure 2.3 in the Southern Hemisphere and at mid-latitudes in the Northern Hemisphere, as more APO tends to accumulate at lower altitudes rather than being mixed aloft in the atmosphere. However, no high-altitude data exist to compare with the altitudinal profiles predicted by different models.

Beyond an understanding of how each model performs relative to the other models, these APO model calculations are important for suggesting new locations where it may be helpful to have oxygen and carbon dioxide measurements to test the existing models and help pinpoint areas in which models need to be improved. For example, whether parameterizations of stronger or weaker vertical mixing are more appropriate could be tested by measurements from vertical profiles in the Southern Hemisphere and at mid-latitudes in the Northern Hemisphere. Because the difference

between models at lower altitudes (950 – 500 mb) in the extra-tropics is greatest in the summer, particular attention should be paid to measurements in the Northern Hemisphere during July – September and in the Southern Hemisphere during January – March.

The Southern Hemisphere can probably be well-described with a zonal array of stations without the need for a longitudinal array. Because of the heterogeneity of land and sea masses in the Northern Hemisphere compared to the Southern Hemisphere, measurement locations spread across different longitudes as well as different latitudes is more important. Horizontal transport can be tested by more measurements in close proximity to areas of large sources and sinks in the Northern Hemisphere; at the present time, at least some stations exist near the large source region in the northern Pacific Ocean although more could be useful. However, no measurements exist in the region of the large source in the northern Atlantic Ocean, a situation that should be rectified by placing stations in eastern Canada and in the British Isles.

Another need is for more land-based stations, especially over the large northern hemispheric continents of Eurasia and North America. Measurements over land, where the net sources and sinks of APO are zero and atmospheric transport can be better isolated, may be significant in evaluating different model parameterizations. Here, seasonal information is important in observing how seasonal cycles in air-sea flux fields propagate over large, mid-latitude continents where no sources or sinks

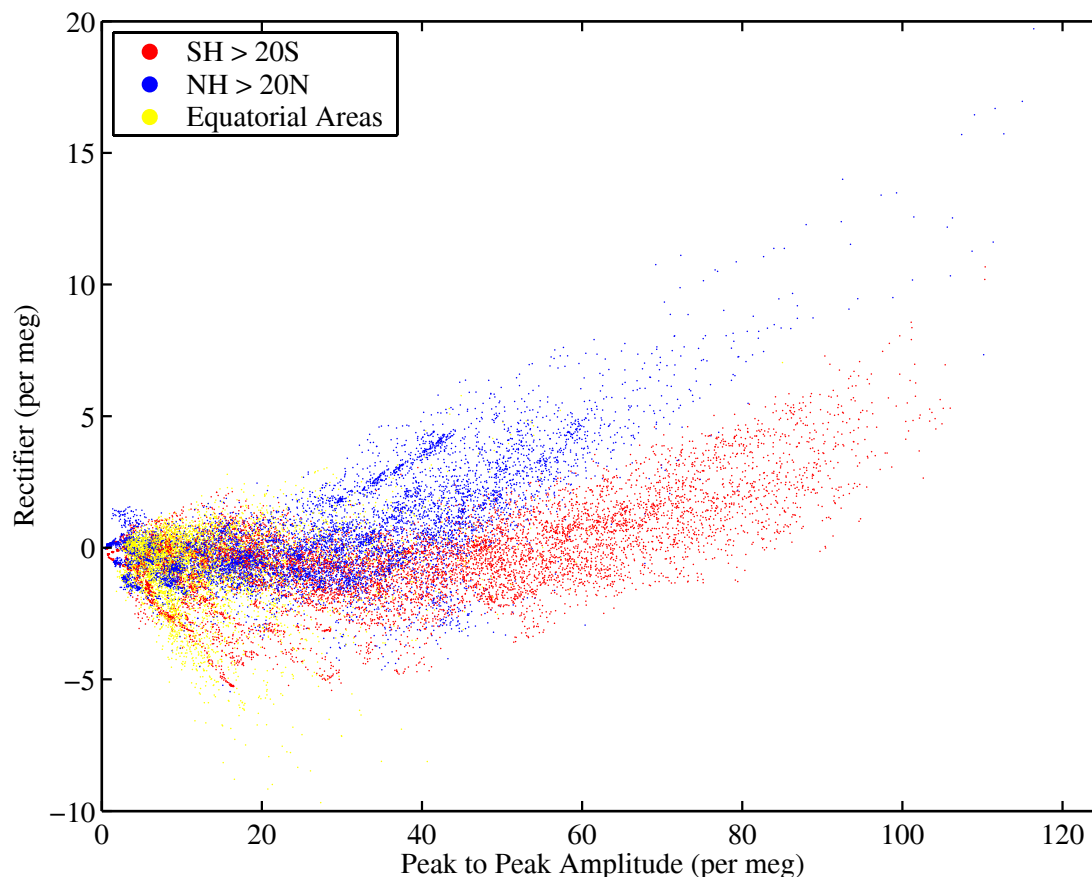


Figure 2.15. Relationship between the peak-to-peak amplitude and the rectifier predictions from all 9 models. The predictions from each model on its respective grid were interpolated onto a new grid with boxes of 20° longitude and 10° latitude from 85°S to 85°N. The 9 pressure levels used for the standard output were retained in the vertical dimension, giving 2916 points per model. The Northern and Southern Hemispheres have distinct relationships between amplitude and rectifier values. The largest rectifier values occur in the Northern Hemisphere, where it can be ~10% of the size of the annual cycle.

exist. Summer transport should also be strongest over land surfaces, leading to significant seasonality in vertical transport. However, land-based stations present measurement challenges associated with localized sources and sinks of carbon dioxide and oxygen as well as pollution. One way to potentially benefit more from measurements over land is to concentrate on vertical profiles.

The rectifiers predicted by models at different stations are correlated with the overall peak-to-peak amplitude of the seasonal cycle. As demonstrated in Figure 2.15, where the cycle is small (less than 20 per meg), the rectifier tends to be close to zero or negative. Above this value, the Southern and Northern Hemispheres have different patterns in all the models: the Northern Hemisphere tends to have larger values of the rectifier than the Southern Hemisphere for the same size amplitude. This result most likely stems from the heterogeneity of land and ocean masses in the Northern Hemisphere. Besides leading to a more complex spatial distribution of sources and sinks, this heterogeneity most likely also leads to a more complex seasonal change in transport due to the effect of heating and cooling on continents as well as seasonal changes above the ocean. In the Southern Hemisphere, among all the models the rectifier effect never is larger than about 7 per meg; in the Northern Hemisphere, the value climbs to 15 per meg at its highest. Also, in the Southern Hemisphere the rectifier value stays close to zero until the seasonal amplitude climbs above 60 per meg; in the Northern Hemisphere, the rectifier starts increasing in concert with the amplitude at about 30 per meg. It is hoped that these model predictions provide a bound on the size of the rectifier resulting from the interaction of the seasonal component in atmospheric transport and tracer fields.

2.5 Conclusions

Through comparison with station APO data, I evaluated the effectiveness of the atmospheric transport models submitted to the TransCom project in modeling a tracer with only oceanic fluxes. Overall, the models correctly predicted the general large-scale surface patterns of APO and the seasonal cycle as compared to APO data from eleven different stations. Some problems with the models have also been highlighted by this comparison. These results are dependent on the accuracy of the initial O_2 and N_2 air-sea flux estimates. However, these results may aid in understanding model predictions and constraints when estimating other variables.

Global maps of the rectifier effect may help identify areas where atmospheric measurements can be considered independently on seasonal time scales and annual averages. In equatorial areas, such an analysis may be very problematic given the small size of annual cycles of many species. The rectifier effect is also larger in the Northern Hemisphere than in the Southern Hemisphere, suggesting that the mean and seasonal signals are less independent in the Northern Hemisphere.

In general, the predictions of the TransCom models show more variability between models in the Northern Hemisphere than in the Southern Hemisphere. Sources and sinks of air-sea gas flux have a heterogeneous distribution because of the distribution of continents, leading to larger localized seasonal cycles in the atmospheric concentration of APO and large land masses over which APO is carried passively. Because westward winds are generally weaker in the Northern Hemisphere (Peixoto and Oort 1992), a zonal band may not mix as fast in the Northern

Hemisphere as in the Southern Hemisphere, leading to greater east-west heterogeneity of concentrations in the lower atmosphere and larger differences in phase.

The results of maps of model predictions suggest that more stations distributed within a particular latitude band would be helpful to test models in the Northern Hemisphere, whereas zonally distributed stations are probably adequate to represent the Southern Hemisphere. Critical areas include the North Atlantic as well as the North Pacific, where models show the greatest disparity in predictions. In these localized areas of sources and sinks, the models show significant variability in describing how these fluxes are transported both horizontally and vertically, and more stations may help to distinguish between different methods of modeling horizontal transport.

Also important are more profiles at altitude, especially in different seasons, as the strength of vertical transport is critical to determining surface patterns. At the present time, it is difficult to test parameterizations of vertical transport solely with monitoring stations at the sea surface. Measurements at different altitudes could resolve differences in atmospheric concentration and phase, helping to understand seasonal differences in vertical transport. Such profiling has rarely been performed because of the expense and the difficulty of repeating such measurements in different seasons. However, these profiles may be necessary to distinguish between different parameterizations of vertical transport and to continue to improve atmospheric transport models.

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Chapter 3

Air-sea heat flux and the related seasonal cycle of $\delta(\text{Ar}/\text{N}_2)$

3.1 Introduction

The sun's radiation falls unequally on the earth's surface, with low latitudes receiving much more radiation than high latitudes. The resultant energy imbalance helps drive the atmospheric circulation as well as the oceanic circulation. Heat is carried poleward both in the atmosphere and in the ocean. Satellite measurements of top-of-the-atmosphere radiation suggest that a peak value of 5 PW is carried northward, of which approximately two-thirds is carried by the atmosphere (Trenberth and Caron 2001; Trenberth and Solomon 1994). The remaining third is carried by the oceans, which take up heat in tropical areas and release it to the atmosphere in the high latitudes. Although the majority of the overall heat transport occurs in the atmosphere, the ocean plays a large role in heat storage, with an maximum amplitude of roughly 12×10^{22} J (18×10^{22} J) in the Northern (Southern) Hemisphere seasonal cycle of heat

content in the upper 275 m of the ocean, whereas the seasonal cycle in the atmospheric heat content has an amplitude of about 3×10^{22} J in the Northern Hemisphere and 2×10^{22} J in the Southern Hemisphere (Peixoto and Oort 1992).

The most recent IPCC report suggests that the increase in radiation at the earth's surface from atmospheric trapping of shortwave radiation by anthropogenic greenhouse gases presently totals about 2 W m^{-2} over the entire earth (Houghton et al. 2001). Levitus et al. (2000) found that the temperature of the ocean increased 0.31°C in the 0-300 m layer between the mid-1950s and the mid-1990s, equivalent to an increase of ocean heat content by 2×10^{23} Joules and a heat uptake of about 0.3 watts m^{-2} per unit area of the Earth's surface. In an updated study, Levitus et al. (2005) conclude that the upper 3000 m of the ocean has warmed 0.037°C between 1955 and 1998. More recently, Willis et al. (2004) find a global ocean warming of $0.86 \pm 0.12 \text{ W m}^{-2}$ in the top 750 m of the ocean between 1993 and 2003. Levitus et al. (2000) quote a maximum heat storage rate of 6 watts m^{-2} in the Labrador Sea, and Gille (2002) finds a warming rate two times as fast as the Levitus global average in the mid-depth Southern Ocean between the 1950s and the 1980s. Much of the excess heat is therefore being stored in the oceans.

Modeling work done by Barnett et al. (2005), Barnett et al. (2001), and Levitus et al. (2001) support the hypothesis that most of this oceanic warming is due to anthropogenic effects of greenhouse gases and the direct effects of sulfate aerosols. In comparison to other estimates of the Earth's heat balance components, the ocean has taken up 14.5×10^{22} J between 1955 and 1998, whereas the continents have only taken

up 0.9×10^{22} J, the melting of the continental glaciers is responsible for taking up 0.8×10^{22} J, and the atmosphere has taken up 0.7×10^{22} J (Levitus et al. 2005). Because the ocean's ability to store heat is so large, this effect may have a significant impact on the amount of overall global warming as well as contributing to localized climate effects. Increased heat storage will also affect the ocean's ability to store greenhouse gases, directly affecting the cycle it buffers. Heat storage may also have significant interannual variability, as evidenced by a decrease of 6×10^{22} J between 1980 and 1983 (Levitus et al. 2005).

Work on long-term changes of the mean ocean heat content has depended on comparison over time of hydrographic surveys of ocean temperature, XBT lines, and, more recently, high density coverage of floats. Data from comparison of ship survey lines or XBT lines tend to be concentrated spatially where it is easy to take ships and temporally when the weather is not threatening. The Southern Ocean in particular has very few ship transect measurements (Levitus et al. 2005). Floats, although getting around such problems better, also have their own problems: they tend to be clustered in particular areas rather than being equally spread spatially, and they also have depth limitations. Although they succeed better at covering geographical areas difficult to reach with a boat and with a higher temporal resolution, they are still limited in their coverage by the fact that they cannot report data from ice-covered areas. Both ocean surveys and floats also tend to be limited by financial considerations. WOCE hydrographic survey data has also been used to calculate the mean ocean heat

transport and the amount of air-sea heat flux expected from the ocean heat transport residuals (MacDonald and Wunsch 1996; Ganachaud and Wunsch 2000).

Less work has been done on the seasonal cycle in the ocean heat content. Peixoto and Oort (1992) show a seasonal heat content change of 12×10^{22} J in the Northern Hemisphere and a change of 18×10^{22} J in the Southern Hemisphere in the upper 275 m of the ocean, consistent with the surface maps of seasonal heat content change in Levitus (1987) and Hsiung et al. (1989). More recent estimates for the upper 250 m show smaller values of 6.5×10^{22} J in the Northern Hemisphere and 10.2×10^{22} J in the Southern Hemisphere (Antonov et al. 2005). These seasonal changes are due to changes in air-sea heat flux and lateral water transport. An improved understanding of this flux may help scientists understand many climate questions better; for example, information on interannual time scales may help explain ocean-atmosphere linkages such as the Pacific Decadal Oscillation or the North Atlantic Oscillation (Trenberth et al. 2002). Air-sea heat flux is also linked to fluxes of climatologically important gases in and out of the ocean, such as CO_2 .

In general, estimates of heat storage rely on atlases of ocean temperature, integrating XBT surveys, or, more recently, using TOPEX data (Wang and Koblinsky 1997; White and Tai 1995). In contrast, estimates of air-sea heat exchange often rely on bulk estimates of surface parameters for sensible and latent heat flux as well as shortwave and longwave radiation. Heat exchanges are also calculated as the residual both of heat transport and storage and of top of the atmosphere radiation measurements combined with estimates of atmospheric heat transport (Trenberth and

Solomon 1994). Ganachaud and Wunsch (2000) calculate divergence of horizontal heat flux and also air-sea heat flux, assuming the system is in steady state.

A new way to estimate air-sea heat exchange and investigate interannual variability involves using measurements of the atmospheric Ar/N₂ ratio. The absence of biological impacts (zero for Ar and negligible for N₂, as discussed in Chapter 1) leaves physical factors as the driving mechanism for changes in the atmospheric Ar/N₂ ratio, the most important of which is heat exchange between the ocean and atmosphere. In general, as the temperature of the ocean surface rises, the solubility of gases in the ocean drops, and gases are naturally released to the atmosphere. The reverse happens with cold water, where the solubility is higher. Because of these solubility changes in the ocean associated with heat flux, changes in the atmospheric concentration of certain species may serve as tracers of air-sea heat flux. Unlike oceanographic measurements, which require many repeat measurements in order to get both spatial and temporal resolution, atmospheric tracers can serve as “integrators,” where a few measurements can help quantify oceanic changes on large spatial scales.

3.2 The seasonal cycle in $\delta(\text{Ar}/\text{N}_2)$: A transient model of air-sea gas flux

The dissolved concentration in the ocean of a particular gas depends both on its solubility in seawater and on whether it has significant sources or sinks, among them air-sea exchange, biological use or remineralization, exchange with the sea floor, and extra production or destruction by radioactive decay (Pilson 1998). The solubility

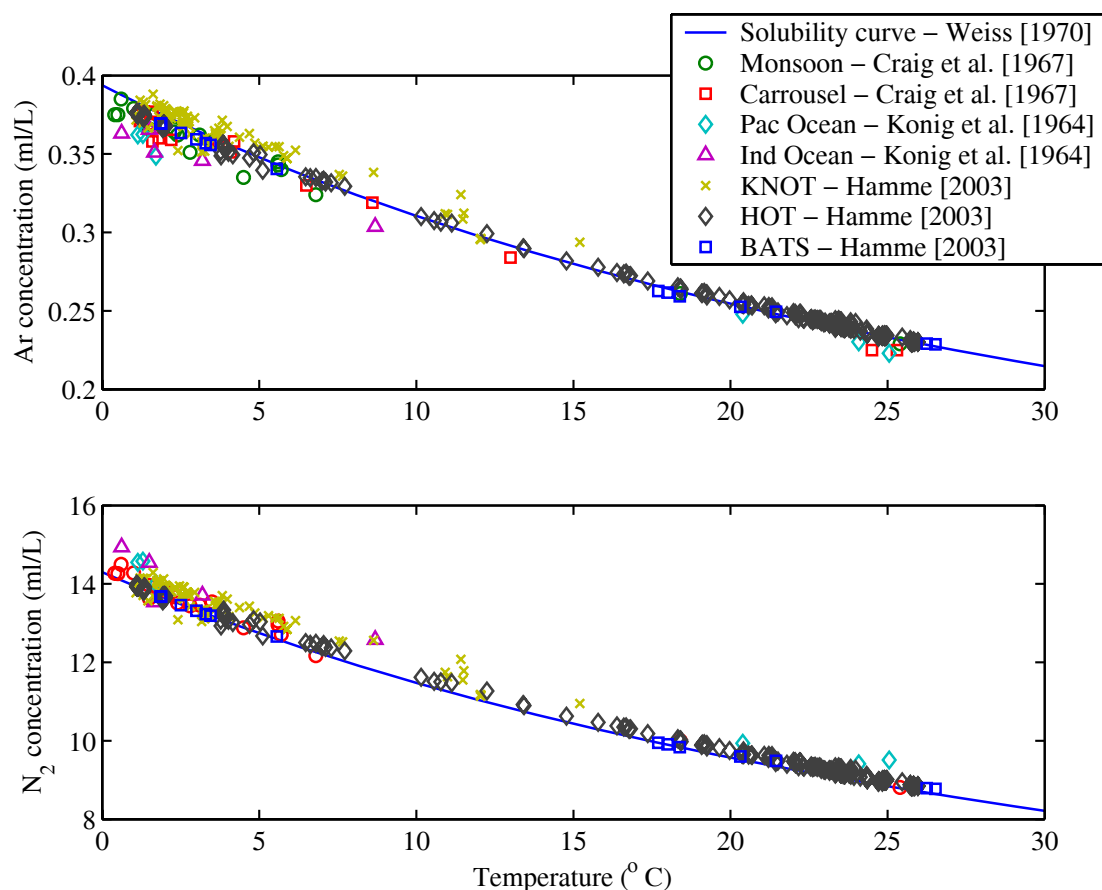


Figure 3.1. Comparison of expected solubility based on temperature and actual ocean measurements for historical data of Ar and N₂ concentrations. The solubility curves are from Weiss (1971). The data come from Craig et al. (1967) and König et al. (1964) in the Pacific and Indian Oceans, and Hamme (2003) for the Hawaii (HOT), North Pacific (KNOT), and Bermuda (BATS) stations. Both Ar and N₂ concentrations show a clear relationship with their predicted solubility based on temperature.

itself depends on the temperature and salinity of the water as well as the gas's atmospheric partial pressure.

Ar and N₂ are two gases whose oceanic concentrations have been shown to be closely related to their predicted solubilities, implying few or no sources and sinks. Historical ocean data of Ar and N₂ have been plotted on Figure 3.1 along with the Weiss (1970) solubility relations based on temperature (salinity effects will be

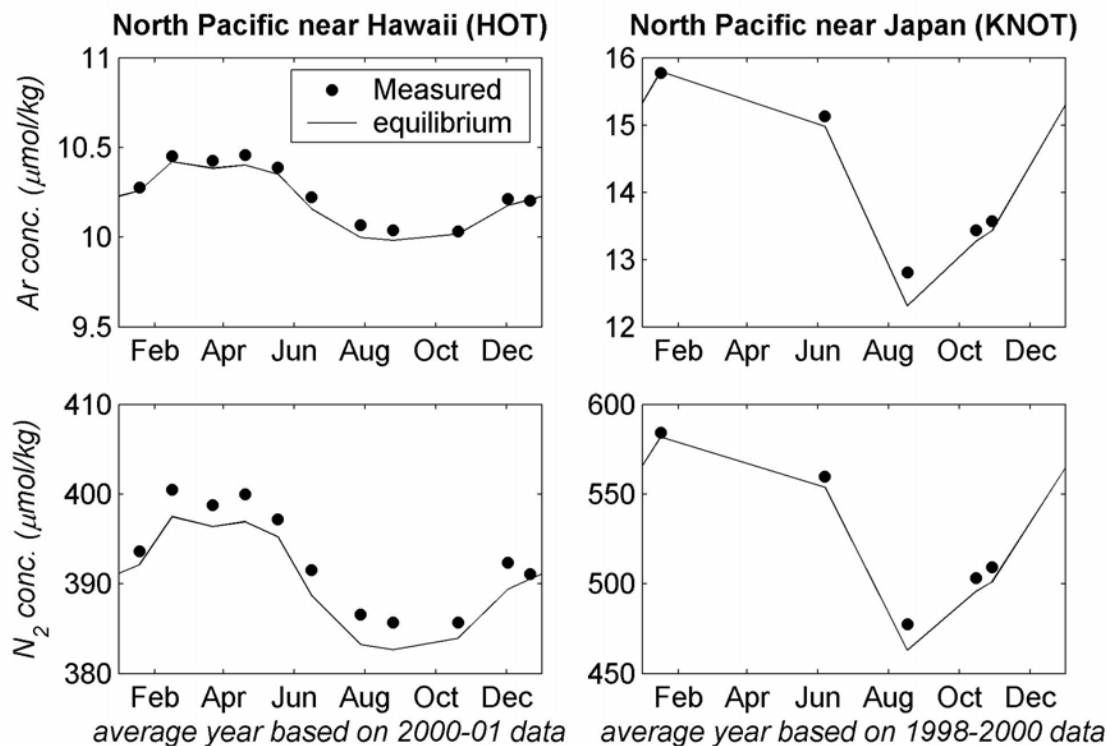


Figure 3.2. Seasonal cycle in surface ocean Ar and N_2 concentrations in temperate and subpolar waters. Figure provided by R. Hamme using data published in Hamme and Emerson (accepted for publication, 2006) and Hamme (2003).

discussed below). Although changes in barometric pressure, bubble injection (Schudlich and Emerson 1996), supersaturation caused by mixing between two water parcels (curvature-induced supersaturation), the stability of the boundary layer, whether surfactants are present, and biological influences on N_2 may all affect the concentration of these gases in the surface layer of the ocean, the dominant influence is still temperature. Seasonal temperature changes translate into seasonal cycles in solubility in both Ar and N_2 , which have recently been documented by Hamme and Emerson (accepted, 2006) and Hamme (2003). The seasonal cycles in the Ar and N_2 concentrations are shown in Figure 3.2 for temperate and subpolar stations.

As mentioned above, solubility depends on salinity as well as temperature. For a range of salinity values from 30 to 36 psu, the solubility of Ar and N₂ varies by about 3-4%. Especially in high-latitude areas, however, the solubility may vary more significantly on seasonal time scales due to changes in freshwater influx and ice formation and melting. Such seasonal cycles could serve either to amplify or reduce the effect of air-sea heat flux on the Ar and N₂ gas fluxes. Near-surface temperature and salinity data from the Gulf of Alaska (Okkonen et al. 2005) show clear seasonal cycles in both variables, ranging between 4-15°C and 18-32 psu. Such seasonal cycles in salinity could result in changes of up to 10% from the expected amplitude of the seasonal cycle in solubility of Ar and N₂ based solely on temperature changes. Near-surface float data in the Labrador Sea (A. Koetzing, pers. comm.) show much smaller cycles in salinity in near-surface waters, potentially leading to errors of less than 1% in estimated seasonal cycles of solubility based solely on temperature. Although it is possible that some regions have large enough cycles in salinity to cause significant changes in gas solubility, I assume a constant salinity on seasonal time scales for the following analysis.

For a gas with no major sources and sinks, assuming that it equilibrates rapidly with the atmosphere, it is possible to estimate air-sea gas flux through the difference in solubility Sol at the initial and final temperatures, T_1 and T_2 :

$$Flux = (Sol(T_1) - Sol(T_2))V \approx \left(\frac{\partial Sol}{\partial T} \right) V \Delta T \approx \left(\frac{\partial Sol}{\partial T} \right) \frac{\Delta Q}{\rho c_p}. \quad (3.1)$$

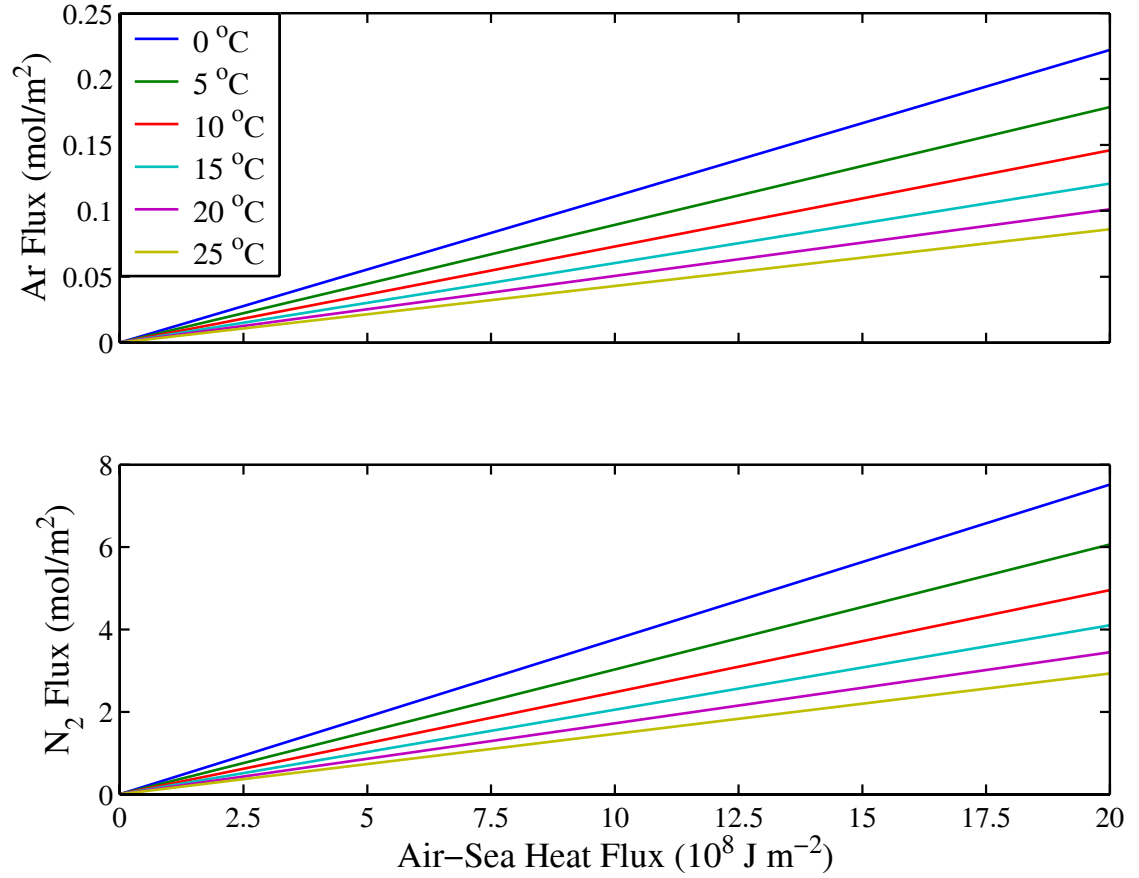


Figure 3.3. Air-sea heat flux and the consequent amount of Ar or N₂ released to the atmosphere through an ocean surface area of 1 m². The amount of gas released depends directly on the temperature of the water; as the temperature rises, the same heat flux causes less gas exchange than at lower temperatures.

where V is the volume of the water parcel, $\Delta Q = \rho c_p V \Delta T$ is the change in heat storage due to heat flux, ρ is the water density, and c_p is the heat capacity. This relationship can be used to relate air-sea heat flux to the amount of gas released to the atmosphere for a specific water temperature change. Imagine a well-mixed atmospheric column above an ocean column, with a surface area of 1 m² where exchange between air and water can take place. As the water column heats up, gas is released to the air column, and the change in the atmospheric gas concentration is directly related to the

integrated temperature change in the volume of water. In Figure 3.3, I show how a specific heat input per square meter of surface would translate into gas release due to solubility changes for both Ar and N₂. Because solubility depends non-linearly on temperature, the derivative ($\partial Sol / \partial T$) is also temperature-dependent, and thus the amount of gas released per unit warming depends on the water temperature. Both c_p and ρ also depend on temperature and salinity, but they vary by less than 6% over the entire range of values of temperature and salinity in the ocean. Using more realistic temperature and salinity values for the mid-latitude surface ocean, they vary less than 0.33% and 0.78% respectively. The range of air-sea heat flux inputs is representative of realistic values from estimates of seasonal heat content, from close to zero at high latitudes to $12 \times 10^8 \text{ J m}^{-2}$ at 40°S (Antonov et al. 2004). Present estimates of long-term global warming also fall into that range: the ocean has taken up the equivalent of about $4 \times 10^8 \text{ J m}^{-2}$ between 1955 and 1998 (Levitus et al. 2005).

In Figure 3.3, the net amount of Ar released is small in comparison to the amount of N₂. However, because the mole fraction of atmospheric Ar (~1%) is much smaller than N₂ (~78%), warming leads to a larger percent change in the amount of Ar than the amount of N₂ in the air, thus causing an increase in the Ar/N₂ ratio. Figure 3.4 shows how these fluxes translate into changes in atmospheric concentration of the Ar/N₂ ratio in the atmospheric column.

The predicted changes in the atmospheric Ar/N₂ ratio are very small. The ratio is expressed as the deviation from a reference according to:

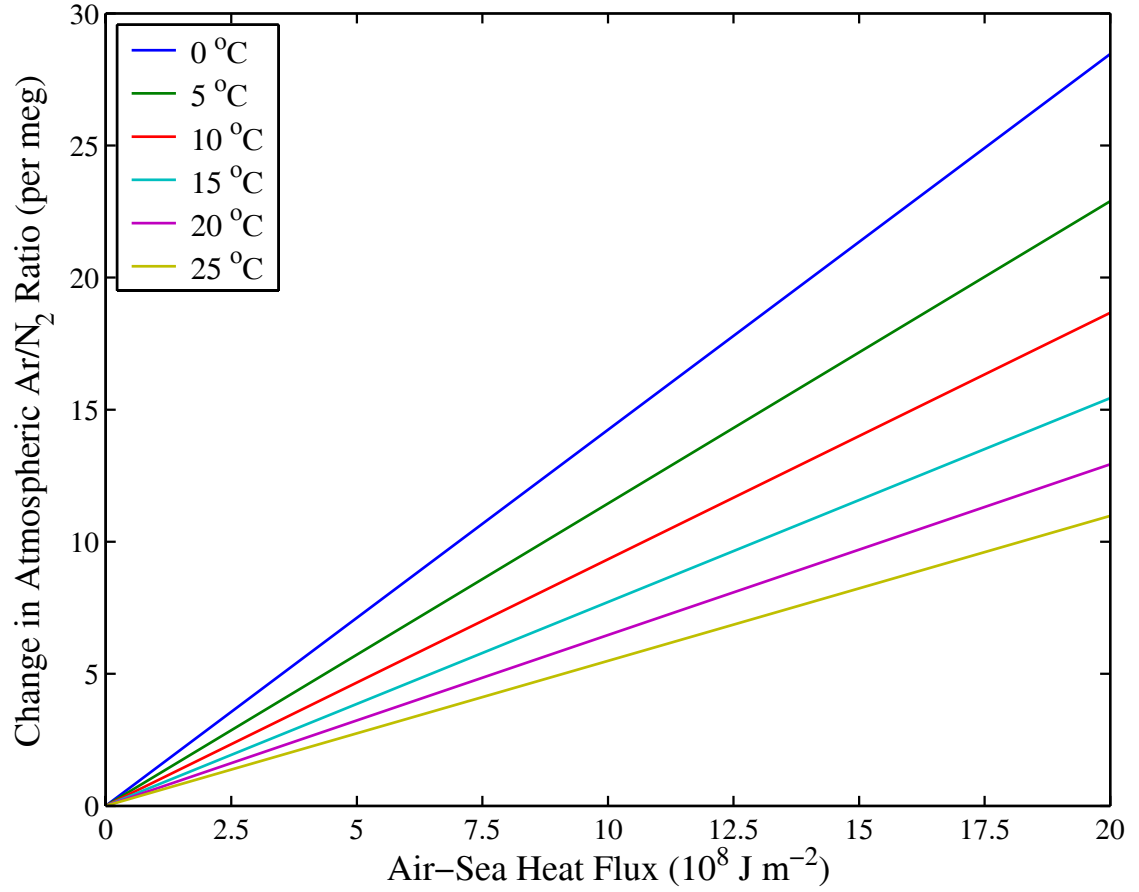


Figure 3.4. Relationship between heat flux and the change in estimated global atmospheric Ar/N₂ ratio. The Ar/N₂ ratio is only about half as sensitive to heat flux as expected from the Ar changes alone because of compensating changes in N₂.

$$\delta(\text{Ar}/\text{N}_2) = \left[\frac{(\text{Ar}/\text{N}_2)_{\text{sample}}}{(\text{Ar}/\text{N}_2)_{\text{reference}}} - 1 \right], \quad (3.2)$$

where $\delta(\text{Ar}/\text{N}_2)$ is typically multiplied by 10^6 and expressed in “per meg” units. An increase of one mole of Ar in 10^6 moles of air corresponds to a 107 per meg change in $\delta(\text{Ar}/\text{N}_2)$, whereas a similar increase in N₂ corresponds to a -1.3 per meg change in the ratio.

Equation 3.1 and the results of Figures 3.3-3.4 assume that atmospheric and oceanic concentrations of Ar and N₂ equilibrate instantaneously and completely. In reality, it takes time for the ocean to equilibrate with respect to the atmosphere. This delay is usually modeled as the following:

$$Flux = K(C - C_{eq}), \quad (3.3)$$

which relates the gas flux to the disequilibrium in the surface water. K is called the piston velocity or transfer velocity, describing how fast gas exchange penetrates through the laminar layer. Theoretical studies of momentum and mass transfer have suggested that K should be dependent on the ratio of transfer coefficients for momentum (the kinematic viscosity ν) and mass (molecular diffusivity D). In practice, the value of K can vary extensively in different environmental conditions and for different gases (Liss and Merlivat 1986; Jähne and Haußecker 1998; Jähne et al. 1987; Jean-Baptiste and Poisson 2000; Wanninkhof 1992).

A two-box model of the oceanic mixed layer and the overlying atmosphere can be used to illustrate the seasonal changes in atmospheric $\delta(\text{Ar}/\text{N}_2)$, allowing for finite rather than infinite K (Figure 3.5). Changes in the concentration of the ocean box are directly dependent on the flux to the atmosphere:

$$V(dC/dt) = -FA, \text{ or } H(dC/dt) = -F, \quad (3.4)$$

where V is the volume of the box, F is the flux to the atmosphere, A is the area of the surface, and H is the depth of the box. The atmosphere and ocean boxes are assumed to be well-mixed. Combining 3.3 and 3.4 and isolating the change in the equilibrium concentration yields:

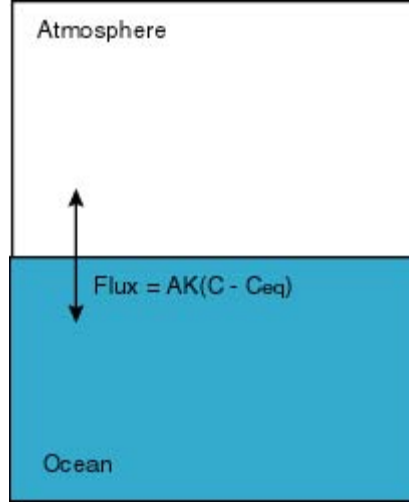


Figure 3.5. Diagram of the transient model showing the gas flux between ocean and atmosphere.

$$\frac{d(C - C_{eq})}{dt} = -\frac{K}{H}(C - C_{eq}) - \frac{dC_{eq}}{dt}. \quad (3.5)$$

This formulation gives an exchange time constant of H/K . Since the salinity and pressure effects on solubility at the ocean surface are small, the term dC_{eq}/dt can be considered as a thermal forcing term, assuming that only changes in the temperature of the ocean surface drive changes in the equilibrium concentration.

Solubility depends almost linearly on temperature over small temperature changes. It is thus possible to estimate the equilibrium concentration of a particular species in water as a linear function of the temperature:

$$C_{eq} = \alpha T + C_1. \quad (3.6)$$

In this two-box model, if we assume that temperature of the ocean box (or mixed layer) changes in a sinusoidal way over time, then we can also write the equilibrium concentration as the following:

$$C_{eq} = \alpha \Delta T \sin(\omega t - \varphi) + C_2, \quad (3.7)$$

where α is the derivative of solubility with respect to temperature, ΔT is the amplitude of the seasonal cycle in temperature, $\omega = 2\pi/365$ days, φ is a given phase, and C_2 is a constant. The equilibrium value of C therefore changes over a year in the same sinusoidal way as temperature.

This model is solved by Keeling et al. (1993) to give the following solution:

$$C - C_{eq} = \left(\frac{\omega H}{K} \right) f \alpha \Delta T \cos(\omega(t - t_{lag}) - \varphi), \quad (3.8)$$

$$\text{where } f = \left(1 + \left(\frac{\omega H}{K} \right)^2 \right)^{-1/2} \text{ and } t_{lag} = \left(\frac{1}{\omega} \right) \tan^{-1} \left(\frac{\omega H}{K} \right).$$

The parameter f basically describes how efficiently the gas equilibrates with the atmosphere, whereas t_{lag} describes the delay between forcing and response. The time-integrated air-sea gas flux and the related heat flux can be written as the following, integrated from zero to a given time:

$$\int F dt = H f \alpha \Delta T \sin(\omega(t - t_{lag}) - \varphi), \text{ and} \quad (3.9)$$

$$\Delta Q = H c_p \rho \Delta T. \quad (3.10)$$

Using these equations to calculate the flux of Ar and N₂, I can then calculate $\delta(\text{Ar}/\text{N}_2)$. For small changes, $\delta(\text{Ar}/\text{N}_2)$ can be approximated by the difference in the relative change of Ar and N₂ in the atmosphere:

$$\delta(\text{Ar}/\text{N}_2) = \left(\frac{(F_{Ar}/M_{atm})}{X_{Ar}} - \frac{(F_{N2}/M_{atm})}{X_{N2}} \right) \cdot 10^6, \quad (3.11)$$

where F_{Ar} and F_{N_2} are the fluxes of Ar and N_2 in moles per m^2 of exchange surface, M_{atm} is the number of moles of air in the atmospheric box per m^2 of exchange surface, and X_{Ar} and X_{N_2} are the average atmospheric mole fraction of Ar and N_2 respectively. The amount of moles in the atmospheric column is calculated from the total number of moles in the atmosphere (1.8×10^{20}) divided by the surface area of the earth. Equation (3.11) can also be written in terms of the heat flux:

$$\delta(Ar/N_2) = \frac{\Delta Q}{M_{atm} c_p \rho} \left(\frac{f_{Ar} \alpha_{Ar}}{X_{Ar}} - \frac{f_{N_2} \alpha_{N_2}}{X_{N_2}} \right) \cdot 10^6. \quad (3.12)$$

For this model, I assume that all the air in this column mixes instantaneously. This is far from the actuality, as air is transported both horizontally as well as vertically, and vertical mixing can have a time constant of months to years. Decreasing the estimated size of this box would increase the expected change in $\delta(Ar/N_2)$.

I calculate the seasonal cycle in $\delta(Ar/N_2)$ due to air-sea heat flux under idealized conditions. The following results assume inputs of approximate values for a temperate ocean mixed layer, with a box depth of 80 m and a seasonal temperature cycle of $\pm 2^\circ\text{C}$ in the mixed layer around a mean temperature of 15°C . This temperature range is consistent with values of average seasonal heat storage estimated for the Atlantic basin by the TOPEX data. I adopt K values of 3.47 m day^{-1} for Ar and 3.64 m day^{-1} for N_2 , following Keeling et al. (1993) and taking into account small changes in molecular diffusion rates between the two species. Figure 3.6 gives the seasonal cycle of atmospheric $\delta(Ar/N_2)$, showing the contributions of both Ar and N_2 . The annual flux cycle for the individual gases are also plotted against heat flux (see

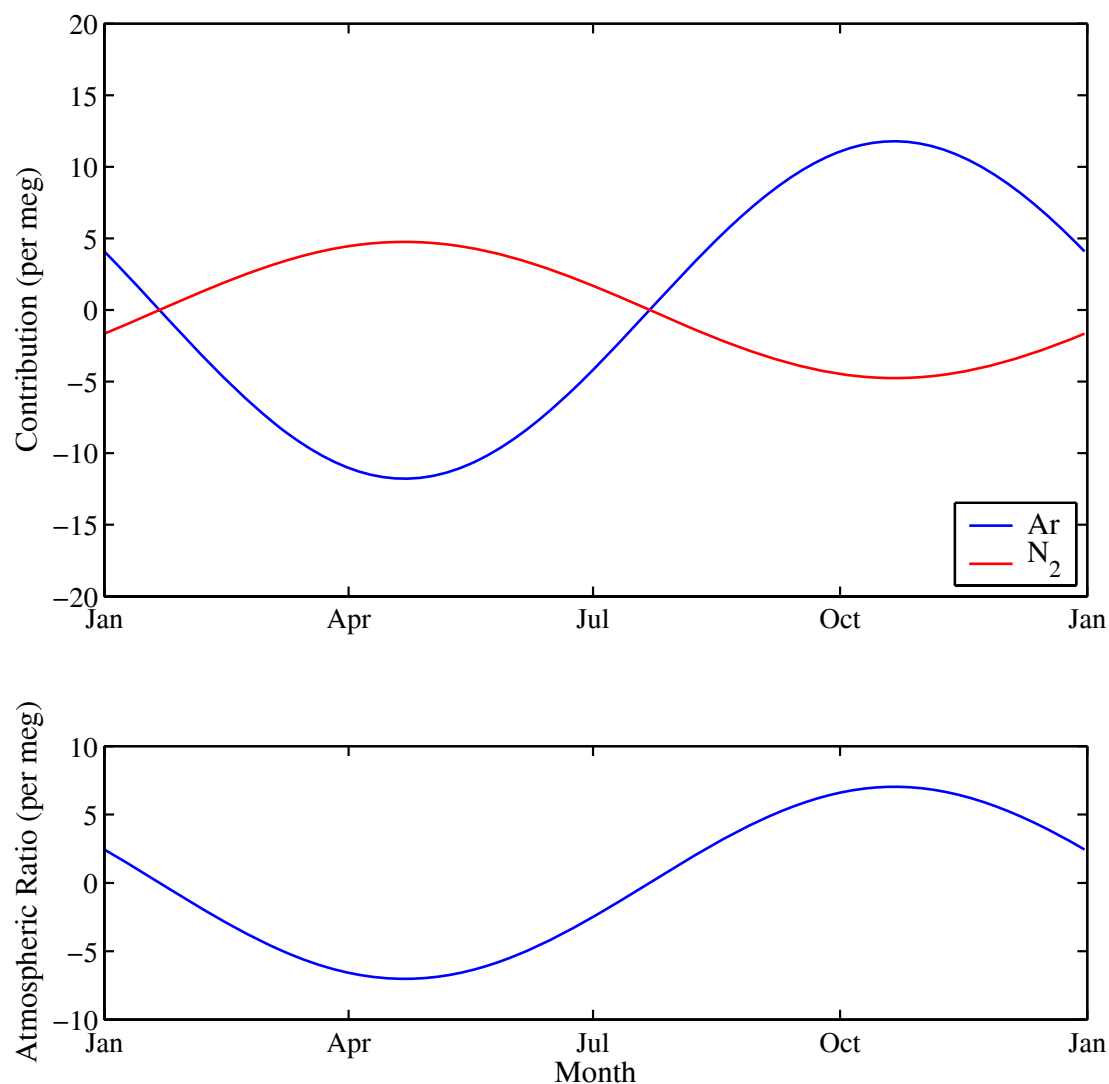


Figure 3.6. The upper panel shows the contribution of each gas to the atmospheric ratio in per meg units. Although the Ar and N₂ fluxes have the same direction, the N₂ flux changes the net Ar/N₂ ratio in the opposite direction from the Ar flux because it is in the denominator of the ratio.

The upper panel therefore shows the N₂ contribution with the opposite sign from the Ar contribution. The N₂ flux is half as large as the Ar flux, so the final $\delta(\text{Ar}/\text{N}_2)$ ratio is only about half as sensitive to heat flux as the Ar flux by itself is. The lower panel shows the atmospheric $\delta(\text{Ar}/\text{N}_2)$ ratio.

Figure 3.7). Because of the delay time in gas equilibrium introduced by K , the relationship between gas flux and heat flux forms an ellipse (the color green represents

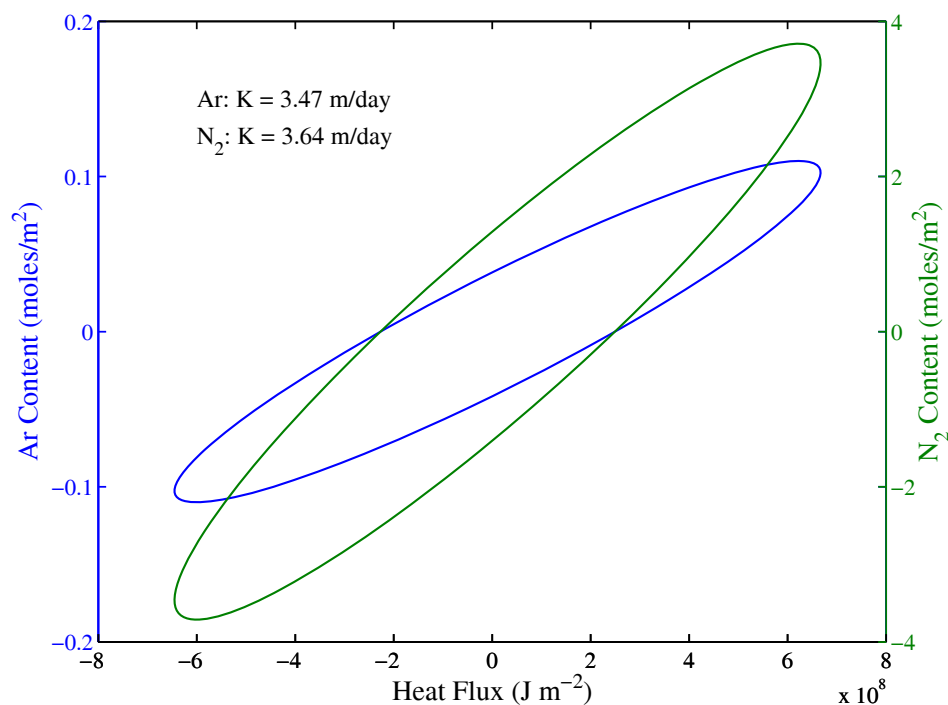


Figure 3.7. The relationship of heat flux to the gas flux of Ar and N₂, assuming a lag in equilibrium time for the ocean layer. The two ellipses are dissimilar due to differences in the K values between gases and how each gas depends on temperature.

the example discussed up to this point). The two gases generally have different piston velocities and different temperature dependences for solubility, and therefore the shape of the ellipses for each gas are not identical. The atmospheric $\delta(\text{Ar}/\text{N}_2)$ ratio shown in Figure 3.8 is a combination of both of these cycles, but the timing of its maximum and minimum values is similar to both of the independent cycles.

We can now look at how changes in K impact changes in the atmospheric $\delta(\text{Ar}/\text{N}_2)$ ratio. When K becomes infinite (instantaneous gas exchange), heat flux and $\delta(\text{Ar}/\text{N}_2)$ are directly related. However, as K becomes smaller and the time it takes for the box to equilibrate with the atmosphere increases, the linear relationship breaks down (see Figure 3.8). The interaction between seasonal temperature changes and the

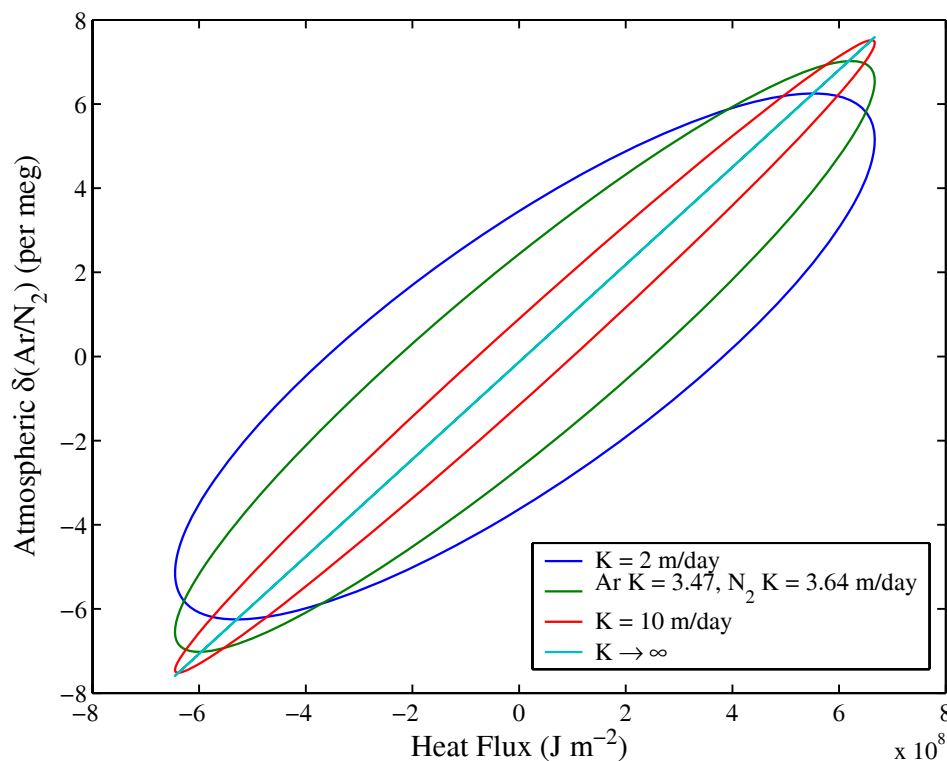


Figure 3.8. Effect of changes of K on atmospheric $\delta(\text{Ar}/\text{N}_2)$. As the equilibrium time becomes instantaneous (K becomes infinite), gas and heat flux become linearly related. As the equilibrium time increases, the relationship between gas and heat flux moves away from a clear linear dependence.

delay in equilibration time causes the linear relationship between heat flux and $\delta(\text{Ar}/\text{N}_2)$ to become elliptical. The change is due in part to a shift in the timing of the $\delta(\text{Ar}/\text{N}_2)$ cycle relative to the timing of the heat flux, but it is also due to changes in the actual flux of Ar and N_2 . Maximum and minimum values of $\delta(\text{Ar}/\text{N}_2)$ are damped; the $\delta(\text{Ar}/\text{N}_2)$ cycle is smoothed out. Figure 3.9 shows how the amplitude and lag time depend not just on K but on the ratio (H/K) . As K becomes large, the ratio is small and the cycle amplitude is at its maximum size. The lag time is also a minimum, as the atmospheric concentration immediately reflects surface temperature changes. This

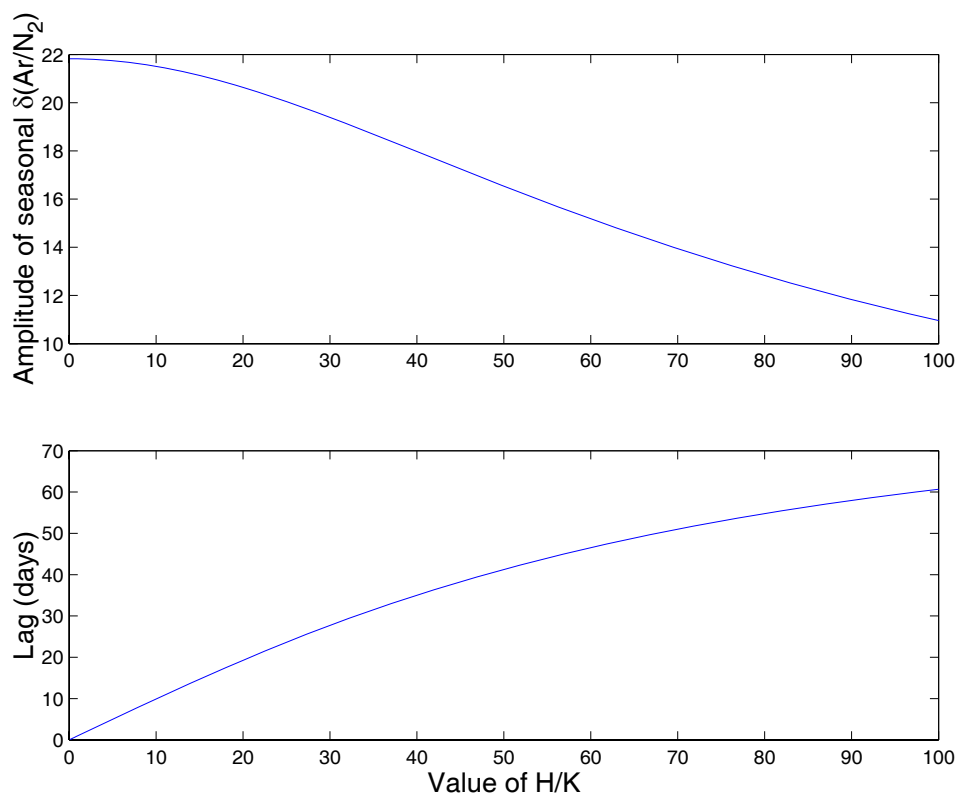


Figure 3.9. Dependence of $\delta(\text{Ar}/\text{N}_2)$ cycle amplitude and lag time on (H/K) . As K gets large, (H/K) gets small, and the amplitude is at its maximum and the lag time is zero, agreeing with Figure 3.8. As (H/K) gets large (either K is small, or H is large), the amplitude decreases and the lag time increases.

model demonstrates the need to be careful about assuming we can calculate seasonal heat flux directly from the atmospheric concentration of $\delta(\text{Ar}/\text{N}_2)$. Assuming a linear relationship between heat flux and gas exchange may lead to an underestimate of the heat flux cycle due to how the $\delta(\text{Ar}/\text{N}_2)$ cycle is damped. The timing of the heat flux cycle may also not be directly correlated with the timing of the $\delta(\text{Ar}/\text{N}_2)$ cycle.

However, with some assumptions about the appropriate values of K and the depth of the mixed layer, it may be possible to develop a better estimate of the heat flux cycle

than we could calculate from an assumption of a linear relationship alone. A good guess of the value of (H/K) for a mixed layer depth of 50 m and a piston velocity of 3.5 m/day is on the order of 15 days, which yields a damping of the cycle of less than 5% and a lag time on the order of two weeks. The example above, with a depth of 80 m and a similar piston velocity, yields an annual cycle with about 10% damping.

This simple model is useful in that it gives a rough estimate of the amplitude of the $\delta(\text{Ar}/\text{N}_2)$ cycle we can expect to see on seasonal time scales, although it cannot be assumed to represent a particular location or set of atmospheric and oceanic conditions. Battle et al. (2003), who first documented flask measurements of $\delta(\text{Ar}/\text{N}_2)$ in the atmosphere, show that the ratio does vary seasonally with approximately the magnitude expected from estimated air-sea heat fluxes.

3.3 A note on latitudinal gradients

The seasonal cycle in the Ar/N_2 ratio is likely superimposed on a latitudinal gradient in the underlying annual mean concentration. In the real world, there are places where the ocean is generally taking up or losing heat on an annual-mean basis, and transport of water masses in the ocean carries both heat and gases. In order to roughly estimate the size of the gradient in the Ar/N_2 ratio that results from this transport, I developed the simple model shown in Figure 3.10. The overturning time in the ocean and the overturning time in the atmosphere are both important to determining latitudinal variations in the $\delta(\text{Ar}/\text{N}_2)$ signal.

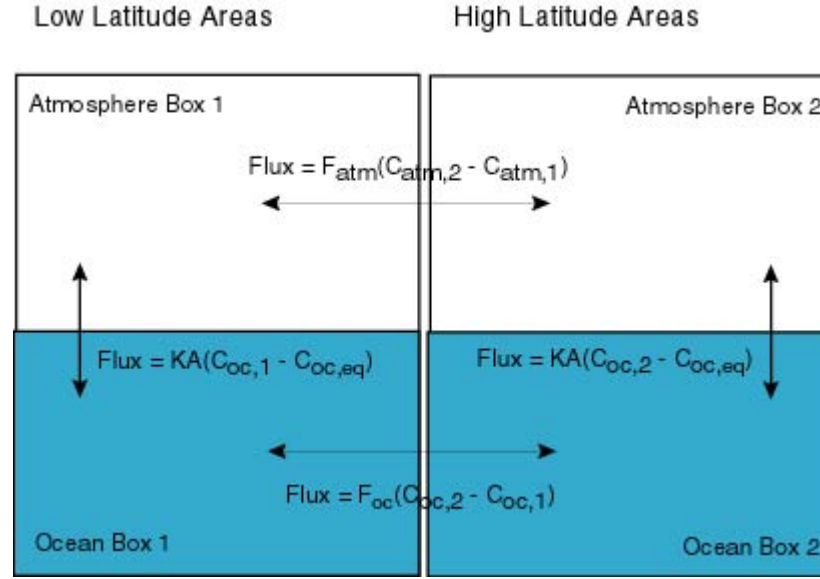


Figure 3.10. Diagram of the steady-state model showing high and low latitude boxes. Gas is exchanged between the atmosphere and ocean, and at the same time gas is transported between ocean boxes and between atmospheric boxes.

In this model, I prescribe steady-state ocean temperatures for both ocean boxes in order to concentrate on the effect of mixing between the two boxes rather than on transient seasonal effects. Imagine that one box is in tropical areas, whereas the other is at high latitudes. If we assume a border of about 30° and a constant ocean depth, both boxes have approximately the same surface area and volume:

$$V(dC_{oc,1}/dt) = -KA(C_{oc,1} - C_{oc,1,eq}) + F_{oc}(C_{oc,2} - C_{oc,1}) \quad (3.13)$$

$$V(dC_{oc,2}/dt) = -KA(C_{oc,2} - C_{oc,2,eq}) - F_{oc}(C_{oc,2} - C_{oc,1}), \quad (3.14)$$

where V is the volume of the ocean boxes; C represents the gas concentration in a given box, the subscript “eq” referring to the equilibrium concentrations based on the temperature of the water; K is the piston velocity; A is the surface available for air-sea gas exchange; and F_{oc} is the water exchange between the two ocean boxes.

In the previous model, the equilibrium concentrations in the ocean have a seasonal cycle dependent on the temperature of the water. The air-sea gas fluxes are small in comparison to the amount of gas stored in the ocean, and so the atmospheric Ar/N₂ ratio changes in response to the ocean equilibrium concentration. As stated above, however, the temperature of the water and the equilibrium concentrations in each box in this model are fixed in order to focus on the gradient due to ocean heat transport. The atmospheric boxes are therefore decoupled from the oceanic boxes. The solutions for the gas concentrations in the ocean boxes are the following:

$$C_{oc,1} = \frac{C_{oc,avg} + \gamma \cdot C_{oc,1,eq}}{1 + \gamma}, \quad (3.15)$$

$$C_{oc,2} = \frac{C_{oc,avg} + \gamma \cdot C_{oc,2,eq}}{1 + \gamma}, \quad (3.16)$$

$$\text{where } \gamma = \frac{KA}{2F_{oc}} = \frac{(V/F_{oc})}{2(H/K)} = \frac{\tau_{mix}}{2\tau_{eq}}.$$

V/F_{oc} represents the exchange time τ_{mix} of water masses between the two boxes, or how quickly the water in one box is replaced, whereas H/K , seen also in the first model, represents the gas equilibrium time τ_{eq} with respect to air-sea exchange.

The atmospheric concentrations of Ar and N₂ are forced by the fluxes in and out of the ocean box. However, exchange between the atmospheric boxes also influences the final, equilibrium concentration. The changes in the atmospheric box concentrations are described by the following:

$$V(dC_{atm,1}/dt) = KA(C_{oc,1} - C_{oc,1,eq}) + F_{atm}(C_{atm,2} - C_{atm,1}) \quad (3.17)$$

$$V(dC_{atm,2}/dt) = KA(C_{oc,2} - C_{oc,2,eq}) - F_{atm}(C_{atm,2} - C_{atm,1}), \quad (3.18)$$

where $C_{atm,1}$ and $C_{atm,2}$ are the respective atmospheric concentrations above the ocean boxes, and F_{atm} is the air exchange between atmospheric boxes. For the rest of the discussion, I assume that $C_{atm,avg} = 0$ and look only at the difference in the concentrations between the two atmospheric boxes. In this case, the solutions are as follows:

$$C_{atm,1} = C_{atm,avg} - \left(\frac{F_{oc}}{2F_{atm}} \right) \left(\frac{\gamma}{1+\gamma} \right) (C_{oc,1,eq} - C_{oc,2,eq}), \text{ and} \quad (3.19)$$

$$C_{atm,2} = C_{atm,avg} + \left(\frac{F_{oc}}{2F_{atm}} \right) \left(\frac{\gamma}{1+\gamma} \right) (C_{oc,1,eq} - C_{oc,2,eq}), \quad (3.20)$$

For subsequent analysis, I assume that K is the same for both Ar and N_2 . I fix the ocean transport at 50 Sv and the box temperatures at 13°C for the low latitudes and 3.75°C for the high latitudes, consistent with estimates of a 2 PW heat flux carried both by eddy transport and thermohaline circulation in the Northern Hemisphere (Talley 1999). The atmospheric transport is assigned to be 8.7×10^{12} moles of air per second, consistent with an intrahemispheric overturning time of two months.

Figure 3.11 shows the value of atmospheric $\delta(\text{Ar}/N_2)$ relative to γ . γ describes how the gas equilibrium time relates to the exchange time of water masses between the two ocean boxes. As γ becomes small, the concentrations in both ocean and atmosphere boxes approach each other and the gas flux drops. In contrast, as γ becomes large, the concentration of each box approaches its equilibrium concentration. In practice, it is difficult to come up with a good measure of γ . With an 80 m mixed layer, Ar and N_2 have an equilibration time constant of about a month.

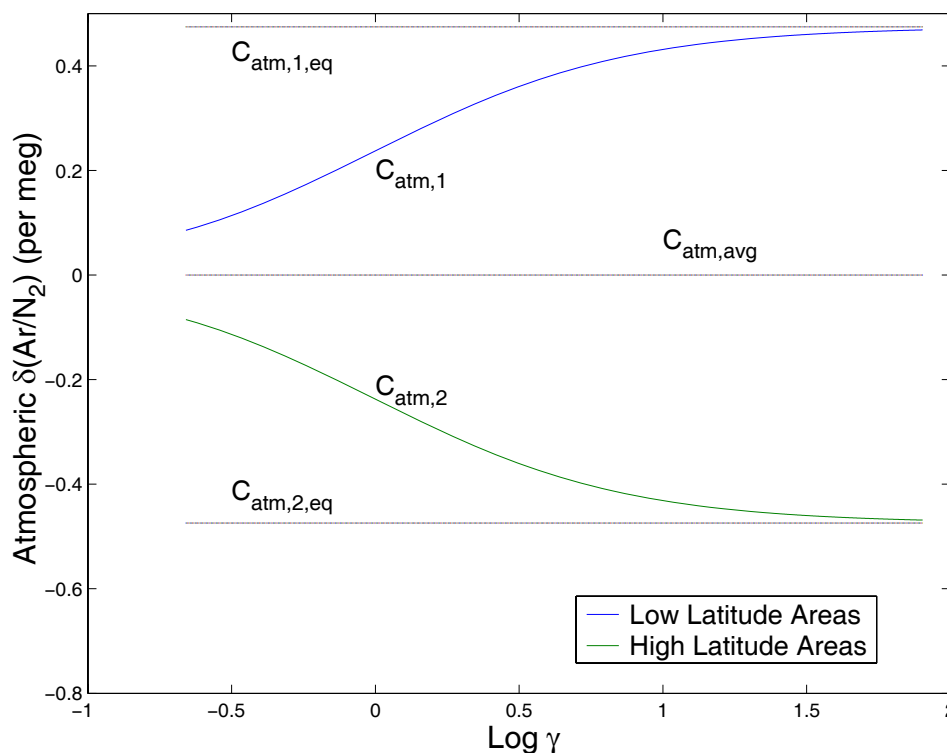


Figure 3.11. Shows the $\delta(\text{Ar}/\text{N}_2)$ concentration of the two atmospheric boxes relative to γ . As γ becomes large (the oceanic turnover time is long in comparison to the chemical equilibrium time), the resultant atmospheric $\delta(\text{Ar}/\text{N}_2)$ diverge between high and low latitude areas.

However, it is unclear how we should take into account mixing into deeper layers in the ocean. It is also difficult to come up with an estimate of ocean overturning. Should we only use the volume of water moving in the conveyor belt? Should we use the time it takes water to move from equatorial areas to high latitudes in the Gulf Stream or ocean gyres? Nevertheless, it is probably safe to say that the real value of γ is at least 10, and most likely much higher.

The concentrations of $\delta(\text{Ar}/\text{N}_2)$ in the atmospheric boxes are forced by air-sea gas flux as well as by the amount of transport in the atmosphere. When the atmospheric turnover time is rapid, the atmospheric box concentrations approach each

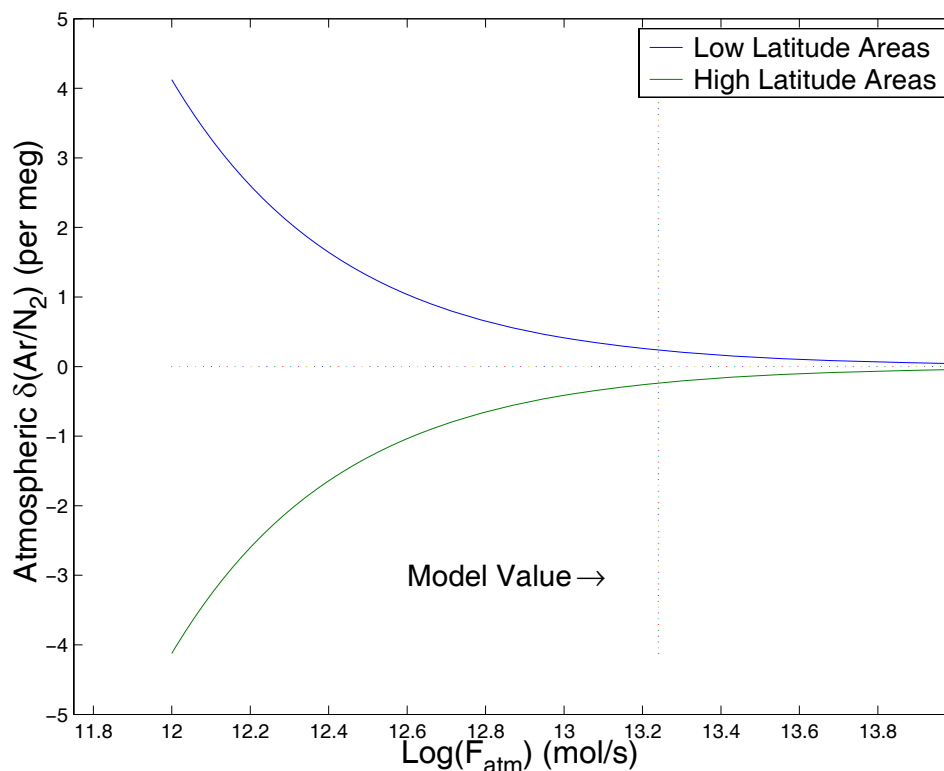


Figure 3.12. Concentration of atmospheric $\delta(\text{Ar}/\text{N}_2)$ at high and low latitudes as the atmospheric exchange changes. The model value used in Figure 3.11 is marked on the plot.

other, whereas when transport in the atmosphere is weak, the concentrations diverge (see Figure 3.12). Although the latitudinal gradient in our model depends directly on $(1/F_{\text{atm}})$, this relationship may be much more complex in the real world. Atmospheric transport is not constant; at certain times of the year, transport is greater than at others. The latitudinal gradient between high and low latitudes may fluctuate irregularly over the course of a year, and it may therefore have both steady-state and seasonal components.

However, given that the predicted size of the latitudinal gradient steady-state component is on the order of 1 per meg, the influence of seasonal variations in

transport is likely to be even smaller. My estimate of the latitudinal gradient is most likely low; in my model, I assumed both instantaneous horizontal and vertical mixing. In reality, surface concentrations are likely to be higher due to slow mixing times, and we may see a larger gradient in annual mean concentrations, particularly at the surface.

The latitudinal gradient in atmospheric $\delta(\text{Ar}/\text{N}_2)$ is likely to be small in comparison to the seasonal cycle in $\delta(\text{Ar}/\text{N}_2)$ at any given station. A higher level of measurement precision may be required to determine and compare the annual mean concentration at stations along a latitudinal gradient.

3.4 Global maps of the expected seasonal cycle in surface $\delta(\text{Ar}/\text{N}_2)$

The previous models provide rough estimates for the changes in the Ar/N_2 ratio in an atmospheric column in response to ocean warming and cooling and for a latitudinal gradient. However, they cannot provide realistic predictions of the ratio at a given location. Here I use atmospheric transport models to develop more realistic estimates of the seasonal variations in the Ar/N_2 ratio.

In order to develop maps of the seasonal cycle (ignoring any mean values), I used the predictions of atmospheric N_2 concentrations from the models in Chapter 2. The N_2 fluxes were calculated from the same principle (Equation 3.1) as that used in the conceptual box model described in section 3.2. Because the effect of the air-sea flux of N_2 in atmospheric per meg units is very similar to that of Ar, I multiply the change in the atmospheric N_2 concentration by a constant scale factor of 1.48 to

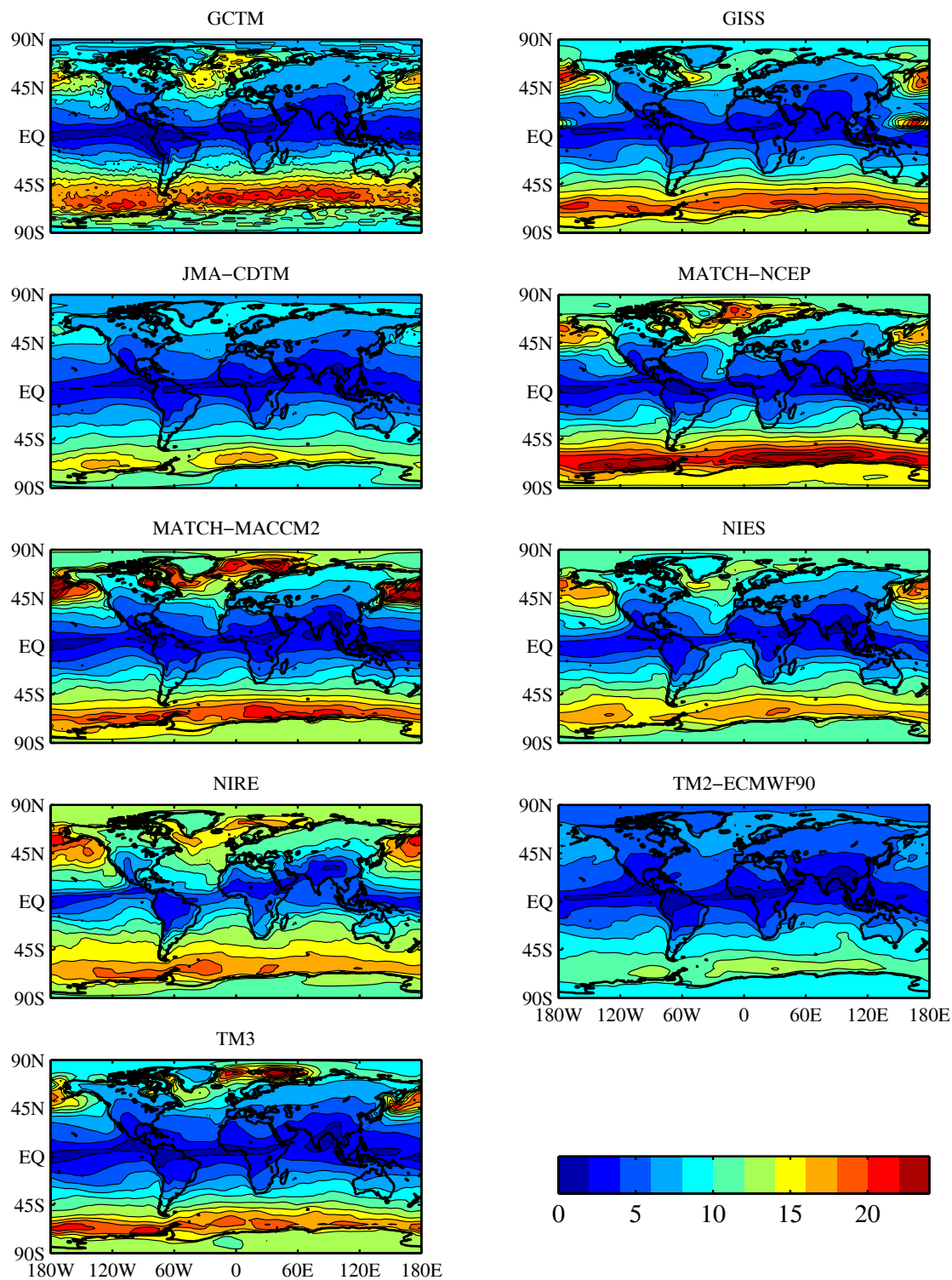


Figure 3.13. Predictions of the annual peak-to-peak $\delta(\text{Ar}/\text{N}_2)$ cycle in the atmosphere at the earth's surface from 9 different transport models. Contoured concentrations are plotted in per meg units.

calculate the expected seasonal concentration of $\delta(\text{Ar}/\text{N}_2)$. This scale factor is taken from the ratio of changes in atmospheric Ar to N_2 in the two-box model described earlier. Although small differences in the relationships between the solubility of Ar and N_2 with temperature should cause this factor to change slightly, it is not enough to be significant. The seasonal peak-to-peak amplitude predictions are shown in the model maps in Figure 3.13. The largest annual cycles correspond well, not surprisingly, with the areas with the largest seasonal air-sea heat flux, in the northern and southern latitudes of 45-60°, and are smallest in equatorial areas.

Most importantly, these maps give an idea of how well we need to be able to measure the atmospheric $\delta(\text{Ar}/\text{N}_2)$ ratio in order to contribute useful information on air-sea heat fluxes. The predictions suggest that we need to be able to accurately measure a seasonal cycle of 12-17 per meg at mid- to high-latitude stations where air-sea heat flux is most important, and to be able to measure an even smaller seasonal cycle to get useful information at lower latitudes. Because the models also use winds from different years, the variation between the models may give us an idea of the size of interannual variability in the $\delta(\text{Ar}/\text{N}_2)$ cycle, possibly ranging from 10-25 per meg in peak-to-peak amplitude at some places.

3.5 Conclusions

The present state of ocean measurements of air-sea heat flux and ocean heat content suggests the need for independent methods for measuring ocean heat uptake

on seasonal and interannual time scales. Because of the close correlation in air-sea heat flux and atmospheric $\delta(\text{Ar}/\text{N}_2)$, regular measurements may serve to independently estimate air-sea heat flux and provide information on its temporal variability.

Atmospheric tracer transport models suggest how well we need to be able to measure the annual $\delta(\text{Ar}/\text{N}_2)$ cycle in order to gain new information: the goal needs to be measurements good enough to identify an annual peak-to-peak cycle of 12-17 per meg in mid-latitude areas. Better measurements may be necessary to look more closely at interannual variability in air-sea heat flux.

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Chapter 4

Development of a continuous method for determining atmospheric $\delta(\text{Ar}/\text{N}_2)$

4.1 Introduction

The primary work in the atmospheric oxygen laboratory at the Scripps Institution of Oceanography has revolved around the maintenance of long-term station records of the atmospheric O_2/N_2 ratio and CO_2 concentration from flasks collected at an array of stations and measured on a suite of instruments. Five-liter flasks are collected in triplicate at nine stations. In methods used for the first 15 years of the records, air extracted from the flasks at a rate of about 300 ml/min flowed through a Siemens CO_2 analyzer and then entered an interferometric O_2 analyzer (Keeling et al. 1998). As the air was drawn from the flasks, tank air flowed in through a second inlet in order to maintain a constant pressure in the flasks.

More recently, a custom-built mass spectrometer with eight collectors, allowing for measurements of $\delta(\text{Ar}/\text{N}_2)$, $\delta(\text{O}_2/\text{N}_2)$, and $\delta(\text{CO}_2/\text{N}_2)$ as well as other

isotopic ratios, has been introduced into the standard flask analysis. Two different methods of analyzing flasks were developed with the introduction of the mass spectrometer: in one technique, flask air was extracted and traveled through a LiCor CO₂ analyzer and then the mass spectrometer, bypassing the interferometer setup. In a second technique, flask air was extracted on the rack used for the Siemens and the interferometer. Gas traveled through the Siemens CO₂ analyzer, then was split into two flows: one entered the interferometer, the other entered a LiCor CO₂ analyzer followed by the mass spectrometer. This second technique, in which gas extracted from flasks is analyzed on four independent instruments, became the dominant flask analysis technique in the lab.

My work builds on this earlier development work in our lab and in a laboratory at Princeton University to measure Ar/N₂ in flask air collected at globally distributed stations (Battle et al. 2003; Keeling et al. 2004). Battle et al. (2003) demonstrate the feasibility of detecting seasonal cycles related to heat flux in and out of the ocean. However, both Battle et al. (2003) and Keeling et al. (2004) found that the measurement precision is significantly limited due to problems in collecting and extracting flask air samples.

As part of my Ph.D. research, I attempted to bypass the problems in the use of flasks to measure the Ar/N₂ ratio. By developing an air intake system that interfaces with the existing flask setup, I was able to perform semi-continuous measurements at the Scripps pier in La Jolla, California, and to determine the annual cycle of Ar/N₂ to a much higher precision than with flask measurements.

In this chapter, I will describe the mass spectrometer system used for analysis and my work to develop a continuous air intake system, including discussions on calibration and on performance tests of the continuous intake system. I will also compare my continuous measurements taken over a year with flask samples taken during the same period.

4.2 Instrument description

Magnetic sector mass spectrometry has generally been used to measure ratios of isotopes of a single element. Bender et al. (1994) first demonstrated that magnetic-sector instruments could be used to measure the molar ratios of atmospheric components as well. In our laboratory, the ratio of Ar to N₂ is measured on a Micromass Isoprime mass spectrometer with a custom inlet system described in Keeling et al. (2004). This instrument has eight collectors, allowing simultaneous measurements of several different elemental and isotopic ratios, including $\delta(\text{Ar}/\text{N}_2)$, $\delta(\text{O}_2/\text{N}_2)$, and $\delta(\text{CO}_2/\text{N}_2)$, which are used in this project. The source, flight-tube, and detector elements are built into one vacuum housing, which permits the wide mass spread (from mass 28 to mass 44) and allows for a single turbomolecular pump to evacuate the system, reducing the instrumental nonlinearity. The collectors have slit widths designed so that the entire beam for each mass falls within the Faraday cups.

This mass spectrometer is fitted with a custom, single-capillary inlet that permits rapid switching between sample and reference gas, which helps to eliminate the effects of instrument drift. Most mass spectrometers have a dual inlet system with

a changeover valve downstream of two capillaries that switches back and forth between reference and sample gas flows. The custom design used for this mass spectrometer has an inlet system with one capillary downstream of the switching valve that allows for 5-sec switching between gases with active pressure control. The ability to switch rapidly between two gases is fundamental to our analysis because it reduces the noise due to instrument drift.

The single capillary system allows errors associated with pressure changes caused by switching between two gases to be minimized. A pause in gas flow during switching can cause errors since gas absorbs onto or desorbs from the filament, thereby leading to nonlinear source effects and increasing the time needed for the signal to stabilize, also known as the equilibration time. However, the single inlet system allows the equilibration time to drop to ~2 sec from ~20 sec for the dual inlet system, thus permitting a much higher switching rate of 5 sec between the sample and reference, which substantially increases precision (Keeling et al. 2004).

Data are reported by the mass spectrometer every ten seconds as a difference between the sample air and an instrument reference gas (shown in Figures 4.1 and 4.2). This differencing procedure allows the effects of any short-term variability in the instrument to be minimized, as such variability is likely to affect both sample and reference gases in the same manner. The 10-second signal is given as the difference between sample and reference, where the reference is an arbitrary gas cylinder filled with air:

$$\delta(Ar/N_2) = \frac{(Ar/N_2)_{sample} - (Ar/N_2)_{reference}}{(Ar/N_2)_{reference}} \times 10^6, \quad (4.1)$$

In parallel with the convention used for measurements of the atmospheric O_2/N_2 ratio, the units of this quantity are called “per meg” (Battle et al. 2003; Keeling et al. 2004). The instrument precision on each 10-second determination is 10-13 per meg in $\delta(Ar/N_2)$, whereas integration over several minutes yields a precision of 2-3 per meg.

The same instrument is used for analysis of flask samples from nine stations primarily located along the Pacific Rim as well as continuous measurements of air from the Scripps pier to be described here. Although not the primary focus of this thesis, the flask measurements will be used for comparison with the continuous measurements at the La Jolla station. Flasks are presently being collected at the nine different stations following the procedure described in Keeling et al. (1998). Samples are collected in 5-l round, glass flasks. Air is normally pumped through a cold trap kept at a temperature of -80°C to remove water in the air by causing the moisture to condense before passing into the flask. At some stations, the three flasks are connected in series, whereas at other stations each flask is individually filled. The pump is run long enough for the air in the flasks to be completely replaced several times before the flasks are closed. Once the samples have been returned to the laboratory, metallic stir bars are inserted into each flask so that the flask air is continually mixed during analysis.

Two different techniques have been used for delivering flask air to the mass spectrometer. In samples measured up to the end of 2002, each sample was attached to a gas handling rack that can accept up to four flasks at a time. The flasks were enclosed in an insulated box and allowed to equilibrate for half an hour before

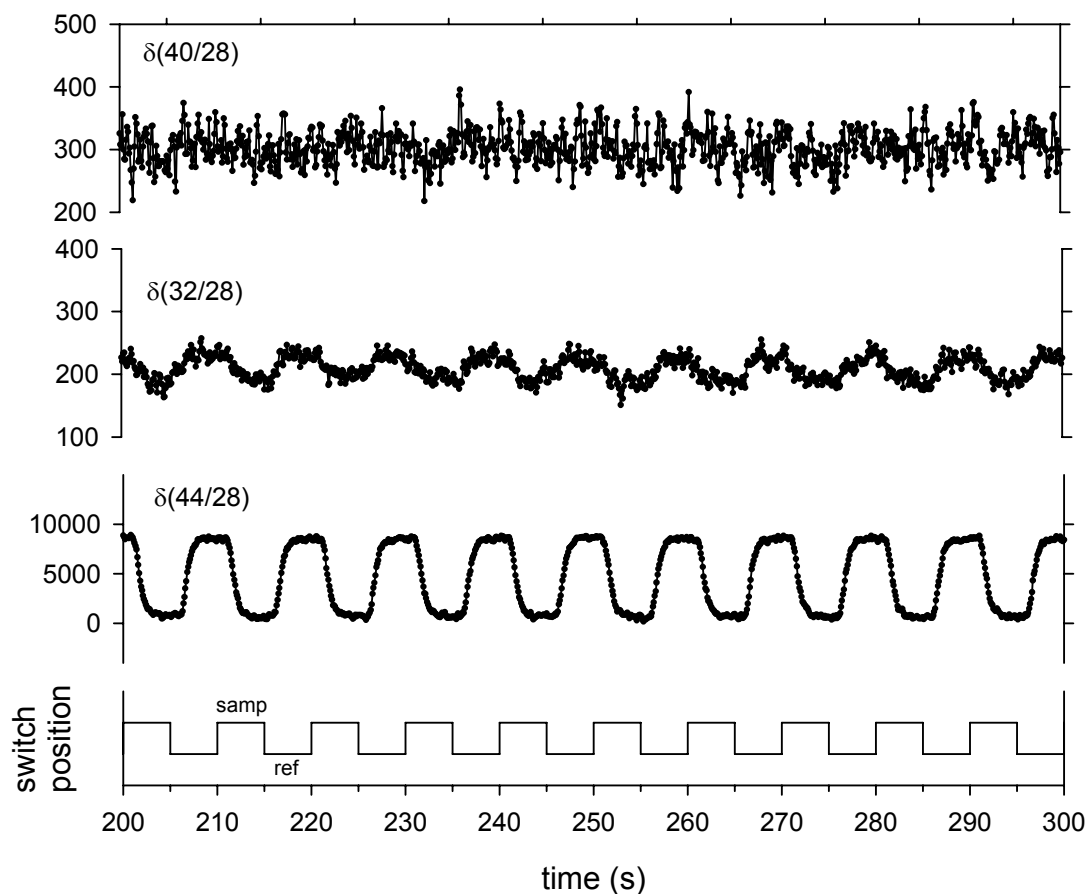


Figure 4.1. Adapted from Keeling et al. (2004). The mass spectrometer output for rapid switching between the sample and the instrument reference gas is marked by the mass number ratios instead of element ratios because the numbers reflect raw beam intensity values, rather than the final elemental ratios of a sample. The ten-second switching between sample and reference gases in the mass spectrometer is clearly visible in the 32/28 and 44/28 ratios, however it is not as clear for the 40/28 ratio because the two gases have similar Ar/N₂ ratios. Of each five-second jog, the first two seconds of data are thrown out, and only the last three seconds are used to calculate the jog value. The data normally saved as output from the mass spectrometer are the 10-second differences between the mean of the sample gas and the mean of the leading and trailing reference baselines.

analysis. When analysis began, gas from a given flask was pumped out at a rate of about 5 ml/minute. It then passed through a LiCor CO₂ analyzer before a much smaller flow, on the order of 10⁻³ ml/min, was picked off to enter the mass spectrometer. The remainder of the gas was discarded. More recently, the flasks have been attached to a three-flask handling rack. A gas of known concentration flows into the flasks as the sample is measured in order to maintain a constant pressure inside the flask. The data analysis procedure accounts for the dilution effect. This method allows for the flasks to be measured simultaneously on different instruments; the oxygen interferometer, the mass spectrometer and both a Siemens CO₂ analyzer and a LiCor CO₂ analyzer are used.

A schematic of the continuous air intake system bringing air from the Scripps pier to the analysis laboratory is shown in Figure 4.2. Two independent, parallel lines lead from the pier to the laboratory. The inlets of the system are located on the landward end of the Scripps pier. Initially it was attached to an existing gate, about 2.5 meters above the concrete pier and about 8 meters total above the beach. Later, the inlet was relocated inside a commercial aspirator used for weather measurements that provides a constant air flow over the inlet and protects it from direct solar radiation. It extends horizontally about 1 m off of the pier, so that it is no longer directly above the concrete structure. The development process resulting in the existing setup will be further discussed in Section 4.4.1.1.

Air is pumped through ~600 feet of Synflex 1300 tubing from the Scripps pier to the laboratory containing the mass spectrometer system. The tubing, also known by

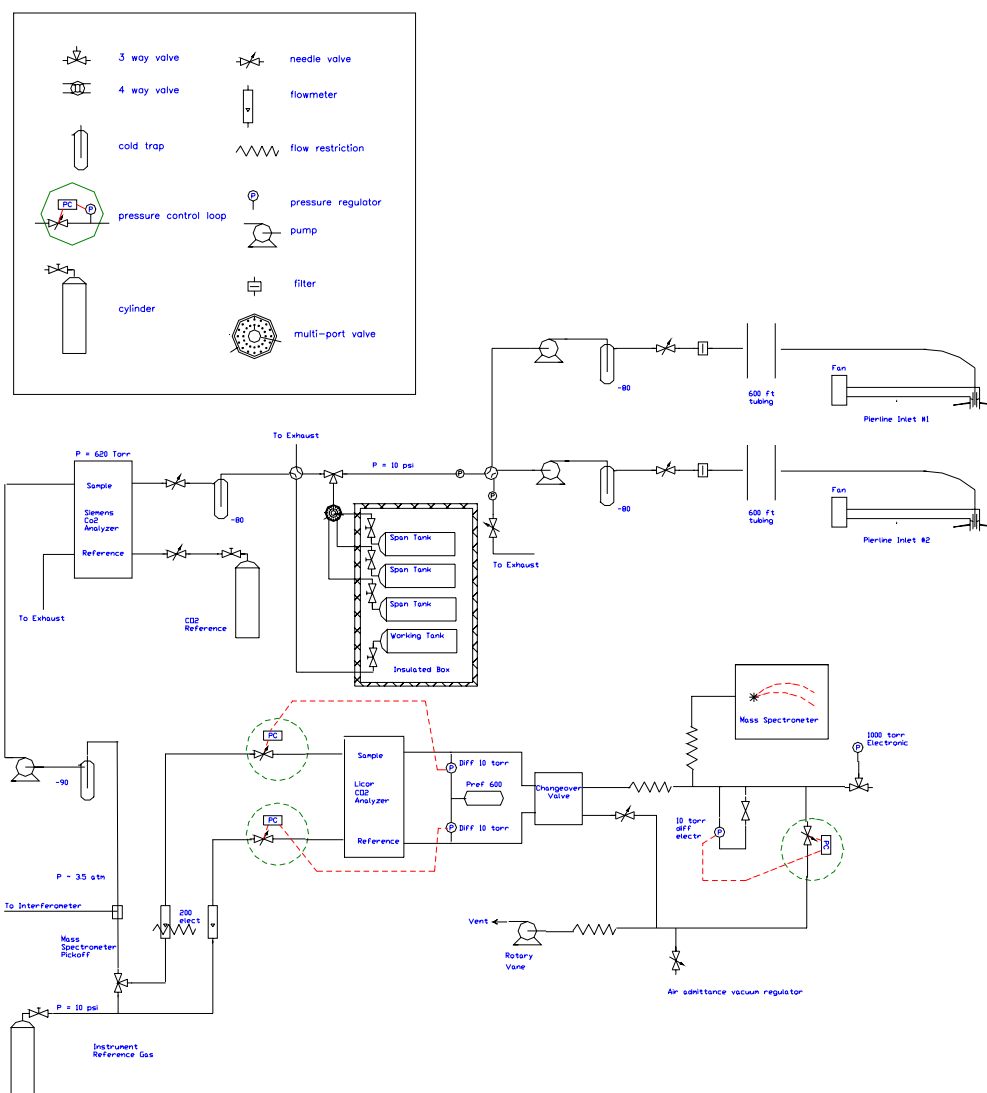


Figure 4.2. Schematic of the continuous measurement system from the inlet on the pier through all laboratory instruments.

the trade names of Dekoron or Dekabon, has an outside layer of high-density polyethylene fully bonded to an internal layer of aluminum. Additional polyethylene film covers the aluminum on the inside. We initially used tubing with a $\frac{1}{2}$ " external diameter (~ 0.4 " internal diameter) that was replaced with tubing with a $\frac{1}{4}$ " external diameter (~ 0.15 " internal diameter) on March 10, 2004. With this change, the time that the air spends in the tube was reduced from approximately 43 minutes to approximately 16 minutes (see Figure 4.3). Although the line has joints, it does not have any tees because of the difficulty of eliminating fractionation effects at tees (Manning 2001).

Once the line enters the lab, it passes through a Valco particle filter (ZUF2) with a stainless steel, pressed frit of $2\text{ }\mu\text{m}$ and enters a stainless steel cold trap maintained at -80°C to freeze out any water in the air. In order to increase the amount of time before the cold trap at -80°C clogs itself from the volume of ice frozen out of the air, an early version of the system included a stainless steel trap placed in a small household refrigerator (similar to the one used in Manning 2000) and cooled to about 1°C . The cold trap had a hole of $\sim \frac{1}{4}$ " in diameter at its base that was attached via tubing to a peristaltic pump in order to continuously remove condensate from the bottom of the trap. However, different iterations of this arrangement all reduced the precision of 10-minute averages. I eventually abandoned this setup in favor of increasing the size of the trap maintained at -80°C .

Downstream, the pier air passes through a second trap and all tank air entering the system passes through a third trap in the same cryogenic unit. On the pierline, this

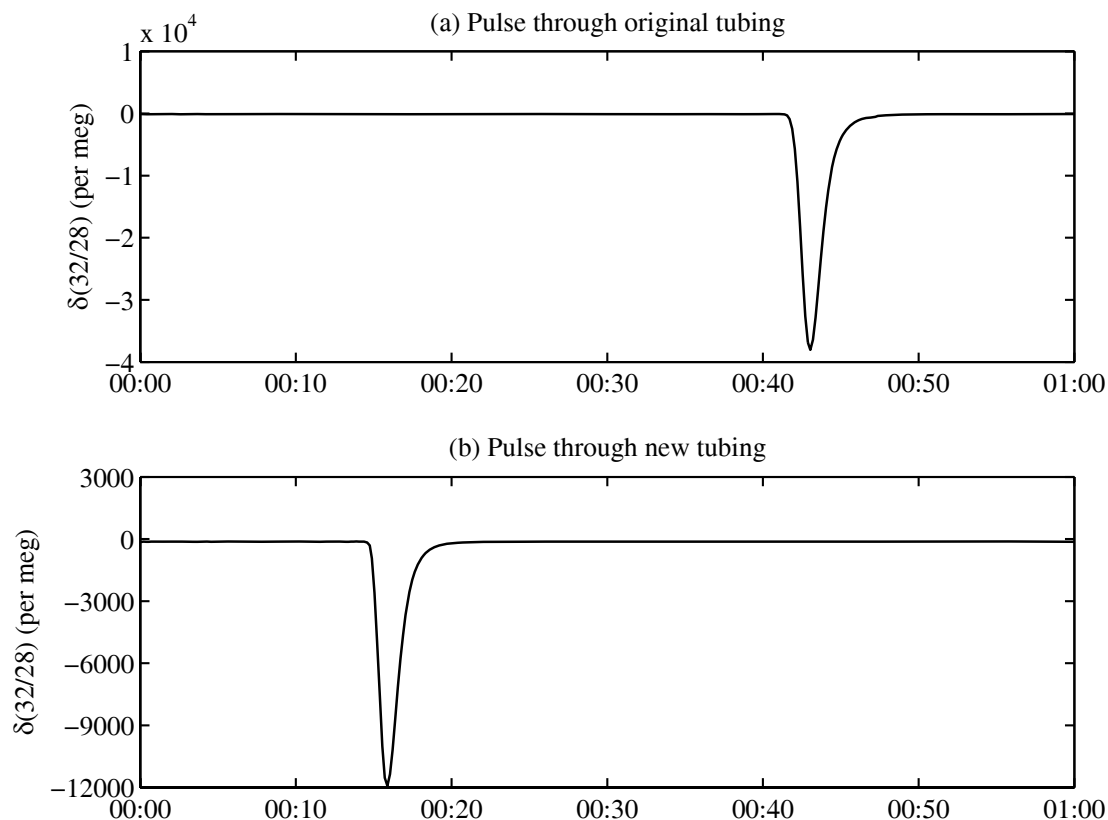


Figure 4.3. (a) Travel time and shape of a pulse through the ½" OD Synflex tubing. (b) Travel time and shape of a pulse through the new, ¼" OD Synflex tubing installed on March 10, 2004. The time 00:00 corresponds to the time that the pulse air entered the inlet. The travel time was reduced from about 43 minutes to about 16 minutes with the change of tubing size.

trap is located before the pump in order to reduce corrosion of salt and water on the pump and downstream pressure control valves. The gas passes through a Neuberger diaphragm pump that maintains the air flow from the pier.

Two independent lines come from two inlets on the pier, with independent systems of cold traps and pumps. Downstream of the pumps, a four-port changeover valve selects air from one of the two pierlines for delivery to the mass spectrometer system, while air from the other line is exhausted into the lab so that gas flow from the pier is constantly maintained. In both sample and exhaust lines, the air stream then

passes through a second filter and a pressure regulator (Porter 40000AMVS30) which maintains the line pressure at 10 psig. The sample flow passes through a Siemens CO₂ analyzer. Fifteen ml/min out of a flow of approximately 310 ml/min is routed to the mass spectrometer setup, of which a much smaller flow, on the order of 10⁻³ ml/min, is picked off to enter the capillary to the mass spectrometer. The rest of the flow enters the interferometer.

Because of the need to share the instruments with other projects in the laboratory, use of the continuous measurement system is normally restricted to weekends, with occasional longer runs. The instrument alternates between the pierlines at the end of every hour, so that each line is sampled for up to 12 hours per day. The pier air stream is run for 50 minutes followed by 10 minutes of air from a designated internal standard tank for a repeatable hourly cycle (see Figure 4.4). This tank is known as the “working tank”. About five minutes of data after any switch between pierline and working tank air are discarded and not used for calculations, in order to take out any transient effects of the switch. For each hour, the mean pierline concentration is calculated as a difference from a five-hour mean of the working tank concentration. This five-hour working tank mean is used because the working tank concentration stays very stable over several hours, and the precision of the ambient air measurement increases as more points are used to calculate the working tank mean. The concentration of the working tank air is determined on a weekly basis by comparison with a suite of three other reference cylinders. The working tank concentration is thus allowed to vary slightly in comparison to tanks used less

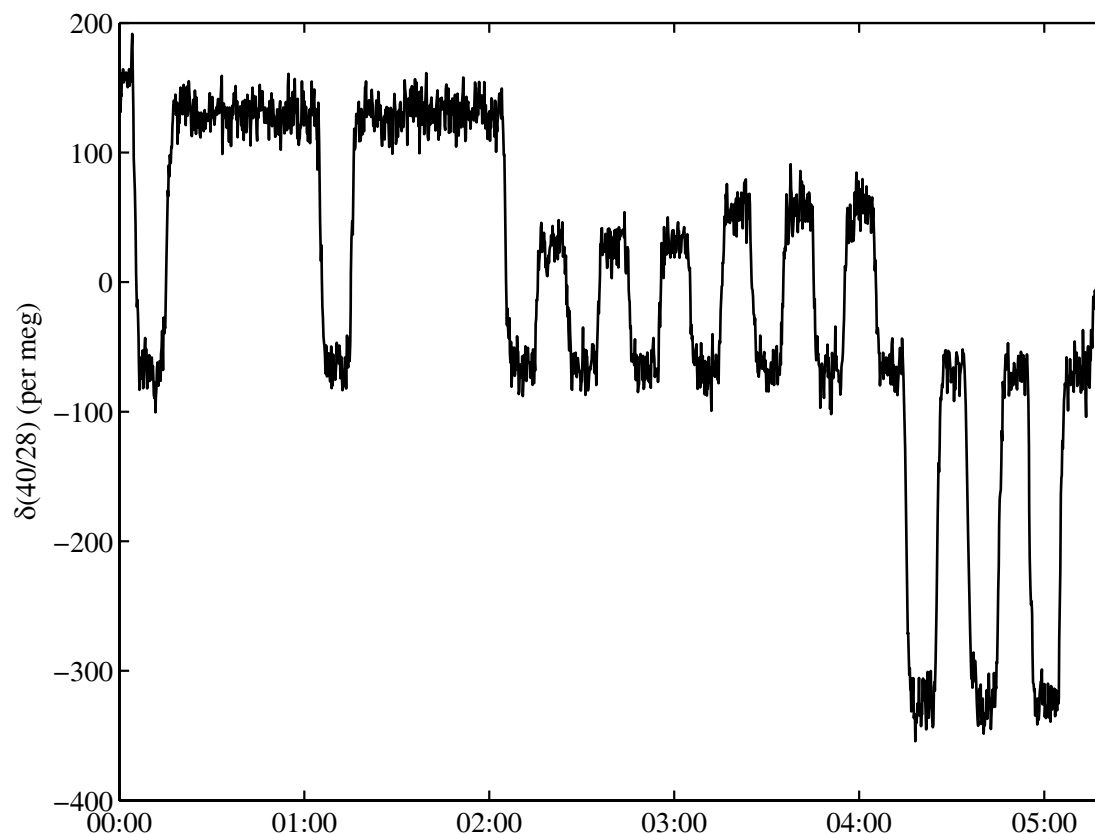


Figure 4.4. Example of raw data output from the mass spectrometer. The left side shows the normal pierline run, with 50 minutes of pier air followed by 10 minutes of working tank air. The right side shows a run against three reference cylinders, with triplicate “jogs” of each reference tank against the working tank. Each “jog” consists of 10 minutes of a working tank baseline, 10 minutes of reference tank, and 10 minutes of a second working tank baseline. These reference tanks are run once per week in order to determine the working tank concentration.

frequently. These reference tanks in turn are calibrated against a suite of other tanks on 4-, 6- and 18-month cycles. The three reference tanks are run against the working tank in a set of three, 10-minute jogs (see Figure 4.4). The lines are initially flushed using a “fast purge”, and then during the test the tank air not presently selected continues to be purged at a slower rate. If any of the three jogs differs statistically from the mean, it is discarded and only two jogs are retained. Dedicated working

tanks last about 2-4 months for continuous measurements and are replaced when their pressures fall below 200 psig.

Working tanks and reference tanks are filled with an oil-free compressor (RIX Industries) and dried to below 5 $\mu\text{moles mole}^{-1}$ of H_2O . Any adjustments in the concentration needed for particular reference tanks are made by adding small amounts of pure CO_2 , N_2 , O_2 . At this stage, none of the tanks are adjusted for Ar/N_2 . Tanks are stored horizontally in an insulated box so that air is withdrawn from the vertical center of the tank and temperature fluctuations are reduced.

4.3 Calibration

4.3.1 Establishing Ion Sensitivities

The mass spectrometer output consists of a voltage that is related to the actual atmospheric abundances of certain masses. The process of deriving the atmospheric abundance ratios from this signal output involves several steps that take into account interferences from other atmospheric species, nonlinearities of the system, and regular comparison with reference gases (mentioned in the previous section). Following Keeling et al. (2004), these effects can be described by the equations:

$$\delta(\text{Ar}/\text{N}_2) = A_1\delta(40/28) + B_1\delta(32/28) + C_1\Delta\text{CO}_2 + D_1, \text{ and} \quad (4.2)$$

$$\delta(\text{O}_2/\text{N}_2) = A_2\delta(32/28) + B_2\delta(40/28) + C_2\Delta\text{CO}_2 + D_2, \quad (4.3)$$

where A represents nonlinearities, B and C represent interferences, and D represents changes in the instrument reference gas, laboratory reference gases, and working tank gases. The ratios are written as mass number ratios (e.g. $\delta(40/28)$) to represent the

mass spectrometer raw signal output, and as element ratios (e.g. $\delta(\text{Ar}/\text{N}_2)$) to represent actual atmospheric abundance ratios. CO_2 is mass 44, Ar is mass 40, O_2 mass 32, and N_2 mass 28. Note that CO_2 is more often reported as a dry air mole fraction in parts per million (written as $[\text{CO}_2]$ or just CO_2), rather than as a relative change measured in per meg ($\delta(44/28)$).

The primary interference comes from carbon monoxide (CO) fragments, which have essentially the same mass as N_2 . When CO_2 is ionized in the mass spectrometer, a small portion of the ions breaks into CO fragments. I developed a correction factor for this interference as well as system nonlinearities by bleeding small amounts of gas of known mixtures of CO_2 , O_2 , and Ar into the working tank of the mass spectrometer. The gas mixtures used included 99% pure CO_2 and accurately prepared gravimetric mixtures of CO_2 in O_2 and CO_2 in Ar. These tests relied on two other instruments with established techniques to determine the changes in CO_2 and O_2/N_2 : a Siemens CO_2 analyzer and an interferometer which measures the O_2/N_2 ratio, described above in the suite of instruments. With the CO_2 numbers from the Siemens instrument, I was able to determine the specific amount of CO_2 added to the working tank and to calculate the amount of additional O_2 and Ar. I could then compare these amounts with ratios measured on the mass spectrometer. The interferometer O_2/N_2 measurements served as a check on some of these calculations. These tests and the calculations are described in depth in Appendix 1.

Using the pure CO_2 gas, I was able to determine the effect of CO_2 interference on the Ar/N_2 and O_2/N_2 ratios as measured by the mass spectrometer. Panels in Figure

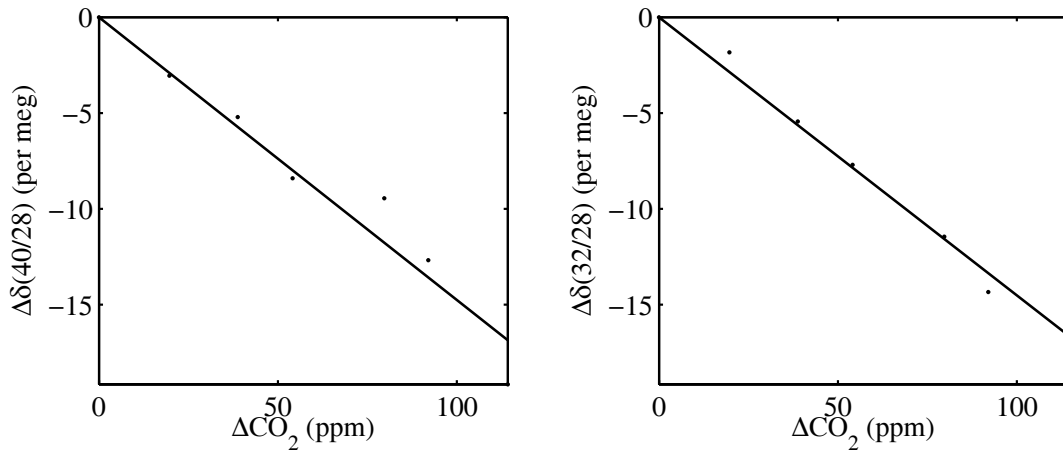


Figure 4.5. Bleed test relationships between known amounts of introduced, 99% pure CO₂ gas (on the x axis) and the measured values on the mass spectrometer (on the y axis) relevant for determining the mass spectrometer correction factors summarized in Table 1. The air into which gas is bled has a CO₂ concentration of 354.6 ppm.

4.5 show a strong linear relationship between the amount of CO₂ introduced to the system (ΔCO₂) and the change in the values of the other ions (Δδ), as expressed by:

$$\Delta\delta(40/28) = \gamma_1 \Delta CO_2, \text{ and} \quad (4.4)$$

$$\Delta\delta(32/28) = \gamma_2 \Delta CO_2. \quad (4.5)$$

The values of γ_1 and γ_2 are listed in Table 4.1 along with error estimates. The two constants are equal to within the measurement errors, which is consistent with interference at mass 28.

The other two gas mixtures test for interferences and nonlinearities associated with changes in the Ar/N₂ and O₂/N₂ ratios. The CO₂/O₂ mixture gives the values of β_1 and α_2 through the following equations:

$$\Delta\delta(40/28)_{adj} = \beta_1 \cdot \Delta\delta(O_2/N_2)_{exp}, \text{ and} \quad (4.6)$$

$$\Delta\delta(32/28)_{adj} = \alpha_2 \cdot \Delta\delta(O_2/N_2)_{exp}, \quad (4.7)$$

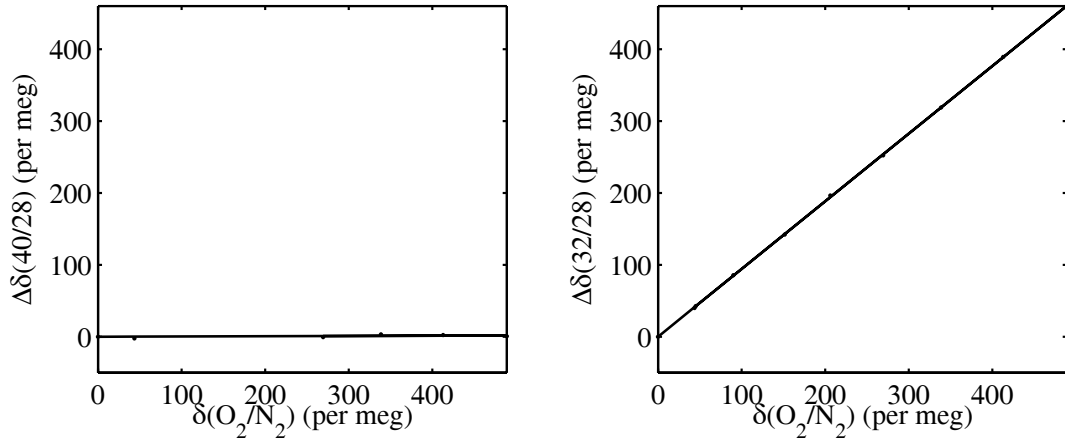


Figure 4.6. As for Figure 4.5. The introduced gas in this case is a combination of CO_2/O_2 , in order to look at interferences and nonlinearities associated with O_2 .

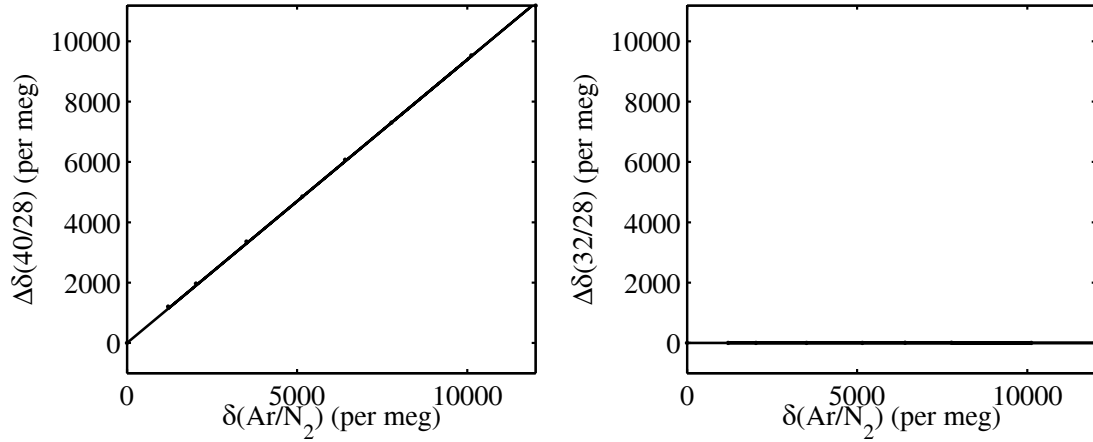


Figure 4.7. As for Figure 4.5. The introduced gas in this case is a combination of CO_2/Ar , in order to look at interferences and nonlinearities associated with Ar.

and the CO_2/Ar mixture gives the values of α_1 and β_2 through the following equations:

$$\Delta\delta(40/28)_{adj} = \alpha_1 \cdot \Delta\delta(\text{Ar}/N_2)_{exp}, \text{ and} \quad (4.8)$$

$$\Delta\delta(32/28)_{adj} = \beta_2 \cdot \Delta\delta(\text{Ar}/N_2)_{exp}, \quad (4.9)$$

where the subscript “*exp*” represents the additional amount of a given species as

Table 4.1. Constants describing interferences and nonlinearities.

Measured Variable	Variable Name in Appendix 1	Slope	Error	Variable in Final Equation	Value	Error
α_1	q ₂	0.9392	0.0127	$A_1 = 1/\alpha_1$ (per meg/per meg)	1.065	0.0144
α_2	p ₃	0.9533	0.0062	$A_2 = 1/\alpha_2$ (per meg/per meg)	1.049	0.0062
β_1	p ₂	0.0035	0.0160	$B_1 \approx 0$	0	N/A
β_2	q ₃	0.0001	0.0003	$B_2 \approx 0$	0	N/A
γ_1	m ₂	-0.1476	0.0182	$C_1 = \gamma_1/\alpha_1$ (per meg/ppm)	-0.1572	0.0122
γ_2	m ₃	-0.1451	0.0127	$C_2 = \gamma_2/\alpha_2$ (per meg/ppm)	-0.1522	0.0062

calculated from the additional CO₂ measured on the Siemens analyzer and the subscript “*adj*” represents measured values which have already been corrected for CO₂ interferences (discussed more in depth in Appendix I). Figure 4.6 and 4.7 show these relationships for different amounts of introduced CO₂/O₂ and CO₂/Ar respectively. The values of β_1 and β_2 are essentially zero, demonstrating that the cross-term interference is not important. The values and error estimates of these constants are shown in Table 4.1.

The initial equations in (2) and (3) can thus be simplified as the following:

$$\delta(Ar/N_2) = A_1\delta(40/28) + C_1\Delta CO_2 + D_1, \text{ and} \quad (4.10)$$

$$\delta(O_2/N_2) = A_2\delta(32/28) + C_2\Delta CO_2 + D_2. \quad (4.11)$$

with each constant defined in terms of the measured values as summarized in Table 4.1. This formula has been implemented into our data workup and is used for all mass spectrometer output.

4.3.2 Long-term stability of reference gases

One of the largest problems in gas handling is due to the diffusive separation of different species in gas. Some of the primary causes of this kind of fractionation

are thermal gradients, pressure gradients (including that due to the gravitational field), and the geometry of a passage through which gas flows (Keeling et al. 1998). Because fractionation at the outlet of a tank can lead to the preferential use of gas that has a different δ -value from the overall mean of the gas in a tank, it causes changes in the concentration of the gas remaining in the tank. Such changes have been observed in the working tank concentrations over time for both the $\delta(40/28)$ and the $\delta(32/28)$ ratios over the lifetime of a given tank's use.

In the case of thermal fractionation, atmospheric species with smaller than average mass generally move preferentially towards the warm end of a temperature gradient, whereas species with heavier than average mass generally move toward the cold end (Grew and Ibbs 1952). This effect can be written as the following:

$$\delta = \left(\frac{T_0}{T} \right)^\alpha - 1, \quad (4.12)$$

where δ is the fractional deviation of the gas ratio from the reference gas ratio, T_0 is the temperature of the reference gas, T is the temperature of the measured gas, and α is the thermal diffusion factor, an empirical constant characteristic of a particular gas pair (Severinghaus et al. 1996). For small changes in temperature, this equation can be linearized:

$$\delta = -\alpha \frac{\Delta T}{T}, \quad (4.13)$$

as per Keeling et al. (1998). Fractionation of about -24 per meg in $\delta(\text{Ar}/\text{N}_2)$ is expected for a 0.1°C temperature difference (Grew and Ibbs 1952), which is common in the laboratory between the foot and top of a tank.

The fractionation effect due to gravitational settling is written as the following in Craig et al. (1988):

$$\delta = \exp\left(\frac{\Delta mgz}{RT}\right) - 1, \quad (4.14)$$

where Δm is the difference in mass between two species being compared (here, the species itself and air), and z is the height difference. Heavier species gradually settle to a lower level if the air is not being actively mixed, whereas lighter species rise to the top. A more general, linearized equation describing the fractionation due to pressure differences can be written as per Keeling et al. (1998):

$$\delta = \left(\frac{m_{Ar} - m_{N_2}}{m_{air}}\right) \left(\frac{\Delta P}{P}\right). \quad (4.15)$$

A height difference of 10 cm results in a fractionation of about 5 per meg in $\delta(\text{Ar}/\text{N}_2)$ due to the gravitational gradient.

Both thermal and gravitational fractionation are likely to occur in tanks stored for long periods of time. In our lab, tanks are stored horizontally so that the gas is drawn from the vertical center of the tank, and fractionation due to gravitational settling is unlikely. To minimize short-term thermal gradients, tanks are also stored in an insulated enclosure so that temperature changes in the laboratory are damped and slowed. Thermistors placed in the enclosure have demonstrated temperature differences between the front and back of tanks of up to 0.1°C and variants within the insulated enclosure of up to 2°C (shown in Figure 8). The front-back temperature gradient for a particular tank is likely important in the observed reduction in tank concentration of heavier species such as Ar and O₂ over the lifetime of the tank.

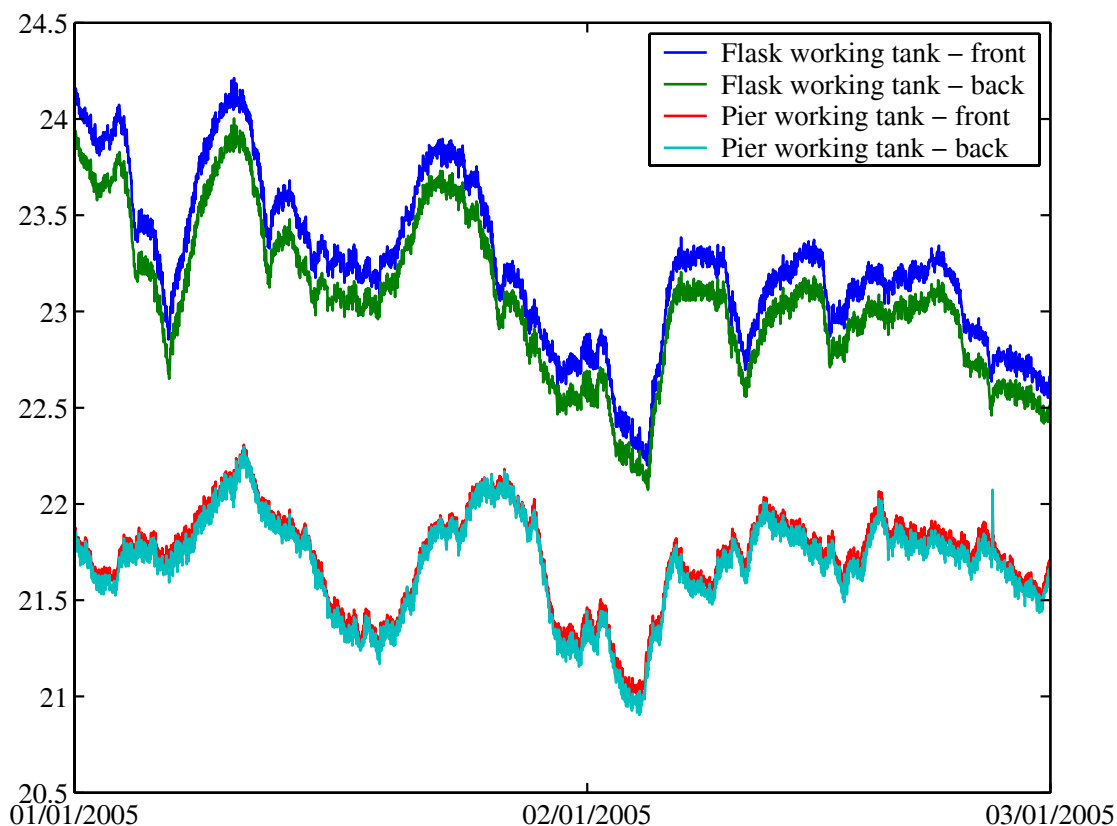


Figure 4.8. Two months of temperature data from within the tank enclosure. Four thermistors are located on the front and back of two different tanks. The flask program working tank was located near the floor on the left side of the tank enclosure; the pierline working tank was located in the upper right corner of the enclosure.

Argon concentrations have sometimes dropped more than 15 per meg (shown in Figure 4.9) and oxygen more than 8 per meg (not shown) over the lifetime of a working tank. For each tank, I fit a line to the working tank determinations, assuming that similar amounts of gas were used between the dates. I then calculated the spread between the first and last estimated value, an approximation of how the concentration of the tank changed over its lifetime. In tanks used between January 2004 and June 2005, the concentration drop was about 6.6 per meg in $\delta(\text{Ar}/\text{N}_2)$.

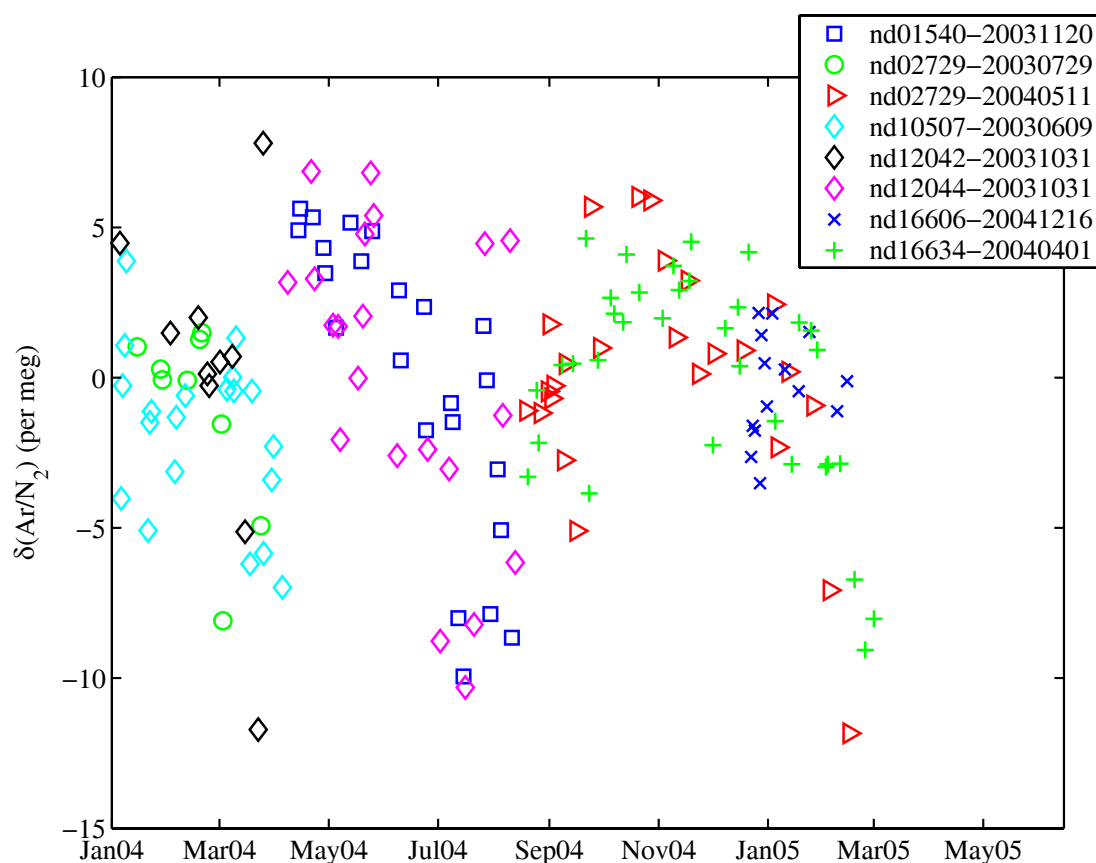


Figure 4.9. Working tank concentrations as determined by comparison with a suite of reference gases on a daily basis. Those tanks marked with a diamond were used in analysis of the continuous pier measurements; other tanks that were run during the same period are shown as well for comparison with the diptube tank results in Figure 4.9.

In early June, 2004, the working tanks used for the continuous setup were changed in order to further minimize the effect of thermal gradients. Instead of sampling from the top of the tank, a diptube was extended into the tank so that the gas is sampled away from the top of the tank, where thermal gradients are expected to be largest. This diptube consists of 1/16" electroformed nickel tubing inside a thin stainless steel column for support that is perforated in order to allow air flow around the internal tube. The end of the diptube droops about 1-2 cm below the vertical

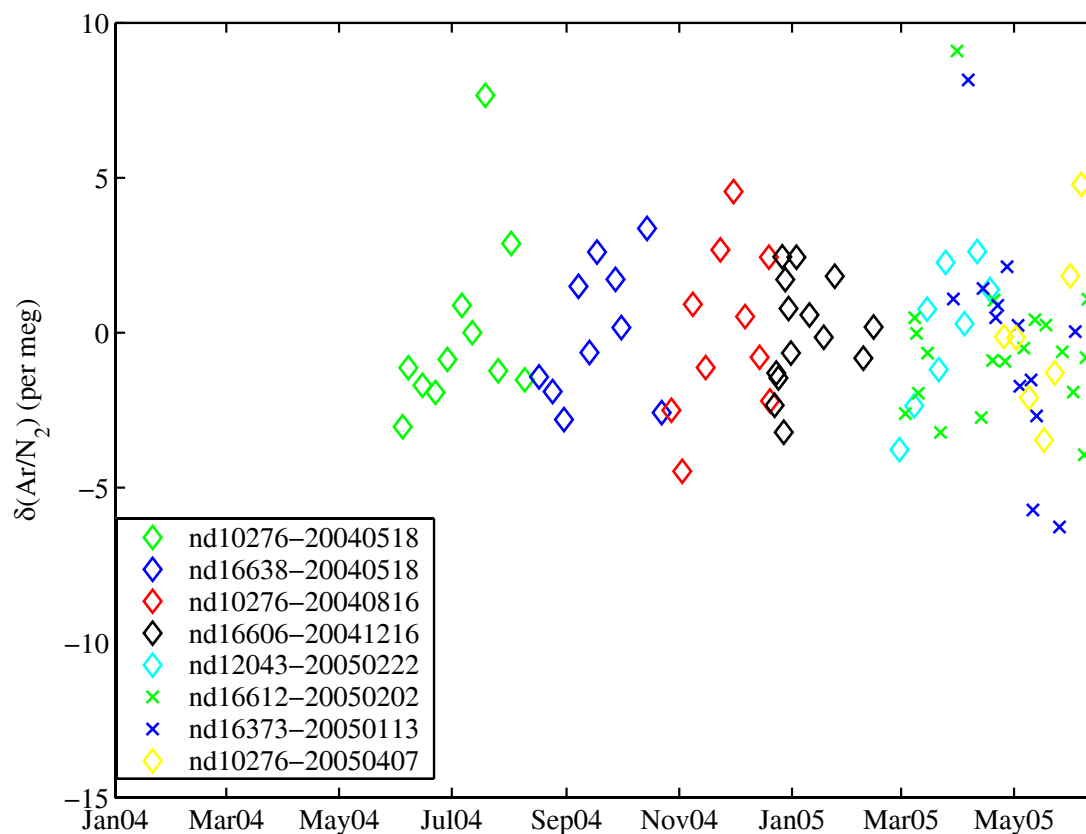


Figure 4.10. Working tank concentrations in diptube tanks as determined by comparison with a suite of reference gases on a daily basis. All of these tanks have been used in the continuous pierline measurements workup.

center of the tank when it is lying horizontally and extends to within about 25 cm of the back of the tank (A. Cox, pers. comm.). The characteristic change in tank concentration over its lifetime, again determined by linear fit, is an average increase of 2.2 per meg in $\delta(\text{Ar}/\text{N}_2)$ (as shown in Figure 4.10). The diptube has significantly improved the stability of the tank on both longer and shorter timeframes, which will be discussed further in Section 4.4.3.

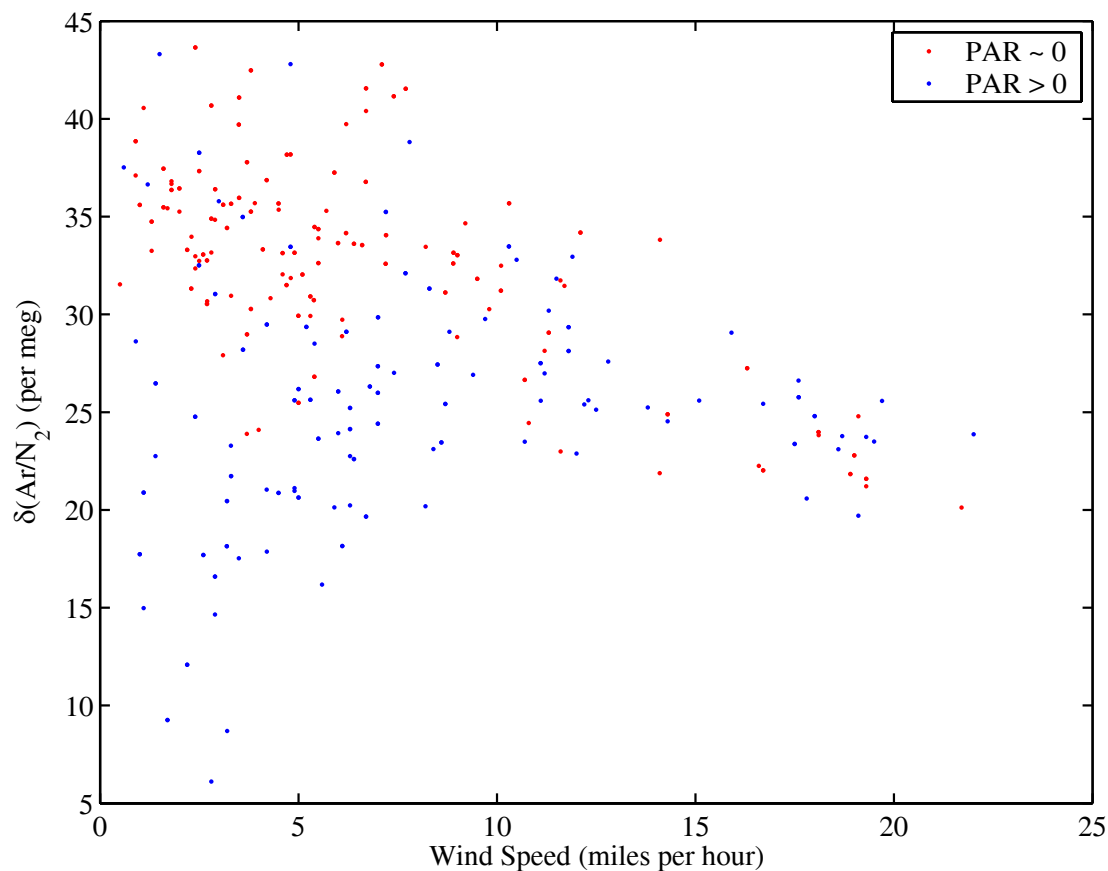


Figure 4.11. Data collected from Dec. 26, 2003 – Jan. 5, 2004. At low wind speeds and high solar radiation (as measured by photosynthetically active radiation, or PAR), low $\delta(\text{Ar}/\text{N}_2)$ values were observed due to thermal fractionation at the inlet. At night, thermal fractionation was caused by radiative cooling of the inlet, leading to high $\delta(\text{Ar}/\text{N}_2)$ values.

4.4 Performance tests

4.4.1 Inlet comparisons

4.4.1.1 Fractionation at the inlet

Early in the development process, I used either Synflex tubing or Synflex tubing attached to a 9" glass tube as a collection inlet on the Scripps pier. Over a period of ten consecutive days from Dec. 26, 2003 to Jan 5, 2004, while using the

glass inlet, the measured $\delta(\text{Ar}/\text{N}_2)$ concentration varied 40 per meg. High values were correlated with low winds and no solar radiation; low values were correlated with low winds and strong solar radiation. During periods when the wind speed climbed above 10 miles per hour, the values during low and high solar radiation were much more consistent (see Figure 4.11). These results suggest that thermal fractionation at the inlet are causing these fluctuations. During the day when the inlet is heated by solar radiation, thermal fractionation would lead to lower $\delta(\text{Ar}/\text{N}_2)$ values, whereas at night, when the inlet cools radiatively, thermal fractionation would lead to higher $\delta(\text{Ar}/\text{N}_2)$ values.

In order to prevent thermal fractionation near the inlet, I installed the pierline inlet inside an aspirated radiation shield (R.M. Young 43408) commonly used in weather stations to protect instruments from solar heating. Formed of two concentric intake tubes with a canopy shade, a blower at the end of the pipe generates a flow of 3.4-7.6 meters per second through the intake tubes and across any sensor. Instead of a meteorological sensor, I have placed Synflex tubing inside the aspirator intake tubes, with the tubing end located approximately 2" above the base of the intake tubes (see Figure 4.2) and exiting the junction box at the top of the radiation shield.

I tested this new setup by switching on an hourly basis between two lines with different inlet systems. The end of one Synflex pierline was placed inside the intake tube of the aspirator as described above. The other Synflex pierline was left unprotected. Over a period of 24 hours, the aspirated line showed a constant $\delta(\text{Ar}/\text{N}_2)$ concentration, whereas the concentration in the unprotected line dropped by up to 80

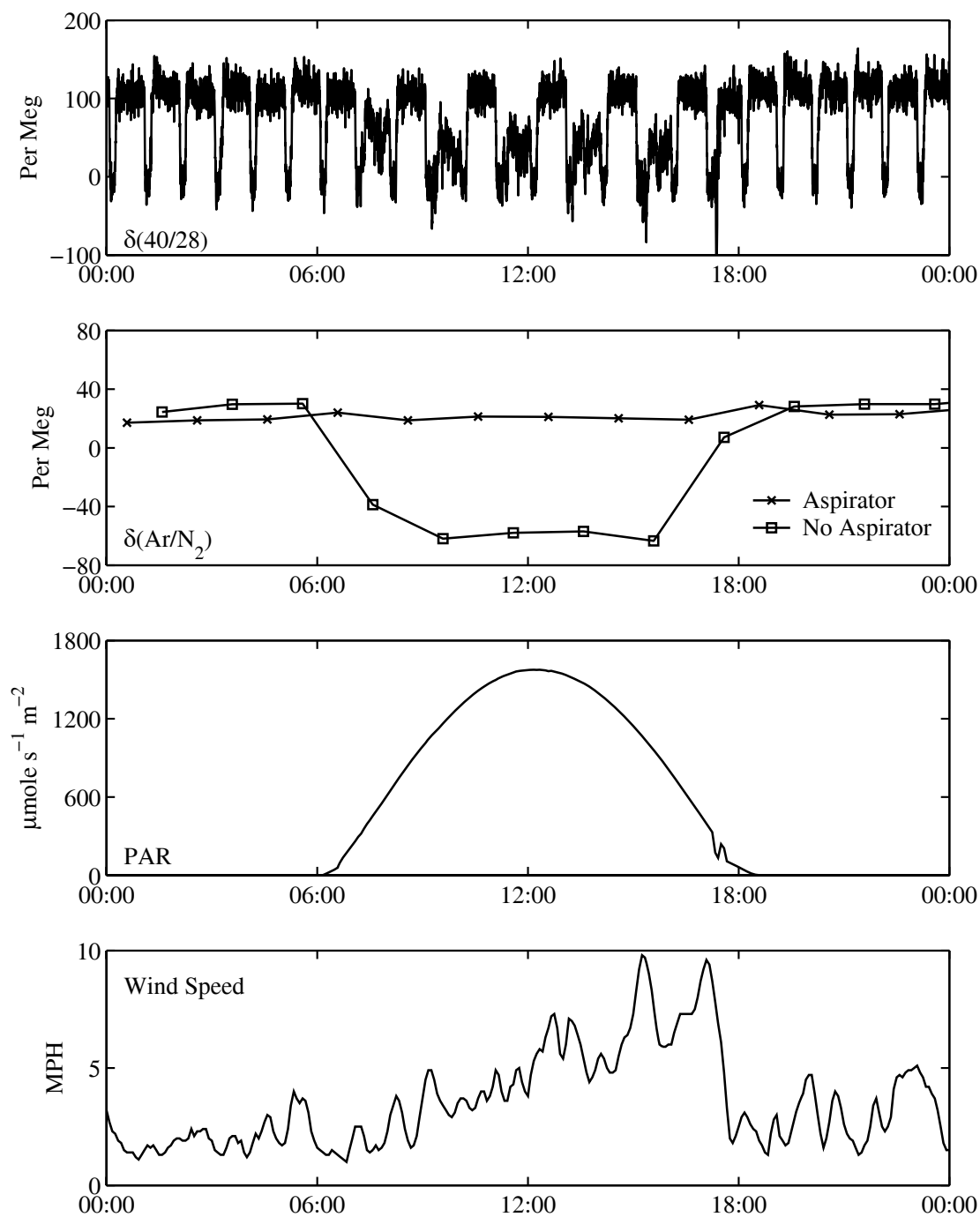


Figure 4.12. Data from March 28, 2004. Every other hour the analyzed air is collected with an aspirated inlet or with an inlet of exposed Synflex tubing. The top panels show the 10-second mass spectrometer output and the derived $\delta(Ar/N_2)$ values. The bottom panels are weather variables: photosynthetically active radiation (PAR) and wind speed.

per meg during the strongest solar heating of the day and increased slightly at night (see Figure 4.12). Leaving the line unprotected would have severely compromised the data, and therefore all data after January 15, 2004, are collected using an aspirated inlet.

4.4.1.2 Variations in line inlet pressure

I tested whether fluctuations in inlet pressure caused any problems with permeation through the pump diaphragm. Generally the air pressure in the line entering the cold trap is about 350 torr below atmospheric pressure. In order to test the measurement sensitivity to line pressure, I compared two parallel lines while dropping the inlet pressure in one and maintaining a steady inlet pressure in the other. In several time steps of 12 hours over three days with a baseline period on each end, I decreased the pressure in one line to about 530 torr below atmospheric using a needle valve placed before the cold trap in the laboratory. At the lowest pressure, the flow was actually too low for the system to maintain the standard pressure of 10 psi above atmospheric pressure entering the instruments.

The 12-hour time step gave six jogs in each line at each pressure (shown in Figure 4.13), which I then averaged. I looked at the difference between the two lines for each pressure level. The difference between the two line means varied from 0.35 ± 0.53 to 2.59 ± 0.87 per meg, with the higher differences actually occurring during baseline periods rather than when the lines had different inlet pressures. In comparison, over two months of data (January -February, 2005) and using twelve-hour

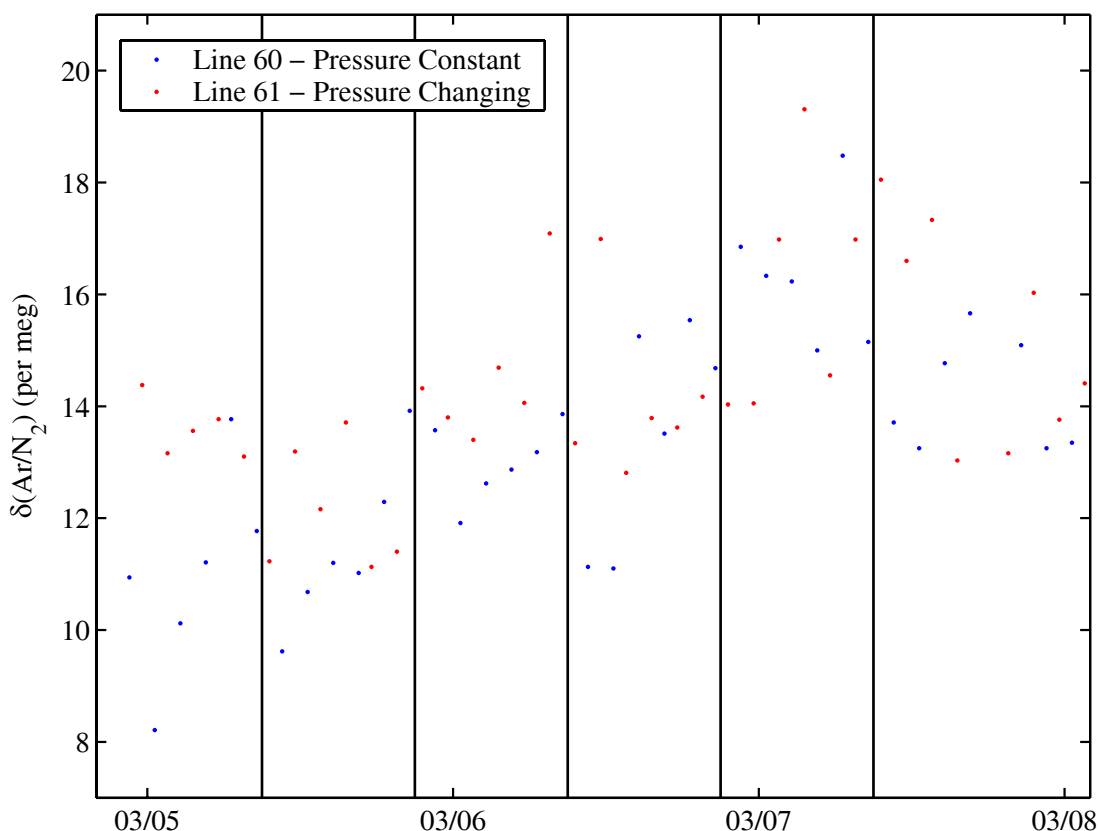


Figure 4.13. Pressure tests during March 4-8, 2005. The first and last windows show how the two lines compare when they are at a baseline inlet pressure of about 350 torr below atmospheric pressure. In the intermediate windows, the pressure is gradually dropped in the red line at 12-hour intervals to 530 torr below atmospheric pressure, while the blue line remains unchanged. The difference between the two lines is minimal.

periods, the difference between the two lines ranged from 0.03 ± 0.74 to 4.61 ± 0.93 per meg, with one line generally higher than the other (an observation which will be further discussed in Section 4.4.3). Thus, the differences measured during the pressure tests are indistinguishable from those normally observed between the lines, and gross changes in the line pressure are unlikely to cause larger differences between the lines.

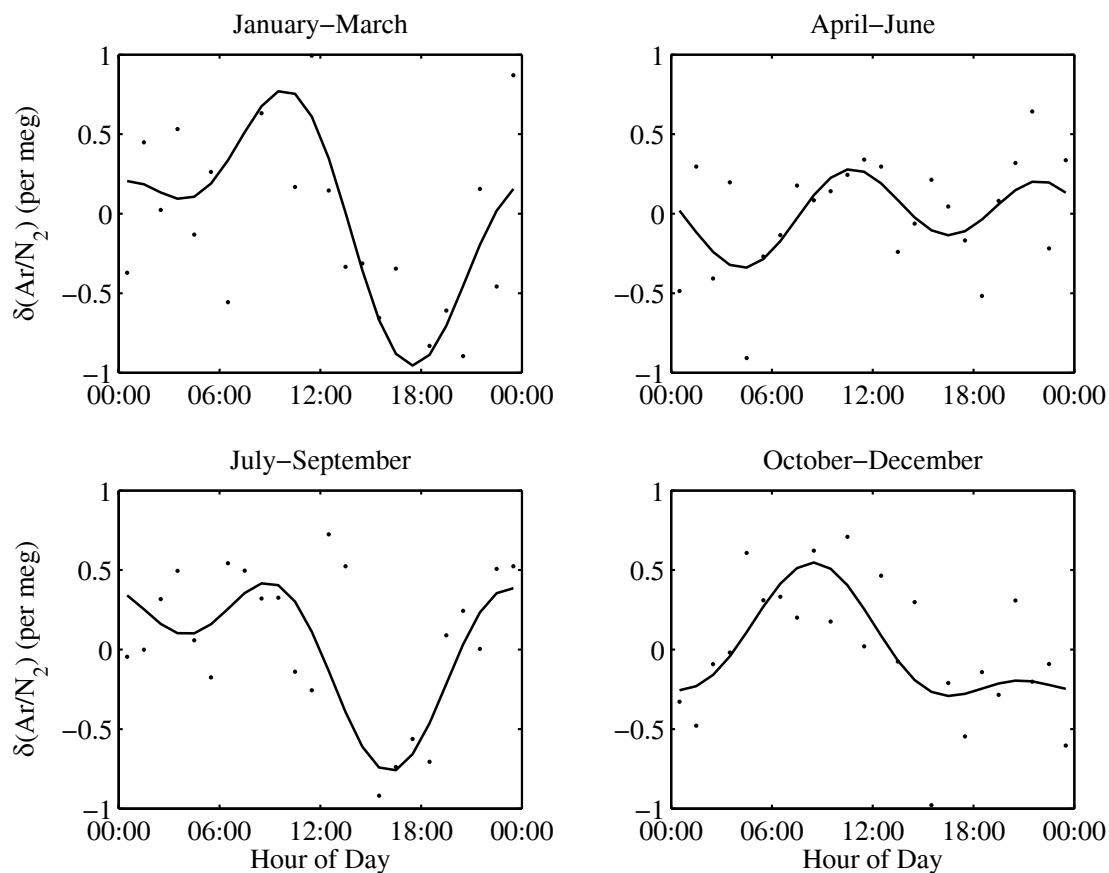


Figure 4.14. Net diurnal cycle in $\delta(\text{Ar}/\text{N}_2)$ as well as the seasonal cycles.

4.4.2 Diurnal cycle

In order to look at whether the continuous data shows any evidence of a diurnal cycle, I extracted all days with 24 hourly determinations of pier air from the data set and calculated the hourly deviations from the daily mean for each individual day. I then binned these points for each hour of the day and calculated the mean value. The results, stratified by season, are shown in Figure 4.14 with a two-harmonic fit to the data. The diurnal peak-to-peak signal in $\delta(\text{Ar}/\text{N}_2)$ is on the order of 1 per meg, with a pattern that changes from season to season. This value basically provides

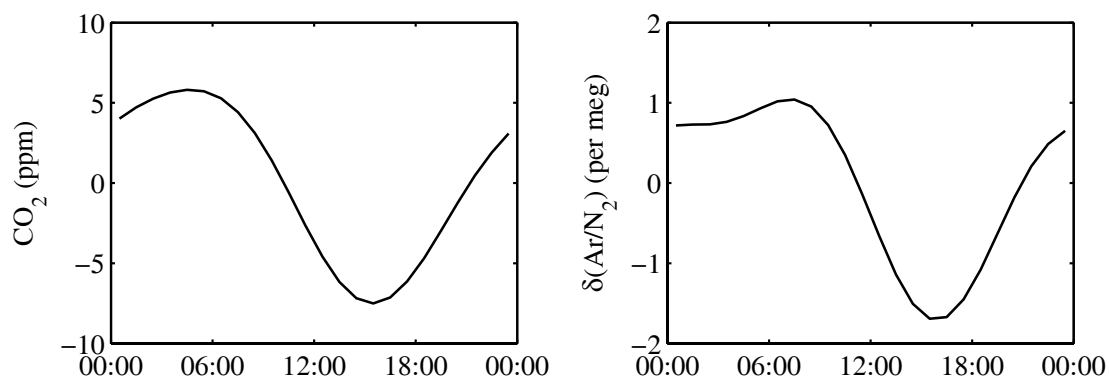


Figure 4.15. Two-harmonic fits to the average diurnal cycle in CO_2 and $\delta(\text{Ar}/\text{N}_2)$ over 14 months of data. The $\delta(\text{Ar}/\text{N}_2)$ signal is shown without the CO_2 correction, in order to show the similarities in the cycle for each species.

a bound on the size of systematic errors in the laboratory that are correlated with daily changes in temperature or pressure.

A diurnal cycle is also visible in both $\delta(\text{O}_2/\text{N}_2)$ and in CO_2 , most likely due to daily changes in wind direction that brings in polluted land air during the night and cleaner air from over the ocean during the day. The $\delta(\text{Ar}/\text{N}_2)$ signal, before being corrected for CO_2 interference, has similar patterns to the CO_2 signal (Figure 4.15). A linear fit between them suggests that the CO_2 correction should be on the order of -0.194 ± 0.0642 per meg/ppm, which agrees well with the value calculated from the bleed tests (-0.157 ± 0.0122 per meg/ppm).

4.4.3 Instrument performance on time scales of 24 hours to several days

On daily timescales, up to 24 hourly determinations of $\delta(\text{Ar}/\text{N}_2)$ are performed. On many days, air from two different pierlines is being tested. As discussed in Section 4.2, the sample air is measured against the instrument reference gas every ten

seconds. This output is then integrated for a given time period in order to give a jog value. Normally this value is differenced against the working tank jog values, but for the following discussion I will be looking at the values of both the pierline and the working tank jogs relative to the instrument reference gas in order to distinguish the performance of each air stream.

Figure 4.16 shows the standard deviation around the mean value for both pierline and working tank determinations over each 24-hour period for which data exists. Many days do not have 24 determinations, and so the number of points used in each daily calculation is included in the third plot. The standard deviation around the mean working tank value (~2.5 per meg) is much higher than around the mean air value (~1.5 per meg) because the working tank integrations are significantly shorter. These calculations were performed regardless of the line being tested at any given time.

The final plot in Figure 4.16 is the difference in the mean between the two pierlines when they were both being used. Two lines were used more consistently after 7/28/05 in order to provide a check on each line. The data between 1/15/05 to 6/1/05 show a small but constant offset with a mean of less than 0.5 per meg between the two sample lines (represented on the plot by the dotted line). During the month of December, 2004, it is evident that one line consistently showed higher values in comparison to the other. This difference may have been due to water leaking into one line and not the other; on January 19, 2005, I used a spare pressurized air cylinder to blow gas through the lines from the inside of the lab in order to dry them out, and

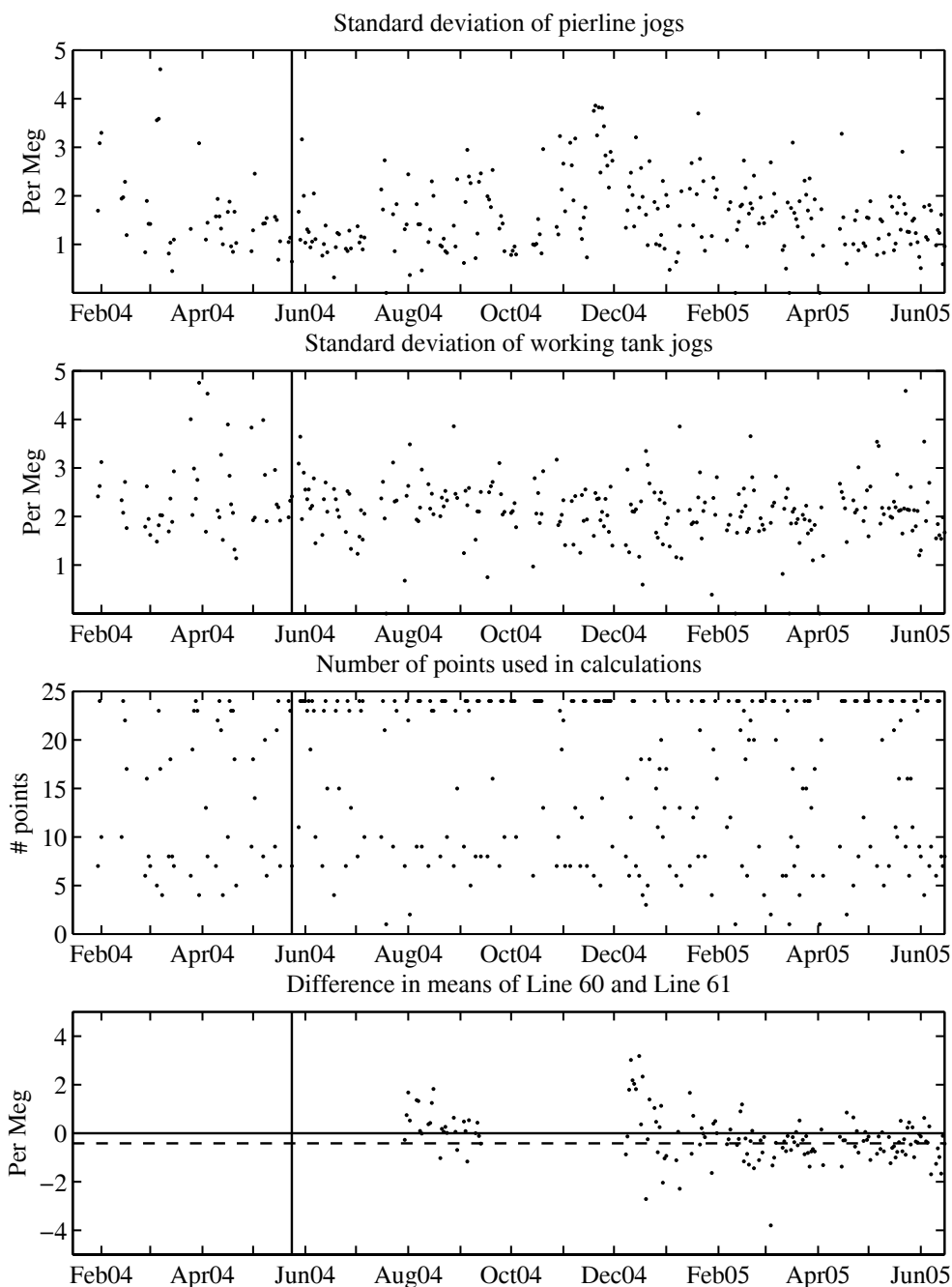


Figure 4.16. The top two plots show the standard deviation around a daily mean $\delta(\text{Ar}/\text{N}_2)$ value in the hourly jogs of pier air and working tank air. Each point represents one 24-hour period, with the number of points actually available in that period shown in the third panel. The pierline values have already been differenced from the working tank averages; the working tank values are relative to the mass spectrometer reference gas. The third plot is the number of points used for every calculation. The last plot represents the difference between the two pierlines when both were being used. The dotted line is the mean difference of all data after 1/15/05, and the vertical line marks the date 5/24/04, when the diptube working tanks were first installed.

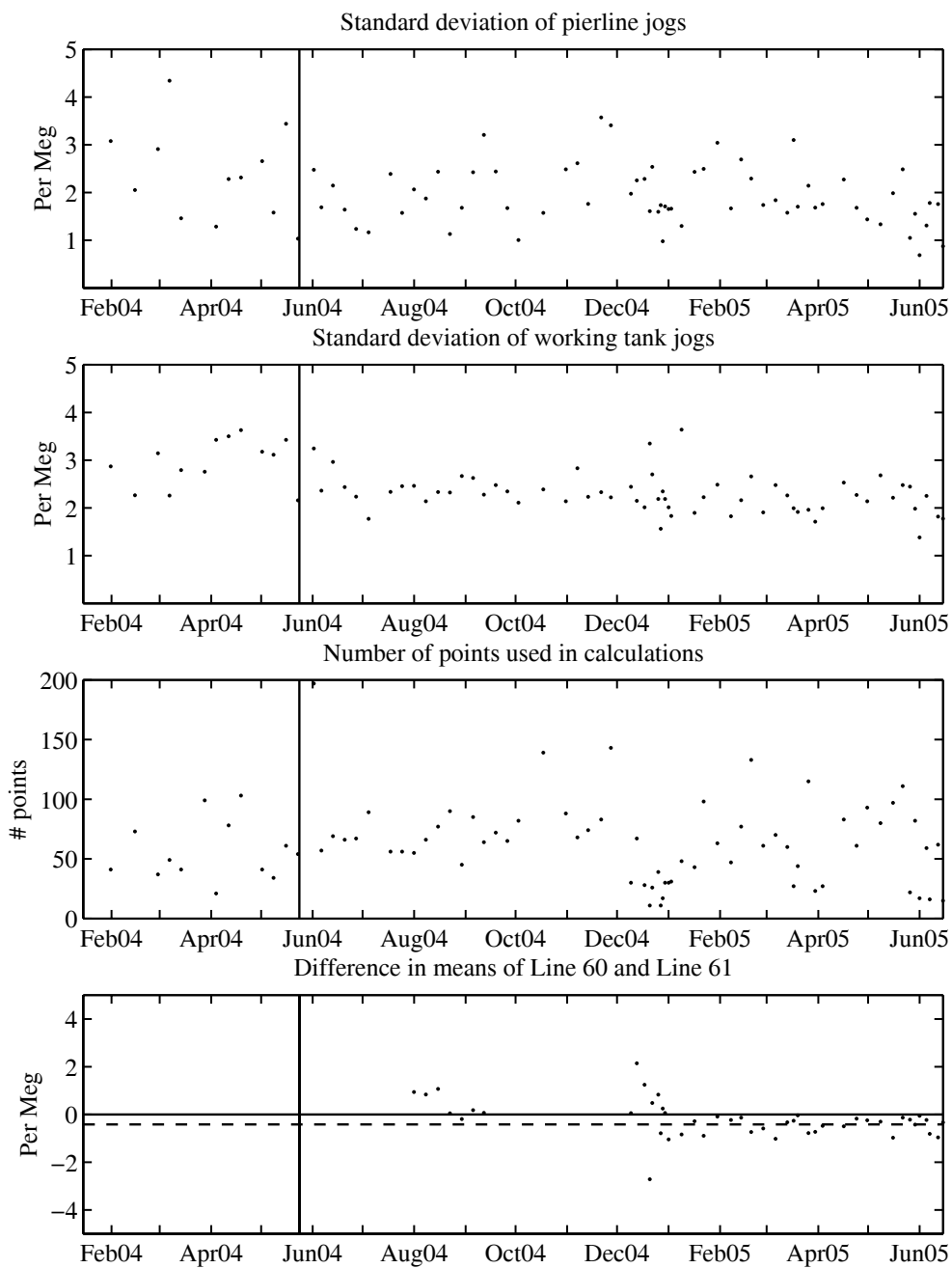


Figure 4.17. As for Figure 5.15, except each point represents each period the pierline was run before being turned off. The time represented by each point can range from 1-8 days. In the working tank jogs, the daily average standard deviation (in Figure 5.15) stayed fairly constant over the entire record.

about 10 mls of water came out of one of the lines. Any openings around the aspirator fittings were also filled in at this time.

Because it is worth looking at possible drift on timescales greater than one day, Figure 4.17 show similar calculations using each weekend of data rather than each 24-hour period. Although the plot showing the standard deviation of pierline jogs is similar to the plot in Figure 4.16, the plot showing the working tank jogs is different. There is a clear shift in the standard deviation from before to after the installation of a diptube in the working tanks on 5/24/04. In the later data, the standard deviation over each period when the pierline was run consistently (up to several days) drops to about the same standard deviation as during a 24-hour period. This observation strengthens the argument for using diptube working tanks in order to obtain more stable working tank concentrations on the order of days to months.

4.5 Comparison of flask and continuous sampling of $\delta(\text{Ar}/\text{N}_2)$ at La Jolla

Figure 4.16 shows data from the first 17 months of continuous sampling for $\delta(\text{Ar}/\text{N}_2)$ at La Jolla, along with all flask measurements during the same period. Also plotted is the first harmonic fit to the seasonal cycle of the continuous measurements. It must be noted that the zero on this scale is arbitrary, because it represents an average of a set of standard gases of unknown composition.

Although these continuous measurements will be discussed in depth in a subsequent chapter of this thesis, it is immediately clear that the continuous data resolve the seasonal cycle much better than the flask measurements. Of the two flask

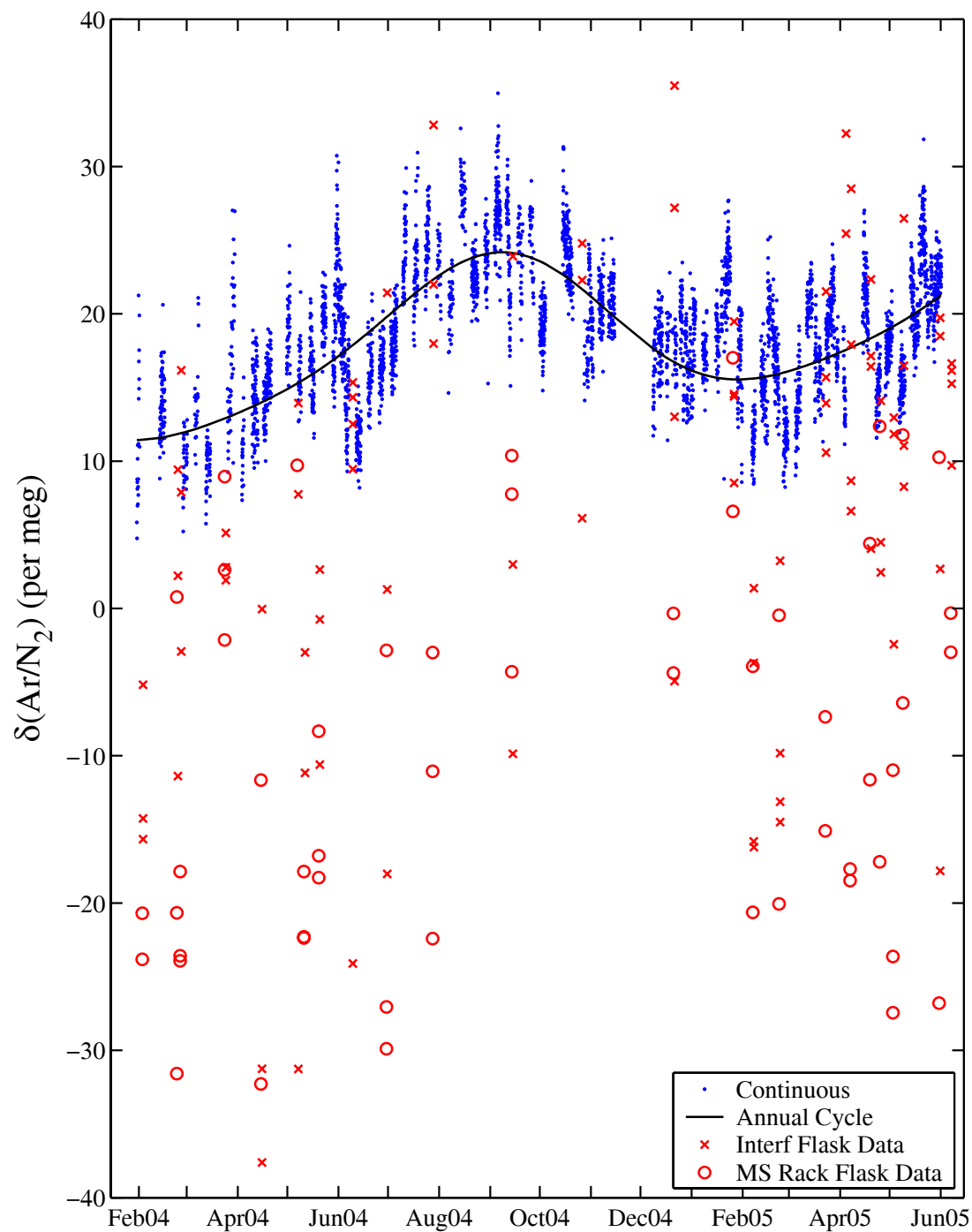


Figure 4.18. The first 17 months of semi-continuous $\delta(\text{Ar}/\text{N}_2)$ data in comparison to the flask measurements taken during the same interval at the Scripps Pier in La Jolla, CA.

analysis techniques, one (Interf) has an annual mean which agrees better with the continuous measurements, whereas the other (MS Rack) shows a significant difference in mean value. This observation raises the question whether the continuous measurements still have some bias, in which the annual mean is higher relative to the flask measurements than it should be. However, it is also likely that the flask measurements have a fractionation bias, most likely towards lighter (or lower) values, because the flasks are sampled in the middle of the day without an aspirator.

The continuous record also shows much more temporal detail. The $\delta(\text{Ar}/\text{N}_2)$ concentration can deviate up to 10 per meg from the fitted seasonal cycle on the order of 1-3 weeks, which is larger than the size of the annual cycle. It is to be hoped that these measurements will give more insight into short-term variability of the $\delta(\text{Ar}/\text{N}_2)$ that has not been previously observed.

4.6 Conclusions

In this chapter, I described a new gas handling system to perform continuous measurements of the Ar/N_2 ratio at the Scripps pier in La Jolla. One-hour averages of a continuous air stream have a precision of 2-3 per meg and are well within the necessary precision to detect the expected seasonal changes in the Ar/N_2 ratio.

The main key to obtaining the precision necessary for measurements of the seasonal cycle was the reduction of thermal fractionation at the collection inlet. Introduction of a commercially available aspirator provides a constantly mixed air stream, which prevents fractionated gases from forming near the inlet. The aspirator

reduced the spread of hourly values over several days from 40 per meg to 8-15 per meg. Given the number of hourly determinations, such a precision permits detection of a seasonal cycle with an amplitude of about 8 per meg. In contrast, although the imprecision on the mean of three flask samples collected together is most likely about ± 11 per meg, real differences between flasks can show a spread of 45 per meg (Keeling et al. 2004). The net change in the concentration of the working tanks over the lifetime of the tank also has been significantly reduced with the introduction of diptube tanks. Better insulation from thermal changes in the laboratory may improve the stability even further.

The continuous data show variability on the order of a few weeks that has never been observed and which may yield insight into geochemical controls on $\delta(\text{Ar}/\text{N}_2)$. Alternatively, it may represent a previously unrecognized laboratory artifact. This variability will be further discussed in a subsequent chapter.

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Chapter 5

Semi-continuous atmospheric $\delta(\text{Ar}/\text{N}_2)$ measurements at Scripps Pier, La Jolla, CA

5.1 Introduction

The oceans have taken up about 84% of the heat due to global warming of the earth system (Levitus et al. 2005). The warming signal now penetrates to a depth of about 100 m in the northern Pacific Ocean and 700 m or deeper in both the North and South Atlantic Oceans, consistent with model estimates of anthropogenically induced warming (Barnett et al. 2005). This warming of the world oceans is expected to lead to emissions of Ar, N₂, O₂, and other gases to the atmosphere because the solubility of these gases in ocean waters generally decreases at higher temperatures (Weiss 1970). Adjustments in ocean stratification and thus convective mixing and deepwater formation (Sarmiento et al. 1998) will also lead to changes in ocean biology and gas fluxes. Time series from 1995-1998 of the concentration of oxygen in the upper 100 m of the ocean, which are associated with a net air-sea oxygen flux, suggest a weak

positive trend (Garcia et al. 2005), and the net ocean signal in measurements of the seasonal atmospheric $\delta(\text{O}_2/\text{N}_2)$ cycle has been roughly estimated (Keeling and Shertz 1992; Manning 2001). The expected change in the ocean oxygen inventory has been calculated based on the increased heat storage of the ocean (Keeling and Garcia 2002). Recent modeling studies attempt to provide estimates of the strength of different causal mechanisms and consequent corrections on estimates of ocean sinks of CO_2 (Bopp et al. 2002). However, no existing measurement record can fully distinguish between different ocean mechanisms on seasonal or interannual timescales for comparison with the models.

The previous chapter established a measurement technique precise enough to reliably determine the seasonal cycle of $\delta(\text{Ar}/\text{N}_2)$ at the Scripps Pier in La Jolla, California. The 17-month record of atmospheric Ar/N_2 from the Scripps Pier in La Jolla, CA, shown in Chapter 4, is presented here with parallel measurements of $\delta(\text{O}_2/\text{N}_2)$ and CO_2 concentration (Figure 5.1). Although continuous measurements of $\delta(\text{O}_2/\text{N}_2)$ and CO_2 exist at other sites, no other dataset like it exists for atmospheric Ar/N_2 . At the moment, the only other published records of atmospheric $\delta(\text{Ar}/\text{N}_2)$, based on flask measurements, are sufficiently imprecise that estimates of the mean annual peak-to-peak cycle at particular stations are possible only with multiple years of measurements (Battle et al. 2003; Keeling et al. 2004).

The $\delta(\text{Ar}/\text{N}_2)$ cycle, closely tied to the seasonal cycle of air-sea heat flux, can serve as an independent constraint on the magnitude of such fluxes in mid-latitude areas. It can also help distinguish between the effect of air-sea heat flux and the effect

of changes in ocean biology and stratification on the seasonal cycle in $\delta(\text{O}_2/\text{N}_2)$.

Eventually, data from stations at various latitudes that show a gradient in mean $\delta(\text{Ar}/\text{N}_2)$ concentration could provide a bound on heat transport in the ocean as well as on localized air-sea heat fluxes, particularly at high latitudes where oceanic measurements are scarce and notoriously difficult to collect. Such measurements may yield important insights into air-sea gas exchange and ocean heat storage, and the consequent effect on atmospheric cycles of important gases as well as ocean biology.

Situated at 32.83°N and 117.27°W, the La Jolla sample site is strongly influenced by its position at the eastern side of the Pacific Ocean. The California Current, part of the North Pacific ocean gyre, carries cold water south from the Gulf of Alaska. Known to be a biologically productive area due to coastal upwelling, upwelling events occur primarily through the spring and fall off of the northern coast, whereas upwelling takes place throughout the year south of the Monterey peninsula (Snyder et al. 2003). During the summer, a strong summertime jet from the north forms in the atmosphere due to the Pacific high and the thermal low over the eastern deserts (Burk and Thompson 1996). The coastal climate is also strongly influenced by the topography of mountain ranges along the California coast, which limits the extent of the marine boundary layer and gives rise to other low level jets (Rogers et al. 1998).

Continuous measurements of atmospheric O_2/N_2 and CO_2 and other trace gases have already provided insights into natural and anthropogenic sources of variability that would not be visible in records based only on flask measurements. Observations of upwelling events recorded in continuous measurements at Baring Head, New

Zealand, have led to the conclusion that short-term changes in atmospheric and oceanic conditions can significantly influence flask measurements, as an air mass can have strong signals of transient events such as upwelling and the source of air arriving at a station can rapidly change (Manning 2001). Continuous measurements at Trinidad Head, in northern California, show changes in the $\delta(\text{O}_2/\text{N}_2)$ and N_2O signals during and immediately after a coastal ocean upwelling event (Lueker et al. 2003). These observations support the conclusion that flask measurements may be inadequate to resolve certain short-term atmospheric variability. In a similar sense, it may be difficult to interpret flask measurements of Ar/N_2 until the short-term variability in the atmospheric Ar/N_2 concentration has been quantified and understood.

In section 5.2, I describe the data workup and the calculation of atmospheric potential oxygen (APO), a tracer that removes the effect of the land biosphere from the $\delta(\text{O}_2/\text{N}_2)$ signal. Section 5.3 takes a closer look at the annual cycle of $\delta(\text{Ar}/\text{N}_2)$ and its relationship to air-sea heat flux. The $\delta(\text{Ar}/\text{N}_2)$ measurements, when combined with CO_2 measurements, are also used to resolve the three main components of the $\delta(\text{O}_2/\text{N}_2)$ annual cycle: terrestrial photosynthesis and respiration, air-sea heat flux, and seasonal changes in ocean biology and stratification.

The semi-continuous measurements not only provide a clear estimate of the annual cycle of $\delta(\text{Ar}/\text{N}_2)$, but also many examples of anomalies ranging from a week to a month in duration. In section 5.4, I take a closer look at these anomalies. While the relationship between deviations in the $\delta(\text{Ar}/\text{N}_2)$ cycle and the APO cycle suggests that they are related to anomalies in air-sea heat flux, the deviations do not correlate

well with estimates of such flux anomalies from the National Centers for Environmental Prediction (NCEP). Some of the anomalies may be due to localized changes in air-sea heat flux or to changes in air masses brought to the station; it is also possible that many of the anomalies are symptoms of measurement issues not yet understood (discussed briefly in Section 5.5). Section 5.6 provides a summary of the results.

5.2 Atmospheric $\delta(\text{Ar}/\text{N}_2)$, $\delta(\text{O}_2/\text{N}_2)$, and CO_2 data

From February, 2004, through June, 2005, air from the Scripps Pier in La Jolla, CA, was analyzed semi-continuously for $\delta(\text{Ar}/\text{N}_2)$, $\delta(\text{O}_2/\text{N}_2)$, and CO_2 concentration, using the instrument system described in Chapter 4. The data were worked up following the procedure described in Chapter 4 and saved as hourly values. Daily averages were also calculated. Because many days do not have a full, 24-hour record, the hourly values were corrected for the diurnal cycle using the seasonal results in Section 4.4.2 in order to generate daily values. Any day with fewer than three hours of data was deleted from the record. Over 4000 hours of data have been collected, on more than 275 discrete days (see Figure 5.1).

In order to allow the data to be separated into the seasonal cycle and short-term anomalies from the seasonal cycle, the hourly data were fit with two harmonics. Employing any larger number of harmonics resulted in the inclusion of anomalies in the estimate of the seasonal cycle. Until more years of data are collected in order to determine whether any of these anomalies are regular features of the seasonal cycle,

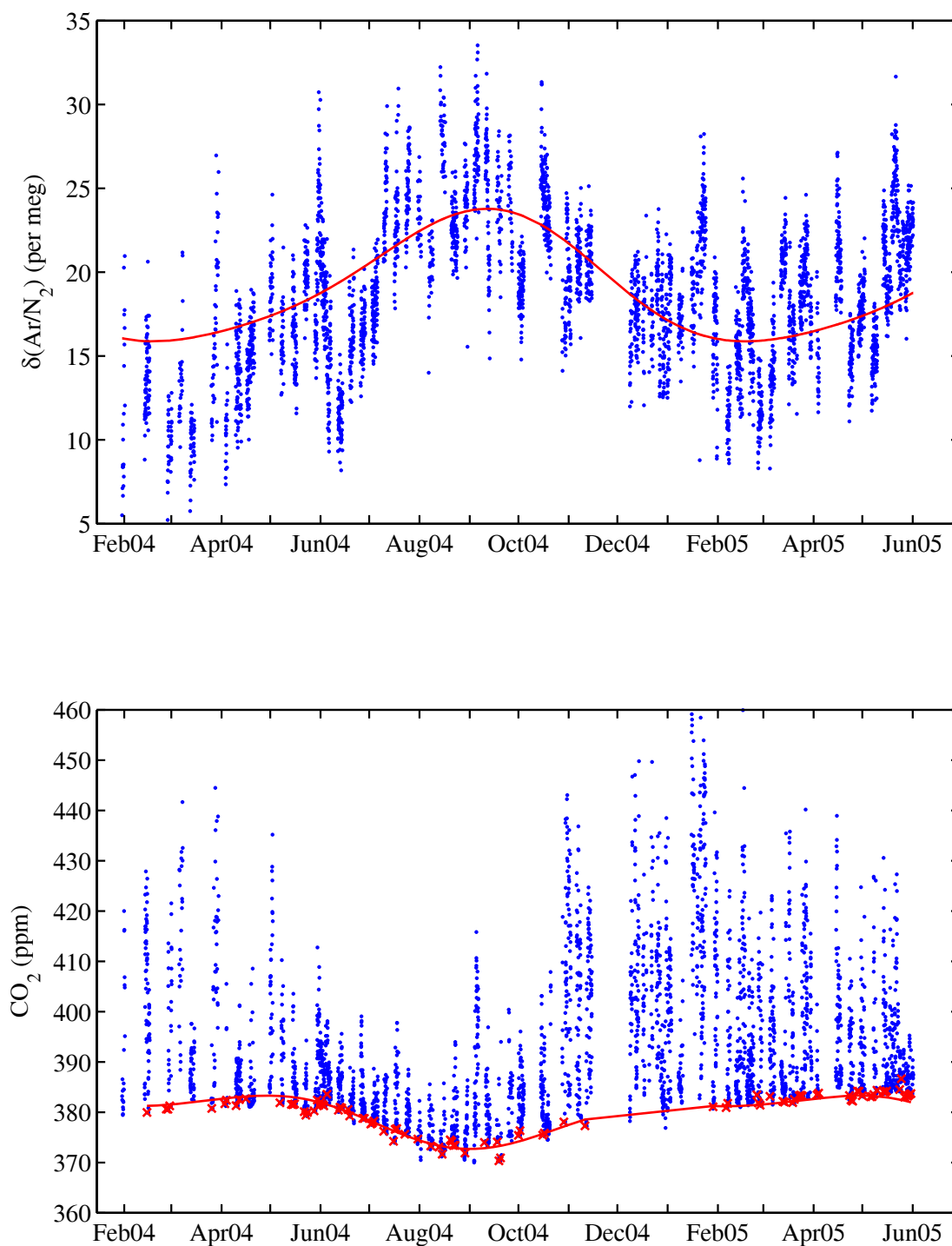


Figure 5.1a. All semi-continuous data for $\delta(\text{Ar}/\text{N}_2)$ and CO_2 (blue). The red line represents the two-harmonic fit to the annual, clean air cycle. The red crosses represent baseline CO_2 concentration, as described in the text.

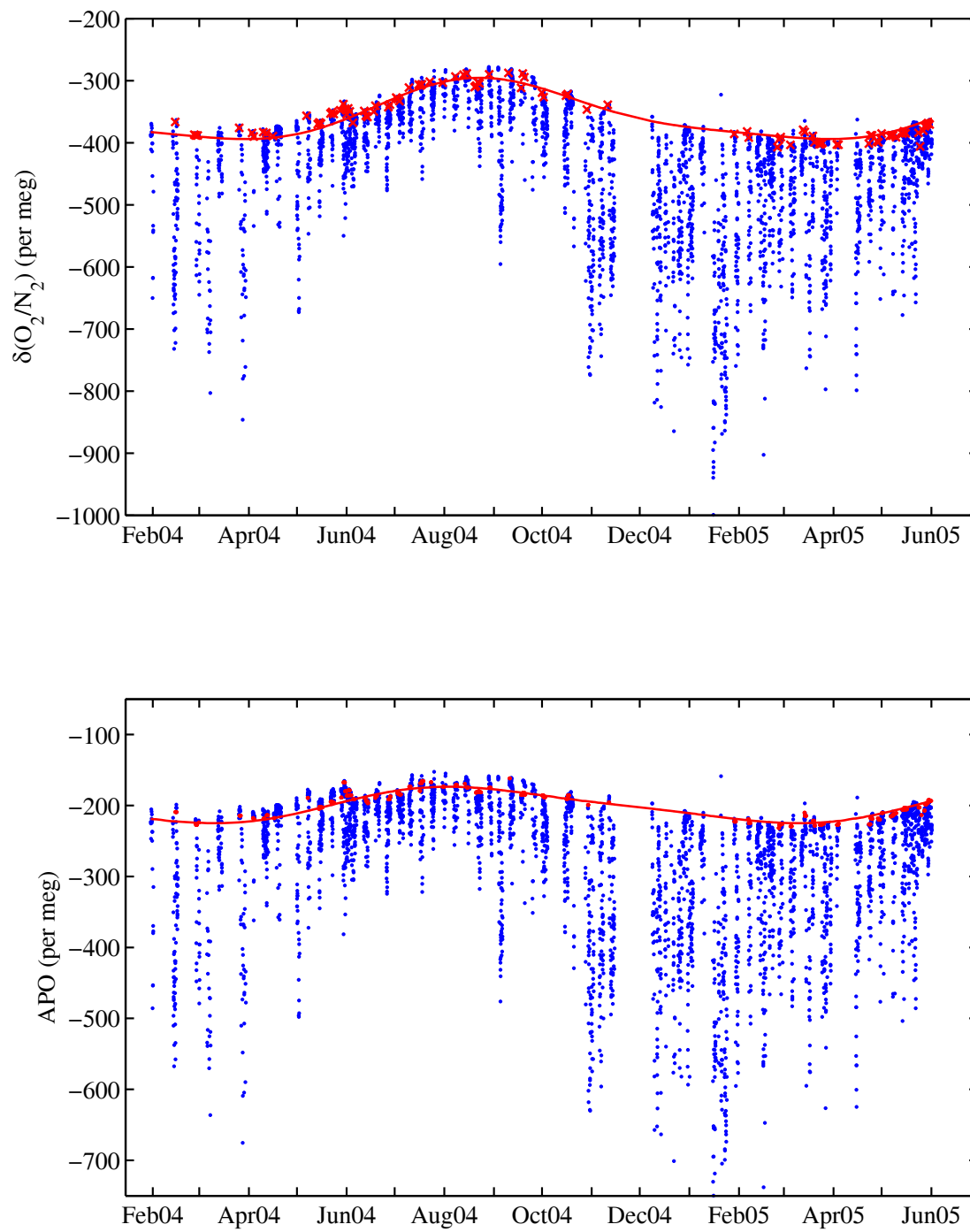


Figure 5.1b. Same as Figure 5.1a, for $\delta(\text{O}_2/\text{N}_2)$ and APO.

they should be viewed primarily as deviations from, rather than as part of, the annual pattern, and therefore two harmonics rather than a larger number were chosen for the subsequent analysis.

Along with the three species directly measured, atmospheric potential oxygen (APO) was calculated from the $\delta(\text{O}_2/\text{N}_2)$ and CO_2 concentrations (Figure 5.1b).

Basically, APO is the amount of oxygen left in an air parcel after the CO_2 cycle due to land photosynthesis and respiration has been removed (see Chapter 2 and Stephens et al. (1998) for a more complete description). APO is conservative to land biology but reflects the oceanic component in the atmospheric CO_2 and $\delta(\text{O}_2/\text{N}_2)$ cycles. On seasonal time scales, the oceanic O_2 exchange is much larger than the CO_2 exchange, and so APO primarily represents the oceanic component of the $\delta(\text{O}_2/\text{N}_2)$ cycle.

To extract baseline APO values, it is necessary to derive a baseline CO_2 concentration that is uncontaminated with local sources of CO_2 . The daily CO_2 minimum in the hourly record was assumed to be a good “first guess” estimate of clean air coming off the ocean and uninfluenced by local sources. It was then tested by looking at the standard deviation around that hourly mean. If the CO_2 concentration during the selected hour had a standard deviation above 30 ppm, showing that the concentration was varying significantly during that time, it was dropped from the record as representing polluted air derived from over land rather than clean air derived from over the ocean. If the daily minimum passed this first test, a second test was conducted that required that the minimum CO_2 value lie within an interval of at least three hours, when the hourly values were all within ± 1 . Once the

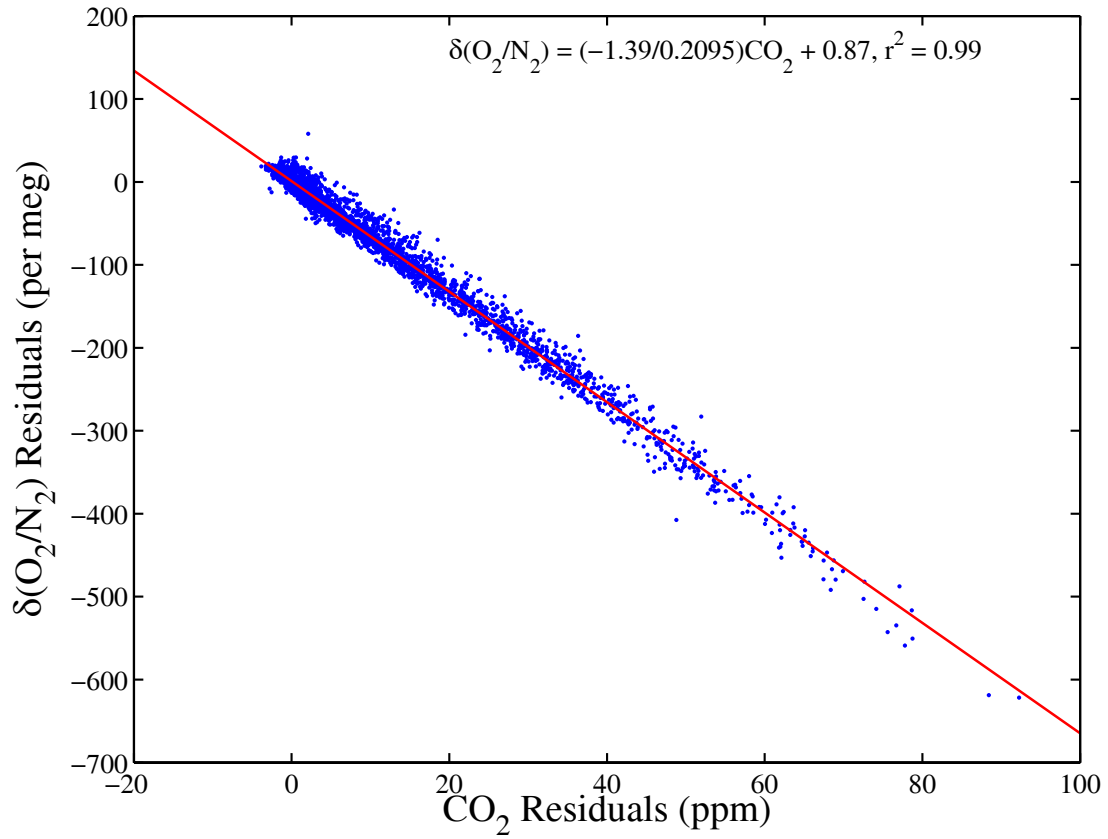


Figure 5.2. The relationship between the residuals to the annual cycle for CO_2 and $\delta(\text{O}_2/\text{N}_2)$. The O_2 and CO_2 cycles are closely correlated, with a ratio of 1.4 due to fossil fuel burning. Because this relationship is so clear, the CO_2 residuals can be used to correct the $\delta(\text{O}_2/\text{N}_2)$ and APO cycles in order to get equivalent, “clean air” values.

CO_2 baseline was determined, baseline APO was calculated using the following formula:

$$APO_{\text{baseline}} = \delta(\text{O}_2/\text{N}_2) + \frac{1.1}{0.20946} (\text{CO}_{2,\text{baseline}} - 350), \quad (5.1)$$

where 1.1 represents the stoichiometric exchange ratio between O_2 and CO_2 in photosynthesis and respiration, 0.20946 represents the equivalency between ppm and per meg units, and $\delta(\text{O}_2/\text{N}_2)$ and $\text{CO}_{2,\text{baseline}}$ represent concurrent measurements.

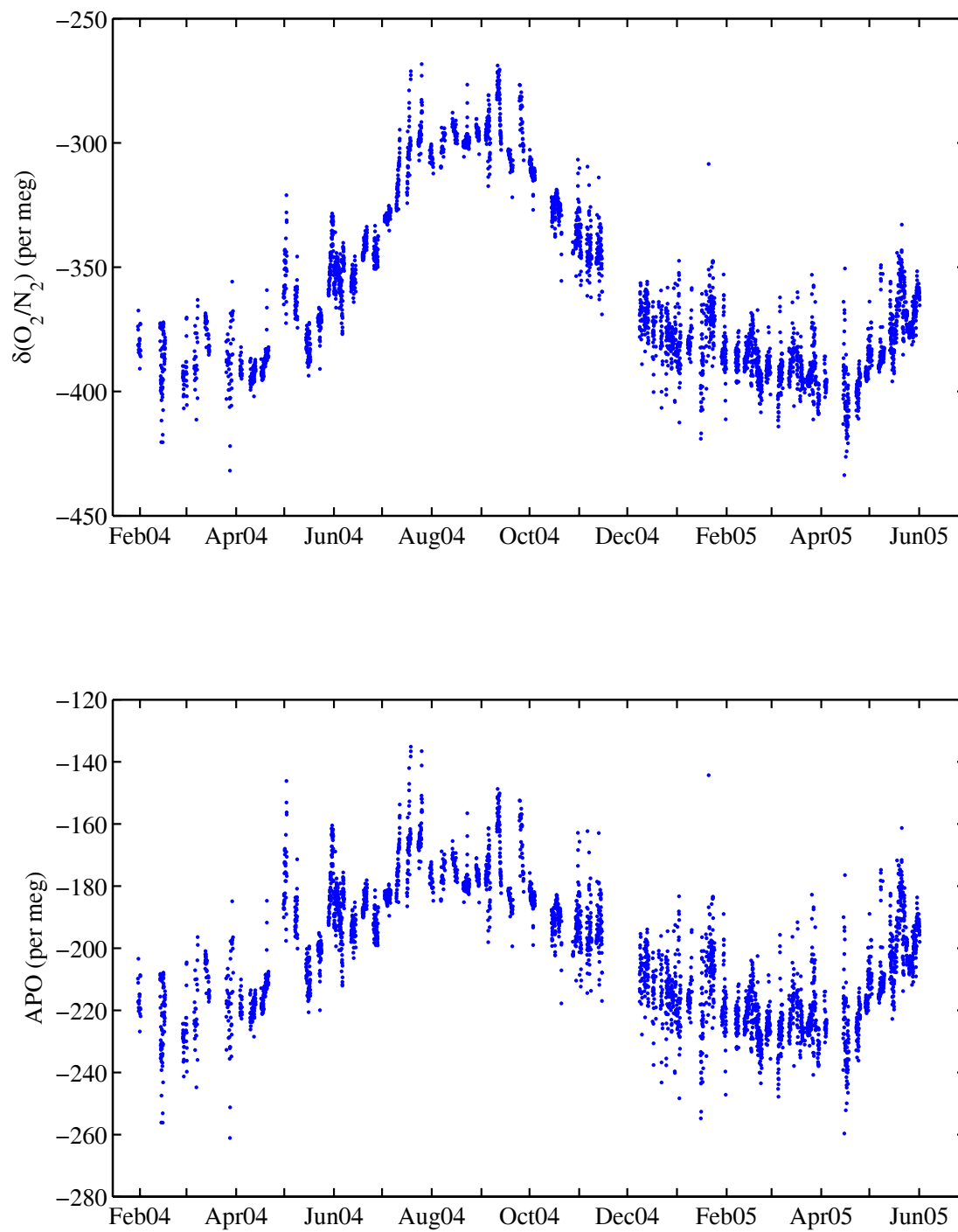


Figure 5.3. Corrected $\delta(\text{O}_2/\text{N}_2)$ and APO cycles based on the CO_2 residuals.

Much of the information in the $\delta(\text{O}_2/\text{N}_2)$ and CO_2 records is lost because of the need to select for clean air conditions. The entire semi-continuous record off of the Scripps Pier reflects significant land-based pollution from burning of fossil fuels, which has a different $\text{O}_2:\text{CO}_2$ relationship. A correlation of the deviations of $\delta(\text{O}_2/\text{N}_2)$ and CO_2 (in per meg equivalent units) from their annual baseline cycles, defined as a harmonic fit to the points retained in the calculation of APO (above), yield a slope of -1.39 with an r^2 value of 0.99 (see Figure 5.2). Although the local ratio will depend on the fuel type, this value is very similar to other published values of the $\text{O}_2:\text{CO}_2$ ratio from burning fossil fuels in Boston (Keeling 1988) and globally (Stephens et al. 1998). I then corrected both the $\delta(\text{O}_2/\text{N}_2)$ and APO signals for pollution in the entire record, thus not losing as much information on the synoptic-scale variability in $\delta(\text{O}_2/\text{N}_2)$ and APO (see Figure 5.3). In order to do this, I calculated the CO_2 residuals from the annual baseline cycle on an hourly basis. I then used the $\text{O}_2:\text{CO}_2$ ratio of -1.39 (found above) to calculate the O_2 -equivalent of these residuals, and I summed these new terms to the hourly $\delta(\text{O}_2/\text{N}_2)$ and APO data.

5.3 Seasonal cycles in the data

5.3.1 Seasonal $\delta(\text{Ar}/\text{N}_2)$ and its relationship to air-sea heat flux estimates

In mid- to high-latitudes, Ar and N_2 are released to the atmosphere in spring and summer and taken up by the ocean during fall and winter. The maximum in the seasonal cycle of the La Jolla $\delta(\text{Ar}/\text{N}_2)$ data occurs around September 15, whereas the minimum occurs around February 7. This seasonal pattern is consistent with patterns

Table 5.1. Estimated annual amplitude based on different methods of calculation.

Time Period	Method used to determine "clean air"	Allow for linear trend?	Mean	Linear Trend (per meg)	Amplitude (per meg)
All data	none	no	19.4 ± 0.063		7.93 ± 0.351
		yes	20.2 ± 0.064	4.10 ± 0.151	11.4 ± 0.329
	APO calculation	no	17.3 ± 0.587		12.3 ± 2.93
		yes	18.0 ± 0.591	2.79 ± 0.866	14.1 ± 2.80
	Sector of wind origin	no	19.0 ± 0.118		9.33 ± 0.627
		yes	19.8 ± 0.116	4.12 ± 0.228	12.7 ± 0.580
All data after 5/27/04	none	no	19.8 ± 0.064		7.23 ± 0.361
		yes	20.3 ± 0.067	5.95 ± 0.308	8.74 ± 0.410
	APO calculation	no	17.4 ± 0.641		12.6 ± 3.28
		yes	18.0 ± 0.653	4.29 ± 1.67	11.5 ± 3.44
	Sector of wind origin	no	19.4 ± 0.120		8.81 ± 0.649
		yes	19.9 ± 0.125	4.94 ± 0.472	8.35 ± 0.713

of thermal forcing as expressed in air-sea heat flux in both phase and amplitude and allowing for atmospheric transport, as will be discussed later. As the ocean warms and the temperature-dependent solubility decreases, both gases are released to the atmosphere; the reverse occurs when the ocean cools.

In Table 5.1, I show the results of calculating the seasonal cycle in $\delta(\text{Ar}/\text{N}_2)$ using several different methods. I use all of the existing data, as well as using subsets of the data representing different definitions of clean ocean air. I also show calculations using only data after 5/24/04, when a change in the design of gas tanks resulted in increased stability of reference gases (discussed in Section 4.3) and thus more reliable data. As a variant, I also allow the cycle to be superimposed on a linear trend.

The annual mean is generally defined statistically to better than 0.2 per meg. However, the possible presence of a trend renders interpretation of the mean unclear. The “best-guess” value for the peak-to-peak annual $\delta(\text{Ar}/\text{N}_2)$ cycle is most likely between 8.8 and 9.3 per meg, with an error of about 0.6 per meg. For comparison, the La Jolla flask measurement record gives a peak-to-peak cycle of 10 ± 3 per meg, using data from June 2001 to June 2003 (Keeling et al. 2004). In order to calculate this value, I defined “clean air” for $\delta(\text{Ar}/\text{N}_2)$ as those hours in which the air comes from the sector off the ocean rather than off land (lying between the bearings $225\text{--}315^\circ$ from due north, as the land is positioned to the west between 350° and 170°) in contrast to the “clean air” definition used for the calculation of APO. This new definition was used because the APO definition threw out too many points, resulting in large error sizes. The APO definition also resulted in an estimate of the amplitude of the annual $\delta(\text{Ar}/\text{N}_2)$ cycle that seemed to be biased low. If all sample hours, clean and polluted air alike, are used for the estimate of the annual peak-to-peak cycle in $\delta(\text{Ar}/\text{N}_2)$, the estimate is 1-2 per meg smaller. Because pollution visible in the CO_2 signal is largest in the winter when $\delta(\text{Ar}/\text{N}_2)$ is smallest, the CO_2 correction, as described in Chapter 4, is largest in the winter as well. If the correction is closer to 12% rather than the estimated 15%, it is possible that polluted air could cause a bias of 1-2 per meg in the annual cycle. It is also possible that the wintertime minimum value is biased upward due to small levels of Ar or N_2 pollution in air coming from the land, due to industrial or laboratory uses.

If the seasonal cycle is calculated allowing for a linear trend, it gives a positive slope of 2.8-5.95 per meg per year (most likely around 4-5 per meg, see Table 5.1). Adding a linear trend improves the r^2 value of the fit (not shown) in every case, however any determination of a linear trend in 17 months of data is dubious at best. The modeled increase in heat content of the earth's oceans is $6.0 \pm 0.6 \text{ W year m}^{-2}$ (Hansen et al. 2005), equivalent to an average change in global heat storage of about $1.9 \times 10^8 \text{ J m}^{-2}$. By comparison, the annual cycle in heat storage is about $7.9 \times 10^8 \text{ J m}^{-2}$ for the entire Northern Hemisphere and $8.7 \times 10^8 \text{ J m}^{-2}$ for the Southern Hemisphere (Peixoto and Oort 1992, p. 340). Roughly estimated, these numbers translate into an annual increase in $\delta(\text{Ar}/\text{N}_2)$ of 0.2-0.3 per meg per year. Thus, the observed trend in $\delta(\text{Ar}/\text{N}_2)$ is most likely not due to long-term ocean warming, but instead due to interannual variability in the air-sea fluxes of Ar and N_2 or unresolved sampling or calibration problems. Keeling et al. (2004) suggest that the interannual variability should be on the order of ± 1 -2 per meg per year, based on estimates of variability in heat storage. Significant interannual variability has already been noted in model predictions and measurements of air-sea fluxes of oxygen: Bopp et al. (2002) project variability on the order of 20% of the average annual emissions of tropical oceans; McKinley et al. (2003) estimate 35-50%, and McKinley et al. (2000) suggests a value of about 40% of the mean flux in the North Atlantic. Garcia et al. (2005) have shown interannual variability of about 25% in comparison to the seasonal cycle of the Northern Hemisphere ocean oxygen content. This variability, caused by changes in ocean stratification, is likely to impact air-sea Ar and N_2 fluxes as well.

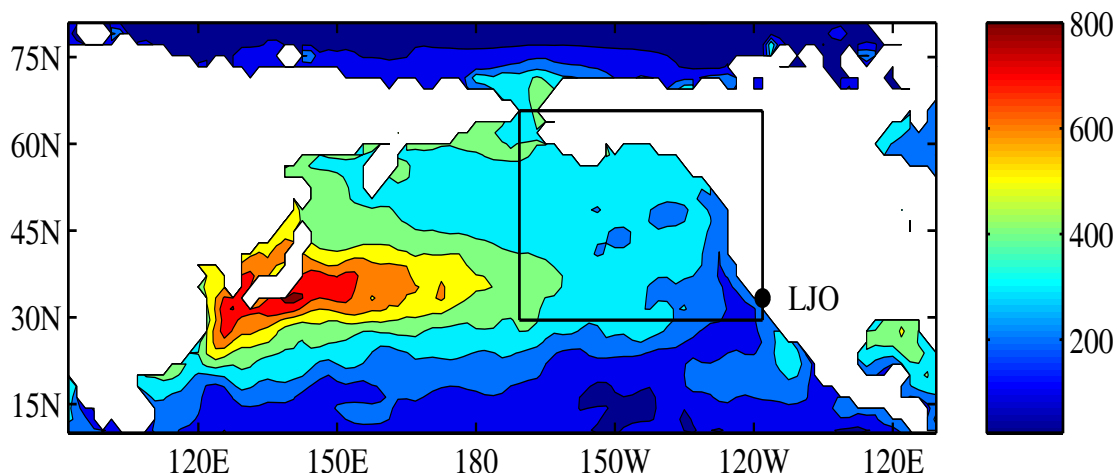


Figure 5.4. Box used to calculate an average air-sea heat flux over the ocean for the east Pacific. The box was drawn so as to contain the end points of most 4-day back trajectories in 2004. The contours represent the amplitude of the seasonal cycle in the NCEP air-sea heat flux in W m^{-2} for the time period of the $\delta(\text{Ar}/\text{N}_2)$ record.

The $\delta(\text{Ar}/\text{N}_2)$ record was compared to air-sea heat flux estimates from the same time period produced by the National Centers for Environmental Prediction (NCEP) reanalysis project. The air-sea heat flux is a combination of four different surface variables: latent and sensible heat flux, and net longwave and shortwave radiation. All of these variables are available from the NCEP project as daily values on a global grid of 1.875° boxes in both latitude and longitude.

I compared the $\delta(\text{Ar}/\text{N}_2)$ data to air-sea heat flux estimates on three different spatial scales. On the most local scale, I used the NCEP reanalysis data for the specific NCEP grid box containing the La Jolla station. For larger spatial scales, I calculated the average air-sea heat flux cycle in both the eastern Pacific Ocean (shown in Figure 5.4) and in the entire Northern Hemisphere. The box used to define the

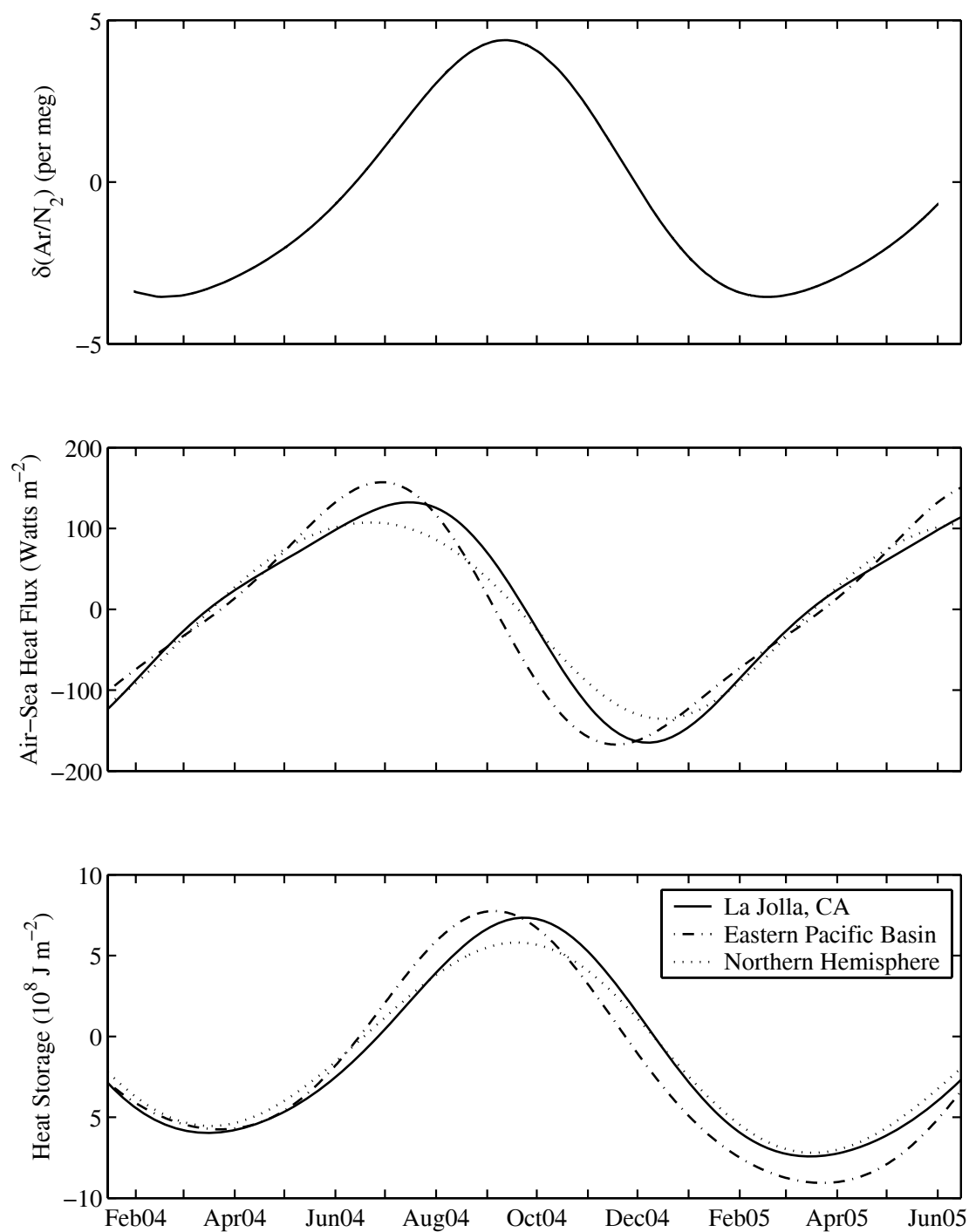


Figure 5.5. Comparison of the two-harmonic fits to the observed annual cycle of $\delta(\text{Ar}/\text{N}_2)$, air-sea heat flux, and oceanic heat storage estimates from the NCEP reanalysis project. The sign convention for air-sea heat flux is positive for flux into the ocean and negative for flux into the atmosphere.

eastern Pacific basin was drawn to contain the end points of most 4-day back trajectories of the air origin in 2004, as calculated using the National Oceanic and Atmospheric Administration Air Resources Laboratory model Hybrid Single Particle Lagrangian Integrated Trajectory model (HYSPLIT) with archived output from the NCEP project (Draxler and Rolph 2003; Rolph 2003).

All three spatial resolutions of NCEP air-sea heat flux yield similar results (Figure 5.5). In the eastern Pacific basin, the heat flux changes from positive to negative values on April 6 and negative to positive values on August 30, whereas the equivalent dates for the local La Jolla grid box are February 15 and October 10. The dates for both of these cycles roughly correspond to the maximum and minimum values of the $\delta(\text{Ar}/\text{N}_2)$ cycle. The shape of the seasonal $\delta(\text{Ar}/\text{N}_2)$ cycle also mirrors that of the local and regional seasonal air-sea heat flux estimates, with a longer period of increase in the atmospheric $\delta(\text{Ar}/\text{N}_2)$ concentration and of heat flux into the ocean, followed by a more rapid decrease in the $\delta(\text{Ar}/\text{N}_2)$ concentration that mirrors a period of more rapid change in the air-sea heat flux.

From the simplified box model of seasonal cycles developed in Section 3.2 (Equation 3.12), I calculate an estimated seasonal cycle in ocean heat storage. Using the amplitude of the measured seasonal cycle in $\delta(\text{Ar}/\text{N}_2)$ to calculate the relative amplitude of the seasonal fluxes in Ar and N_2 , it is possible to solve for ΔT in terms of $\delta(\text{Ar}/\text{N}_2)$. This expression can then be substituted into Equation 3.10. Estimating α (the change in solubility with respect for temperature) for both Ar and N_2 around an average seasonal temperature of 20°C in mid-latitude areas, the seasonal cycle in heat

storage is 10.6 J m^{-2} . However, this estimate comes with a strong caveat; the model is based on idealized atmospheric and oceanic boxes. Given that this calculation assumes instantaneous mixing in the atmosphere, this estimate is likely to be too low. In comparison, the NCEP reanalysis data from this year gives an annual cycle in heat storage of about $13 \times 10^8 \text{ J m}^{-2}$.

To better take account of horizontal and vertical transport and mixing in the atmosphere, the seasonal cycle of $\delta(\text{Ar}/\text{N}_2)$ is shown in Figure 5.6 relative to predictions from the TransCom models used in Chapter 2. These calculations were based on the ECMWF estimates of seasonal air-sea heat flux, rather than the NCEP reanalysis results. The seasonal cycles of the models are calculated using two harmonics, as for the fit to the $\delta(\text{Ar}/\text{N}_2)$ data. I also show the results for the baseline APO cycle.

The TransCom models generally underestimate the peak-to-peak amplitude of the seasonal cycle of both $\delta(\text{Ar}/\text{N}_2)$ and APO. Such discrepancies may be due to problems in the estimates of the air-sea Ar, O₂, and N₂ fluxes or in how atmospheric transport is modeled. The one model (NIRE) which grossly overpredicts the seasonal $\delta(\text{Ar}/\text{N}_2)$ cycle also overpredicts the APO cycle, suggesting a problem with the model rather than with our understanding of air-sea fluxes of Ar and N₂. The models MATCH and NIES predict an earlier peak and a slow and gradual winter decrease in atmospheric $\delta(\text{Ar}/\text{N}_2)$, whereas other models predict the shape of the annual cycle better.

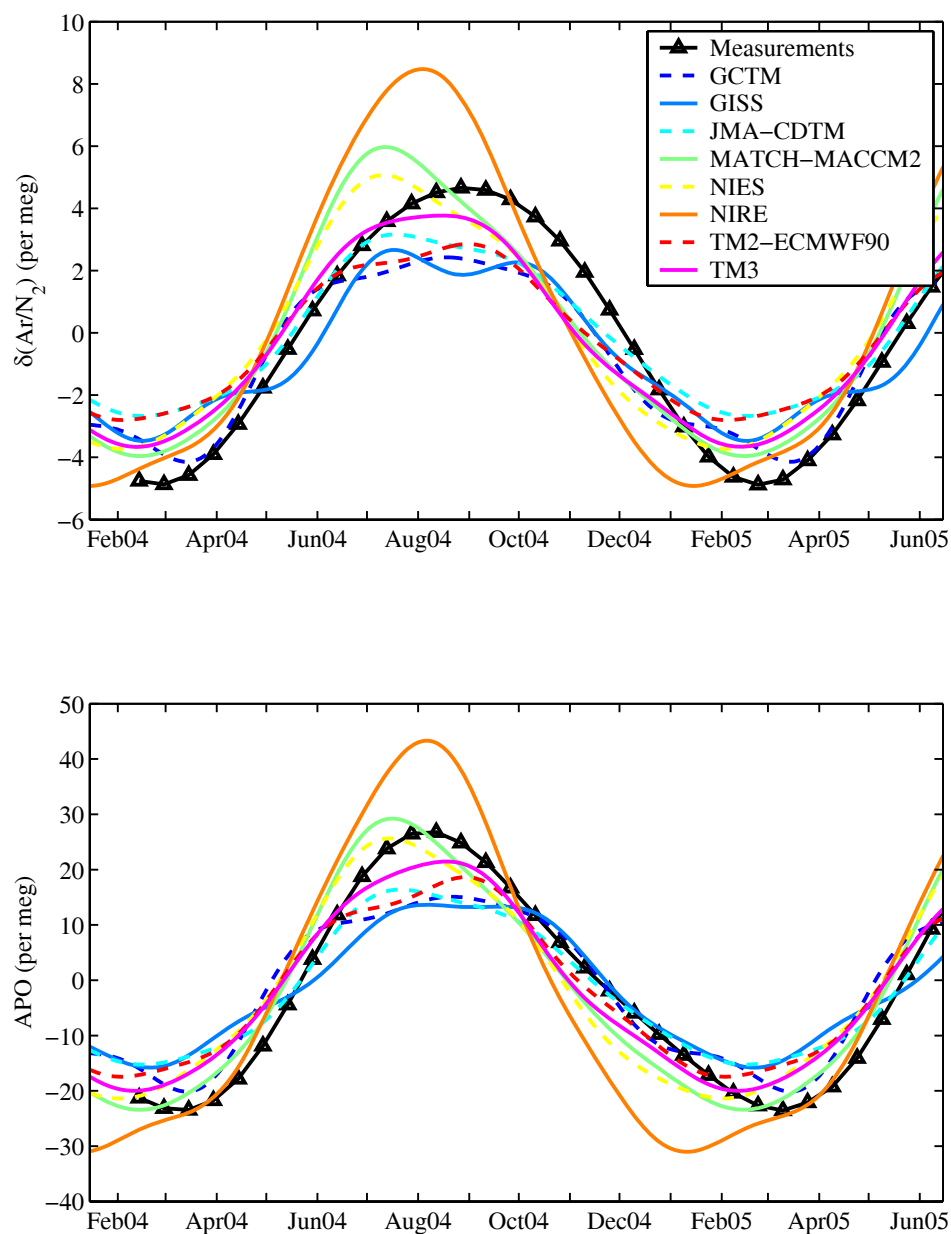


Figure 5.6. Comparison of the measured $\delta(\text{Ar}/\text{N}_2)$ and APO cycles and the output of 9 atmospheric transport models. The annual mean has been removed from the measurements. All transport models were forced with the same air-sea fluxes of argon, nitrogen, and oxygen.

This model/data discrepancy may be due to the wind fields chosen to drive specific atmospheric transport models. It suggests that we may also expect to see such variability in the shape of the seasonal cycle on interannual time scales. The annual maximum and its timing may also be problematic in many models due to seasonal changes in atmospheric transport that are not accurately described. In 2004, for example, the wind speed tended to be low through the summer months. Although the wind speed began increasing again in September, it dropped again in October, a phenomenon that models may not be able to accurately capture. The measured annual cycle may have been affected by weaker vertical mixing in the atmosphere throughout the summertime in comparison to other times, leading to a higher maximum than generally expected. However, differences between predictions and measurements may also be a more systematic problem related to the difficulty of modeling the complexities of atmospheric transport near the La Jolla station. Most likely, the models fail to accurately describe the low-level coastal jets which form above the marine boundary layer, especially during the summer (Burk and Thompson 1996). La Jolla may be receiving more air with a northern origin (and a larger expected seasonal cycle in Ar/N_2) than the models are able to predict.

5.3.2 Seasonal cycles of CO_2 , $\delta(\text{O}_2/\text{N}_2)$ and APO

The peak-to-peak amplitude of the measured clean-air seasonal cycles in the semi-continuous measurements, based on a 2-harmonic fit, are 10.80 ppm in CO_2 , 98.69 per meg in $\delta(\text{O}_2/\text{N}_2)$, and 50.86 per meg in APO (Figure 5.1). These numbers

compare quite closely to the cycles of 10.39 ppm, 103.74 per meg, and 53.99 per meg measured in Scripps Institution of Oceanography flask sampling program since 1989 (described in Chapter 4; Keeling et al. 1998). These numbers provide an important check on the continuous measurement system, showing that any systematic sampling problems are smaller than that which can be generally detected in the $\delta(\text{O}_2/\text{N}_2)$ or CO_2 cycles. They also validate the criterion used for sampling clean air in the flask measurement program.

In parallel with the $\delta(\text{Ar}/\text{N}_2)$ cycle, discussed above, Keeling et al. (1998) observe that atmospheric transport models tend to underestimate the APO cycle at La Jolla, as they do the $\delta(\text{Ar}/\text{N}_2)$ cycle. They hypothesize that there is a discrepancy between the modeled seasonal cycle and the observed one because technicians actively select for steady, west-wind conditions in order to minimize pollution, whereas the model results do not reflect specific wind conditions. Because the data workup selects for clean air times in the sampling record in a similar way to that in which a technician selects for clean air in the flask sampling program, the semi-continuous measurements will likely have a similar bias towards air masses with an origin over the ocean. However, the corrected data shown in Figure 5.3, which are not selected for specific wind conditions, yield an annual amplitude of 98.79 per meg for $\delta(\text{O}_2/\text{N}_2)$ and 50.86 per meg for APO. The difference in predictions for the $\delta(\text{Ar}/\text{N}_2)$ cycle between the best “clean air” estimates and estimates using all data is in the range of 1-2 per meg as well. This observation suggests that the “clean air” cycles are probably not significantly biased by the origin of selected air, in contrast to the explanation in

Keeling et al. (1998), and implies that the discrepancy between models and predictions lie with problems in the models.

5.3.3 Components of the seasonal cycle of $\delta(\text{O}_2/\text{N}_2)$

Based on the solubility of O_2 , Ar, and N_2 in seawater (Weiss 1970), the expected atmospheric $\delta(\text{O}_2/\text{N}_2):\delta(\text{Ar}/\text{N}_2)$ ratio due to seawater warming and cooling ranges from 0.83 at 25°C to 0.85 at 0°C . Keeling and Garcia (2002) suggest that the actual relationship between air-sea heat flux and O_2 flux may be very different from the expected relationship based on heat flux alone; the effects of biological production and respiration and seasonal changes in the ocean structure can be several times larger than the effects of air-sea heat flux on the oxygen cycle. They calculate an estimated oxygen flux per joule of heat flux of 5 nmol J^{-1} in mid-latitudes on seasonal time scales (Keeling and Garcia 2002), with model results predicting 6 nmol J^{-1} (Sarmiento et al. 1998, as quoted in Bopp et al. 2002) and 6.1 nmol J^{-1} (Bopp et al. 2002).

Atmospheric transport model results based on satellite estimates of ocean primary production suggest that 88% of the seasonal $\delta(\text{O}_2/\text{N}_2)$ cycle at the La Jolla station is due to marine biology and ventilation, while changes in solubility account for only 12% (Balkanski et al. 1999), giving a ratio around 7. Keeling and Garcia (2002) suggest an O_2 flux/heating ratio of about 5 nmol J^{-1} for mid-latitudes, based on measurements of ocean oxygen concentrations. Using the estimated relationship between $\delta(\text{Ar}/\text{N}_2)$ and $\delta(\text{O}_2/\text{N}_2)$ due to differences in solubility, this value is equivalent to an expected ratio of 3.5 for atmospheric $\text{APO}:\delta(\text{Ar}/\text{N}_2)$, given an average surface

water temperature of 15-20°C in mid-latitudes. APO is used rather than $\delta(\text{O}_2/\text{N}_2)$ because APO represents the oceanic component of the atmospheric $\delta(\text{O}_2/\text{N}_2)$ signal.

Comparison of the size of the annual cycles in the continuous measurements results in a ratio of APO to $\delta(\text{Ar}/\text{N}_2)$ of 5.5, which fits in with the above estimates. The maximum of the seasonal ocean heat storage cycle in September 2004 minus the minimum in March 2005 gives a cycle on the order of $14.7 \times 10^8 \text{ J m}^{-2}$ in La Jolla and $16.8 \times 10^8 \text{ J m}^{-2}$ in the eastern Pacific basin, compared to the long-term average of $13.7 \times 10^8 \text{ J m}^{-2}$ in La Jolla and $13.1 \times 10^8 \text{ J m}^{-2}$ in the eastern Pacific basin from 1950-2004. The comparison suggests that the heat component of the APO cycle during the 2004-2005 period in which there are semi-continuous measurements may be larger than the average, reducing the ratio between APO and $\delta(\text{Ar}/\text{N}_2)$. Although ocean biology would presumably change in response to the dynamical effects of a larger ocean heat storage cycle, it may not be able to respond as fast or as completely as solubility-driven changes in the air-sea gas fluxes.

Parallel measurements of CO_2 , APO, and $\delta(\text{Ar}/\text{N}_2)$ make it possible to piece out what part of the $\delta(\text{O}_2/\text{N}_2)$ cycle is due to land biology (the difference between $\delta(\text{O}_2/\text{N}_2)$ and APO), air-sea heat flux (the $\delta(\text{Ar}/\text{N}_2)$ cycle times the expected atmospheric $\delta(\text{O}_2/\text{N}_2):\delta(\text{Ar}/\text{N}_2)$ ratio of 0.84 derived from differences in solubility in Weiss 1970), and ocean structural and biological changes (the remainder). All three of these cycles, shown in Figure 5.7, have distinct amplitudes and timing. Garcia and Keeling (2001) conclude that the peak of the O_2 cycle due to ocean stratification and biology is closely correlated with the peak of the timing of the air-sea heat flux. More

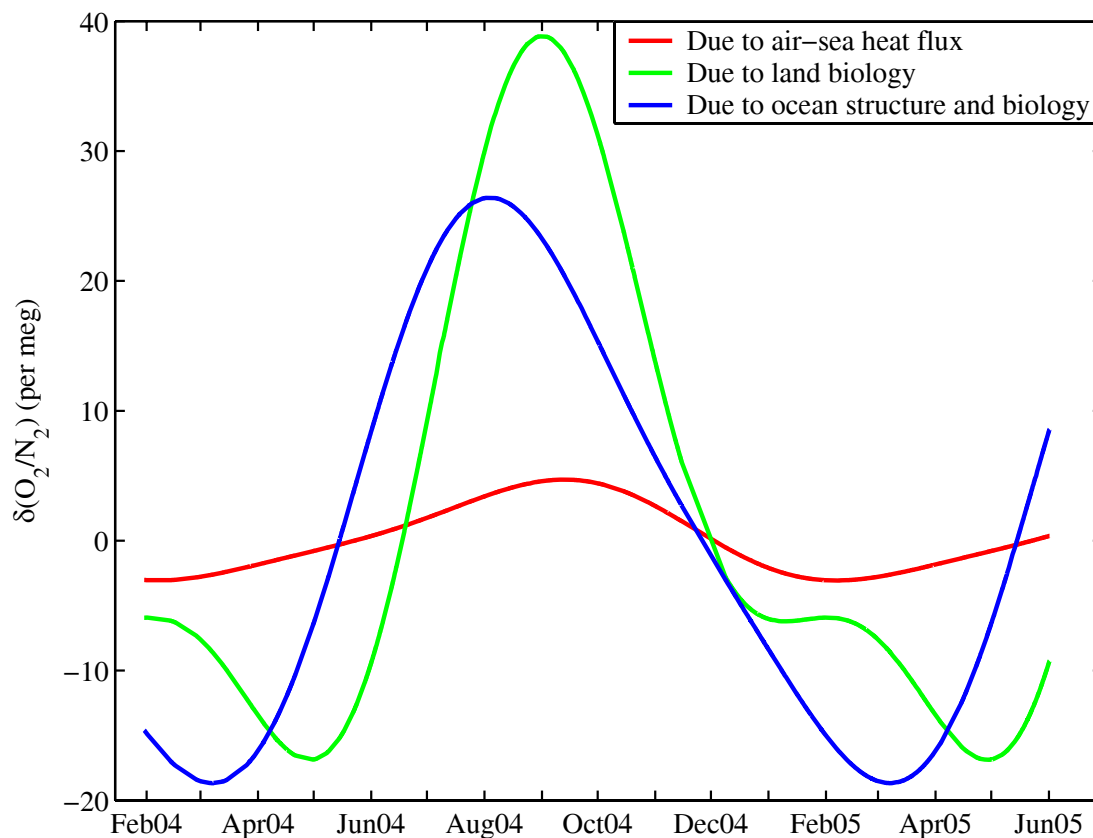


Figure 5.7. Partitioning of the annual $\delta(\text{O}_2/\text{N}_2)$ cycle due to land biology, air-sea heat flux, and changes in ocean structure and biology.

specifically, Bopp et al. (2002) suggest that the ocean should initially release O_2 due to changes in solubility, whereas ocean biology becomes more important later in the season. This pattern holds up in the data: the seasonal rise in the air-sea heat component begins about a month before the component due to ocean structure and biology. This is supported by the $\delta(\text{Ar}/\text{N}_2)$ cycle having an earlier seasonal minimum. However, the ocean component reaches a maximum before the heat flux component; the peaks are separated by about a month.

Models predict significant oceanic changes in surface warming and ocean stratification in response to global warming, which will lead to consequent changes in biological production, export, and remineralization (Maier-Reimer et al. 1996; Sarmiento et al. 1998; Matear and Hirst 2003). Ocean primary productivity as measured by satellite records of chlorophyll is already estimated to have dropped 6% since the early 1980s (Gregg et al. 2003). Changes in coastal areas may be even more important, as they are some of the most biologically productive areas in the world, generating 14-30% of the primary production in the oceans (Gattuso et al. 1998). Although some scientists suggest that upwelling may be increasing along the coasts due to increased wind curl and stronger winds (Snyder et al. 2003), model simulations suggest that increased stratification may reduce the efficiency of upwelling in spite of stronger winds (Di Lorenzo et al. 2005). Measurements of $\delta(\text{Ar}/\text{N}_2)$, especially those at stations like La Jolla which may characterize coastal areas, will help to distinguish between biology and ocean stratification on interannual time scales and as the earth's climate continues to change. It will also help address questions concerning seasonality; Mendelssohn et al. (2004) note that the maximum upper ocean temperature in the California Coastal current occurred 1-2 months earlier in the 1990s than in the 1950s, with significant interannual and decadal variability observed as well. This early attempt to distinguish between causal mechanisms of seasonal changes in the O_2 cycle will become more important as more long-term data is collected.

5.4 Anomalies from the seasonal cycle

5.4.1 General observations

The $\delta(\text{Ar}/\text{N}_2)$ record shows both small scale and large scale deviations from the annual cycle with a duration of a week up to a month (Figure 5.8). These deviations are what remains in the record after a fit using two harmonics and a linear trend (as in Section 5.3.1) is subtracted from the data. The scale of the deviations is similar to the size of the peak-to-peak annual signal, with the largest on the order of 10 per meg. Deviations may be due either to real processes affecting the atmospheric concentration of $\delta(\text{Ar}/\text{N}_2)$ or to instrumental problems that we do not yet understand.

The $\delta(\text{Ar}/\text{N}_2)$ anomalies are shown with parallel calculations of anomalies in APO (Figure 5.8). Figure 5.9 shows a correlation of 0.8 between deviations in APO and $\delta(\text{Ar}/\text{N}_2)$ with a statistical significance to the 0.0001 level. This relationship, while it explains only 10% of the variability, is very similar to the expected correlation of 0.84 due to the differences in solubility between argon and oxygen in the ocean and implies that at least part of the deviations are indeed real.

Such anomalies in the $\delta(\text{Ar}/\text{N}_2)$ record could be due to synoptic variations in weather patterns (discussed later in Section 5.4.4), changes in air-sea heat flux, or other micro-meteorological factors. However, the anomalies correlate with neither local events of upwelling in ocean temperature records nor indices of upwelling along the California coast (not shown). They also do not correlate with continuous measurements of N_2O at the Scripps Pier (Prinn et al. 2000, also not shown), although

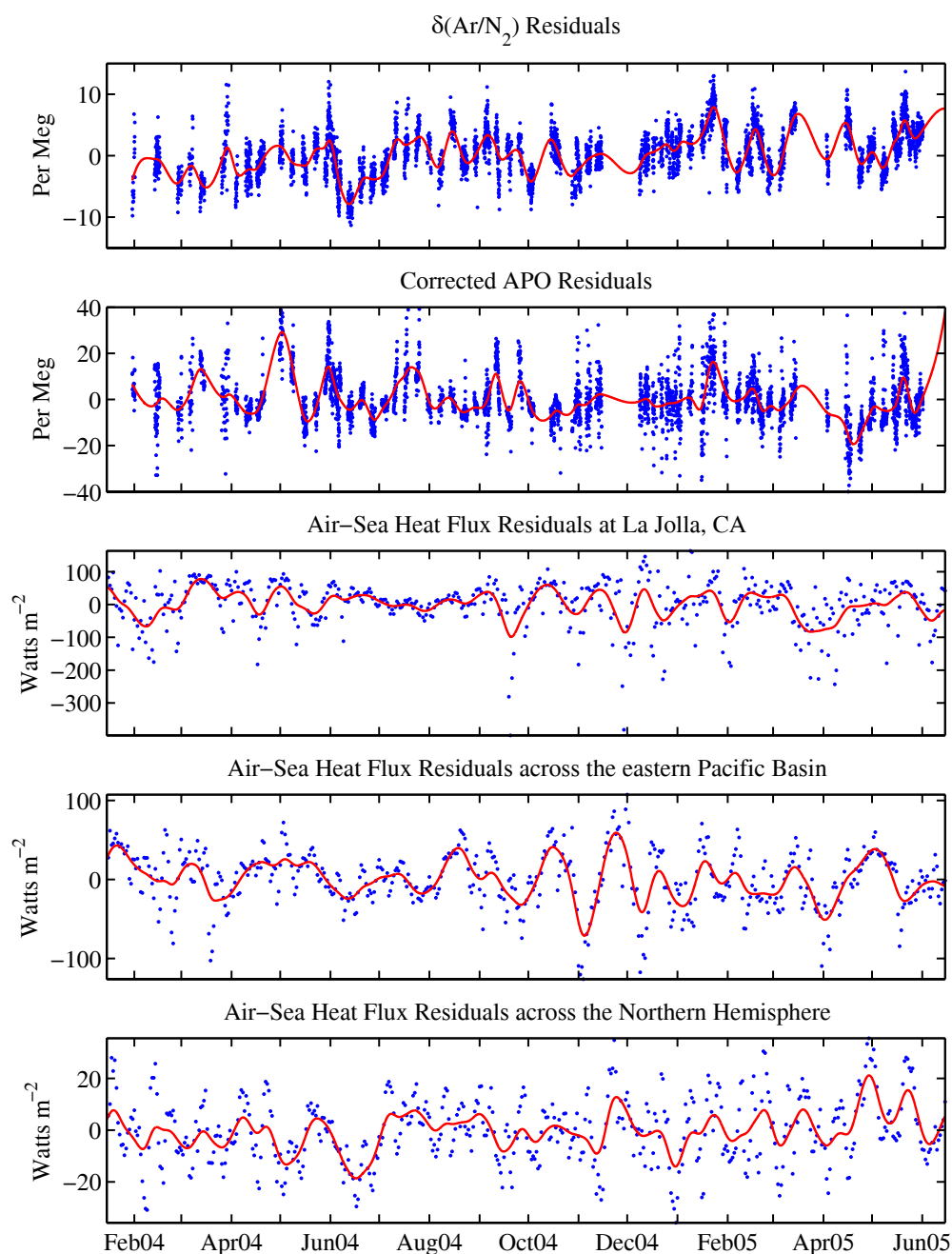


Figure 5.8. The top two plots show the time series of residual $\delta(\text{Ar}/\text{N}_2)$ and APO after the annual cycle (made up of two harmonics and a linear trend) has been removed. The bottom three plots show a similar residual from the annual air-sea heat flux estimate from the NCEP reanalysis project. All curves are fit with a stiff spline fit in order to show the patterns in the residuals more clearly; for example, a large anomaly in $\delta(\text{Ar}/\text{N}_2)$ in June, 2004, also shows up as an anomaly air-sea heat flux residuals in the Northern Hemisphere but not at La Jolla or in the eastern Pacific Basin. As before, positive values for the heat flux signifies flux into the ocean; negative values signify flux into the atmosphere.

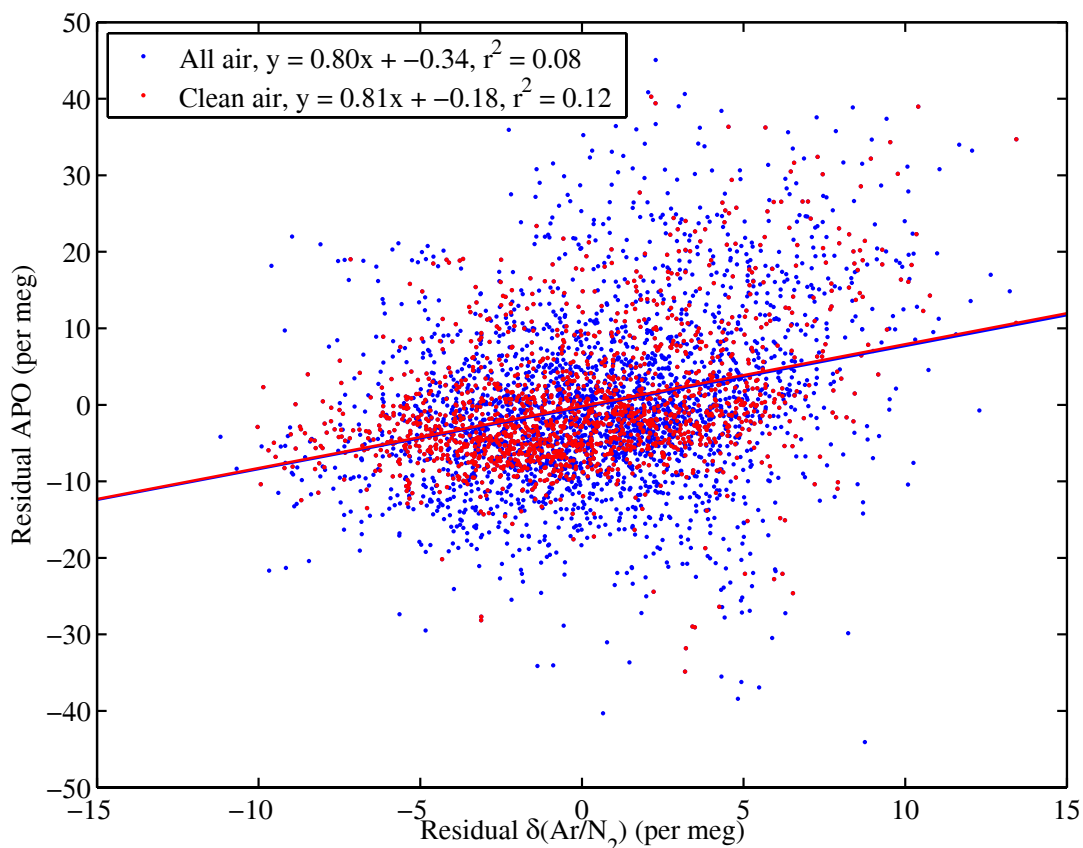


Figure 5.9. Relationship between the APO and $\delta(\text{Ar}/\text{N}_2)$ residuals. The expected relationship based on the solubility of oxygen and argon in the ocean would be about 0.84. The relationship for clean air (in red) and for all measurements corrected for pollution (in blue) is extremely similar. This result suggests that the method of correcting the APO data based on CO_2 anomalies has worked well.

both N_2O and O_2 flux have been shown to be related to upwelling (Nevison et al. 2004; Lueker et al. 2003).

In order to explore the relationship between the $\delta(\text{Ar}/\text{N}_2)$ anomalies and heat, I have also plotted the anomalies in air-sea heat flux in Figure 5.8. The three estimates of deviations from the seasonal cycle of NCEP air-sea heat flux estimates (the model box containing La Jolla, an average value over the eastern Pacific Ocean, and an

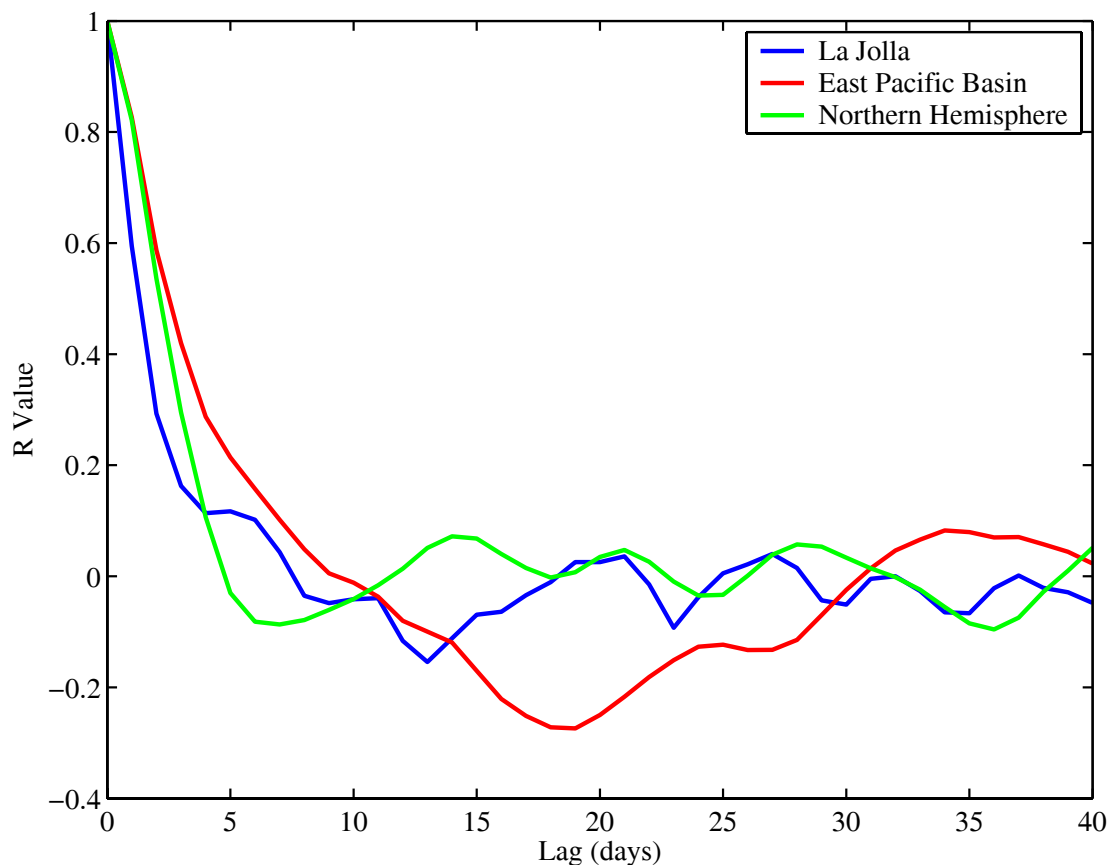


Figure 5.10. Autocorrelation of the NCEP air-sea heat flux residuals.

average value over the entire Northern Hemisphere, all of which were used to look at the seasonal cycle) display autocorrelation on a time scale of 5-10 days (Figure 5.10). This time scale is similar to the typical time scale of 3-7 days for synoptic variations in winds (Peixoto and Oort 1992), and this autocorrelation may be primarily reflecting changes in transport.

Because the time step between measurements is not regular and the data set is very gappy, a standard autocorrelation procedure could not be used on the $\delta(\text{Ar}/\text{N}_2)$ data set. I calculated the product between every value in the $\delta(\text{Ar}/\text{N}_2)$ anomaly record with every other value (as is normally done in an autocorrelation calculation), but I

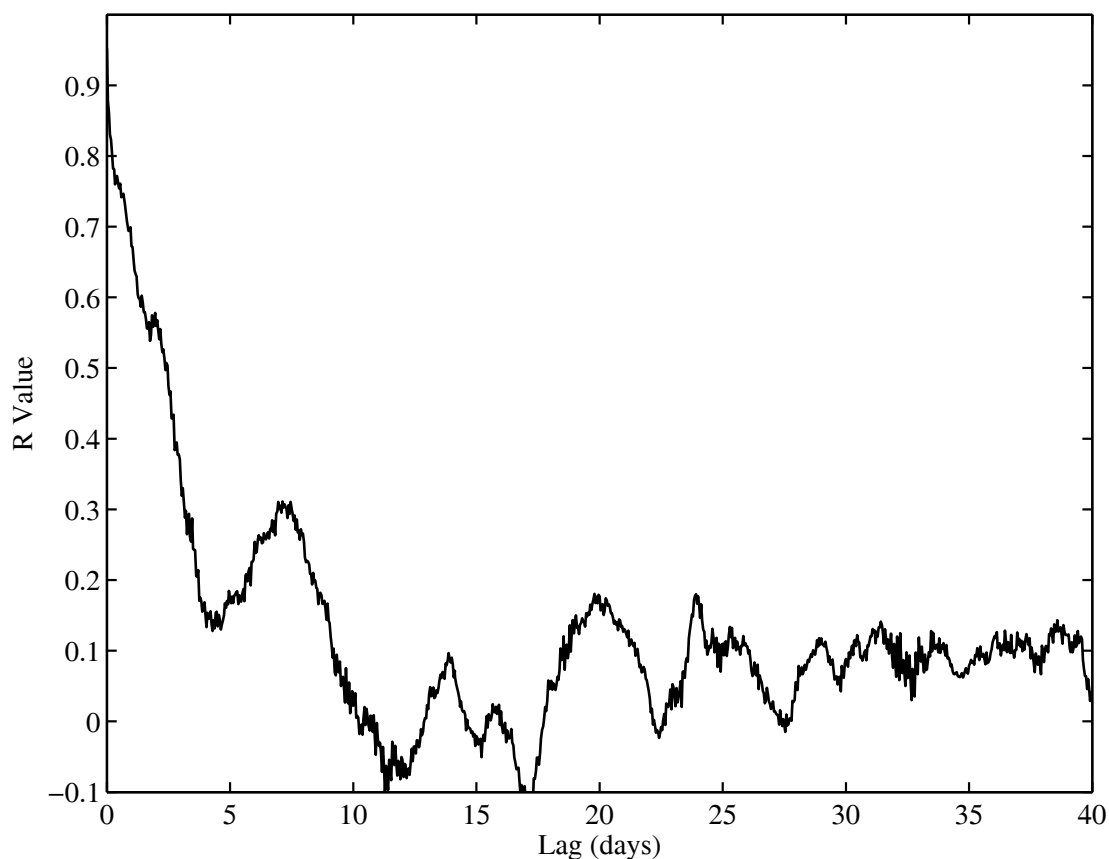


Figure 5.11. Autocorrelation of the $\delta(\text{Ar}/\text{N}_2)$ residuals. See text for description of method.

also recorded the difference in sampling times between each pair of points. I then binned the data for every hour difference in sampling time and averaged the ratios in that bin. The results show that the anomalies are generally correlated on the order of 5-8 days (Figure 5.11), similarly to the estimates of heat flux. Although there are obvious exceptions to this rule (such as the large anomaly in June, 2004), in general the timescale of anomalies is on the order of one week.

The anomalies from the seasonal cycle in the heat flux are on the order of 30-50% of the size of the annual cycle, rather than being close to the size of the annual

signal itself. Although certain peaks in the residuals of the heat flux seem related to peaks in the $\delta(\text{Ar}/\text{N}_2)$ residuals, a statistical comparison of three different estimates for air sea heat flux using the NCEP reanalysis output used for the annual cycle shows that only the La Jolla estimate has any correlation to the variation in $\delta(\text{Ar}/\text{N}_2)$, accounting for less than 5% of the variability. The other two estimates show no correlation between $\delta(\text{Ar}/\text{N}_2)$ and large-scale air-sea heat flux anomaly estimates at all. Comparing NCEP reanalysis output from 1950-2003 with the 2004-2005 anomalies in the $\delta(\text{Ar}/\text{N}_2)$ record actually suggests that previous years' air-sea heat flux estimates sometime correlate better than the 2004-2005 NCEP reanalysis output, thus supporting the conclusion that there is no real correlation.

Although comparison with the anomalies in the NCEP reanalysis output does not suggest a link between deviations in the $\delta(\text{Ar}/\text{N}_2)$ cycle and deviations from the seasonal cycle of large-scale estimates of air-sea heat flux, it is also possible to look at local weather variables for evidence of changes in air-sea heat flux. The weather station on the pier collects information on atmospheric and oceanic variables every five minutes. I then averaged the data into hourly values, more appropriate for comparison with the $\delta(\text{Ar}/\text{N}_2)$ data, and removed the seasonal cycle. Key variables likely to be correlated with $\delta(\text{Ar}/\text{N}_2)$ include ocean water temperature and air temperature, both linked to air-sea heat flux. Other likely candidates include wind speed, wind direction, photosynthetically active radiation (PAR), and barometric pressure as weather systems move through the area. However, both on time scales of an hour and of a day, there are either no or extremely weak correlations. Wind speed,

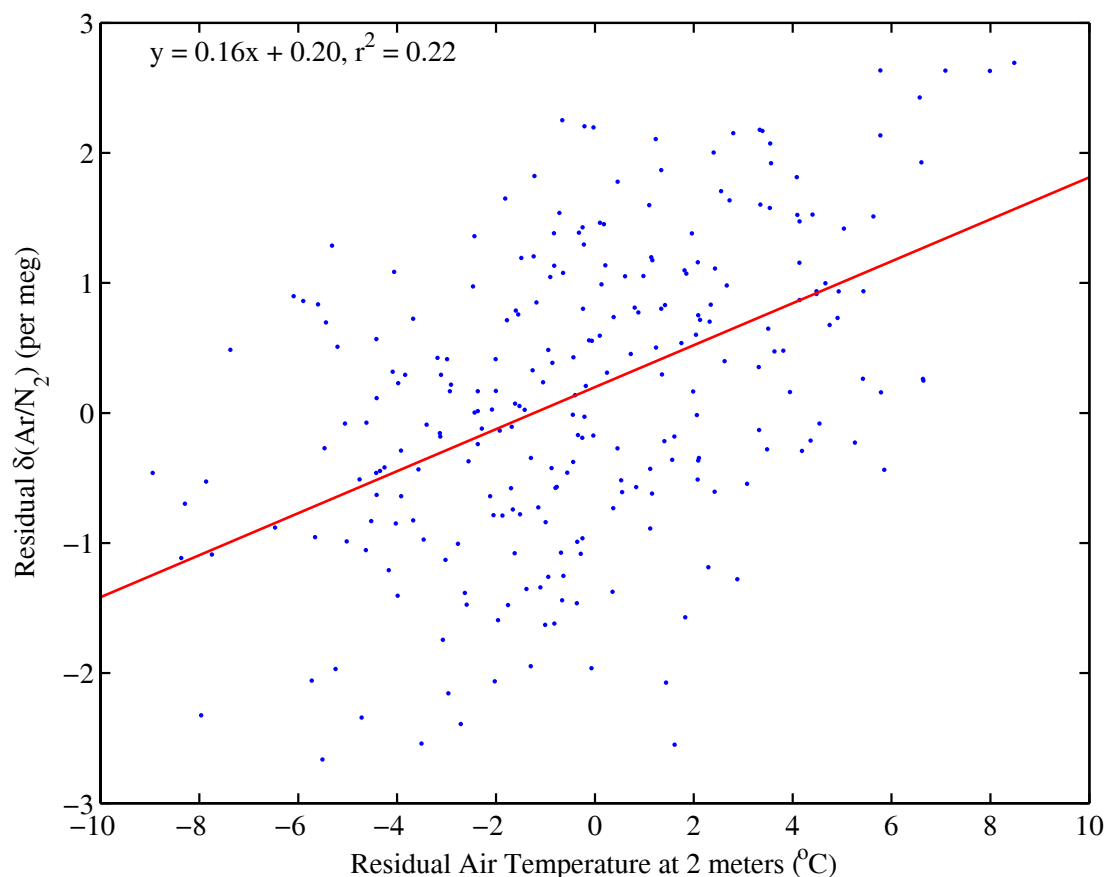


Figure 5.12. Relationship between air temperature residuals and $\delta(\text{Ar}/\text{N}_2)$ residuals from the NCEP database in the reanalysis model grid box containing La Jolla. The $\delta(\text{Ar}/\text{N}_2)$ residuals are not well correlated with air-sea heat flux, although the NCEP reanalysis flux products are known to have large errors. The $\delta(\text{Ar}/\text{N}_2)$ is however correlated with air temperature, which explains over 20% of the variability and which may also be related to heat flux in and out of the ocean.

barometric pressure, and air temperature all could explain 5-10% of the variation, but no more. PAR and ocean water temperature explain none.

Looking at weather variables on a larger scale than that reflected in pier measurements may be better related to $\delta(\text{Ar}/\text{N}_2)$, which is most likely representative of events on a larger scale rather than immediately local scale. Returning to the available

NCEP reanalysis output, daily deviations in estimated air temperature from the seasonal cycle at 2 meters above the surface in the model box containing La Jolla explain about 20% of daily $\delta(\text{Ar}/\text{N}_2)$ deviations (Figure 5.12), which could arguably be tied to air-sea heat flux. A similar correlation is weaker for other variables available from the NCEP dataset, such as surface air pressure and wind direction. An analysis of the power spectrum from seven of the longest gap-free periods with at least three days of data does not show any suggestion of a periodic processes related to the anomalies. Instead, it suggests that any pattern on timescales of less than a month may be attributable to transport of a passive marker in a turbulent system. However, this analysis also isolates three periods with a different pattern, suggesting that the assumption of a stationary stochastic process is not strong, and different mechanisms may be causing the anomalies in different periods (R. L. Parker, personal communication). The first of these periods will be discussed next; the other two fall into the period from 12/1/04-6/1/05.

5.4.2 June 2004 anomaly

The anomaly in June, 2004, is the largest so far in the record. It persists for a month, rising initially to 10 per meg over the seasonal cycle and then dropping in about a week to 10 per meg below the cycle, slowly rebounding over the next few weeks. A comparison of the anomalies in $\delta(\text{Ar}/\text{N}_2)$ and heat flux estimates in Figure 5.8 also shows that the largest negative anomaly in heat flux in the Northern Hemisphere average occurs at the same time, showing up (but not as strongly) in the

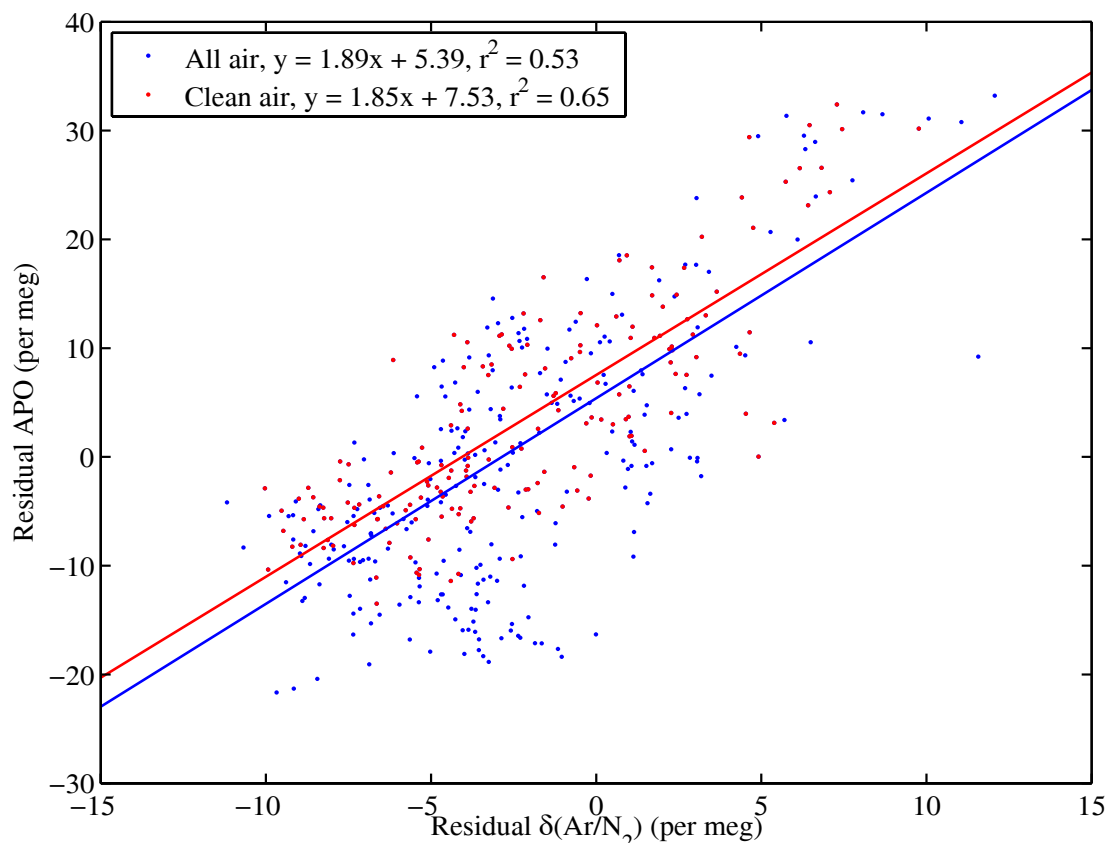


Figure 5.13. Relationship between residuals of $\delta(\text{Ar}/\text{N}_2)$ and APO from 5/29/04 to 6/30/04. The residuals show a clear correlation, although it is different from the correlation of 0.8 over all data (shown in Figure 5.11).

east Pacific basin average as well. A negative anomaly signifies heat flux into the atmosphere and a cooling ocean, which could well explain the decrease in the atmospheric concentration of $\delta(\text{Ar}/\text{N}_2)$. It is possible that the deviation seen in the Scripps station $\delta(\text{Ar}/\text{N}_2)$ measurements may be representing something happening as far away as the Atlantic Ocean, although a large lag would be expected in this case. In the annual cycle, however, an air-sea heat flux cycle of 250 Watts m^{-2} is associated with a seasonal cycle of 10 per meg. By comparison, it may be difficult to argue that a change of 20 Watts m^{-2} could be responsible for an anomaly as large as 10 per meg.

However, it is feasible that a short-term anomaly would not mix as far into the atmosphere and would result in anomalous $\delta(\text{Ar}/\text{N}_2)$ concentrations as measured at the sea surface level.

During this period, the ratio between APO and $\delta(\text{Ar}/\text{N}_2)$ anomalies differs from the ratio of 0.8 common over the entire record; instead, it is closer to 1.8-1.9, and the ratio accounts for 50-65% of the relationship between the two variables, a much larger percentage (Figure 5.13). Thermal fractionation would imply a ratio close to 0.25; although it may not be possible to dismiss the possibility that instrumental problems are the cause of the change in the ratio, this anomaly seems to be real and not just a measurement problem.

This anomaly occurs at the same time as the cloudiest month on record since the beginning of the semi-continuous $\delta(\text{Ar}/\text{N}_2)$ measurements. During this period, the anomaly record of air temperature is close to zero and has little variability compared to the overall record of anomalies. Wind speed anomalies are also small. Although upwelling events occur over the months of May and June, with a large event lasting from 5/30/04 to 6/6/04, a larger and more sustained upwelling event occurs in mid- to late-July when the $\delta(\text{Ar}/\text{N}_2)$ concentration is more stable. However, the $\delta(\text{Ar}/\text{N}_2)$ anomaly is loosely correlated with changes in the record of photosynthetically active radiation (PAR, a measure of incoming solar radiation that falls between 400-700 nm) as measured by the weather station on the Scripps pier. It is possible, though speculative, that the change in PAR represents short-term, localized changes in air-sea heat flux that could result in a sudden change in atmospheric $\delta(\text{Ar}/\text{N}_2)$. An increase in

PAR most likely represents heat flux into the ocean, and thus atmospheric $\delta(\text{Ar}/\text{N}_2)$ values would be expected to increase as well. These results suggest that localized events (such as the strongly stratified marine boundary layer common off the coast of La Jolla in June) can have a significant effect on the measured atmospheric $\delta(\text{Ar}/\text{N}_2)$.

As was shown in the plot of the seasonal cycle in APO due to different components (Figure 5.7), the increase in the air-sea heat flux component precedes the increase of the land biology component and the ocean structure/biology component. This difference in timing may contribute to an increased anomaly ratio. However, other effects may be to blame: the upwelling event in the first week of June (mentioned above) may have brought water depleted in O_2 and with excess N_2 to the surface. Although this colder water may take up more oxygen than expected just based on solubility estimates as it equilibrates with the atmosphere, such uptake might also be balanced by increased productivity. However, along the coast, in upwelling indices off of La Jolla and further up the coast close to the California-Oregon border, upwelling decreases towards July 1. During May and June, the trend is towards decreased upwelling and more flow towards the coasts rather than away from it. Unless the atmospheric $\delta(\text{Ar}/\text{N}_2)$ measurements can reflect an extremely local source, it is unlikely that upwelling is the culprit.

5.4.3 Anomalies from December 2004 – May 2005

Winter 2004-2005 and spring 2005 was a highly unusual period for weather in San Diego. As the third wettest year overall since record-keeping began, the

anomalous weather began in October, 2004, as the wettest October on record since 1850. December, January, and February all had unusually heavy rain (National Weather Service Forecast Office for San Diego; see bibliography for website). This period is similar to a period of large anomalies and rapid changes in the $\delta(\text{Ar}/\text{N}_2)$ record, which appears to last through mid-May. As recorded in both pier weather records and in the NCEP reanalysis weather information, significant storm systems passed through the area with associated changes in air pressure, wind direction and speed, and air temperature.

Although this may be indicative of rapid changes of the origin of air masses arriving in La Jolla, such a speculation is not borne out by a record of the standard deviation of measurements over the period of a weekend (see Figure 4.17). If rapid changes in wind were bringing in air masses with different $\delta(\text{Ar}/\text{N}_2)$ concentrations, it would be expected that the standard deviation of a 24-hour period's measurements or of an entire weekend's measurements would increase during this period (Figures 4.16 and 4.17, respectively). However, it does not change at all.

5.4.4 Back-trajectory analysis

I calculated the five-day back-trajectory for every day in the continuous data set using NOAA's HYSPLIT program. I then compared this record with the daily record of deviations. Figure 5.14 shows the origin of the air in the pier record over the five days before it arrives in La Jolla. A few patterns begin to emerge: the highest anomalies (colored in red and yellow) come from air which has spent several days

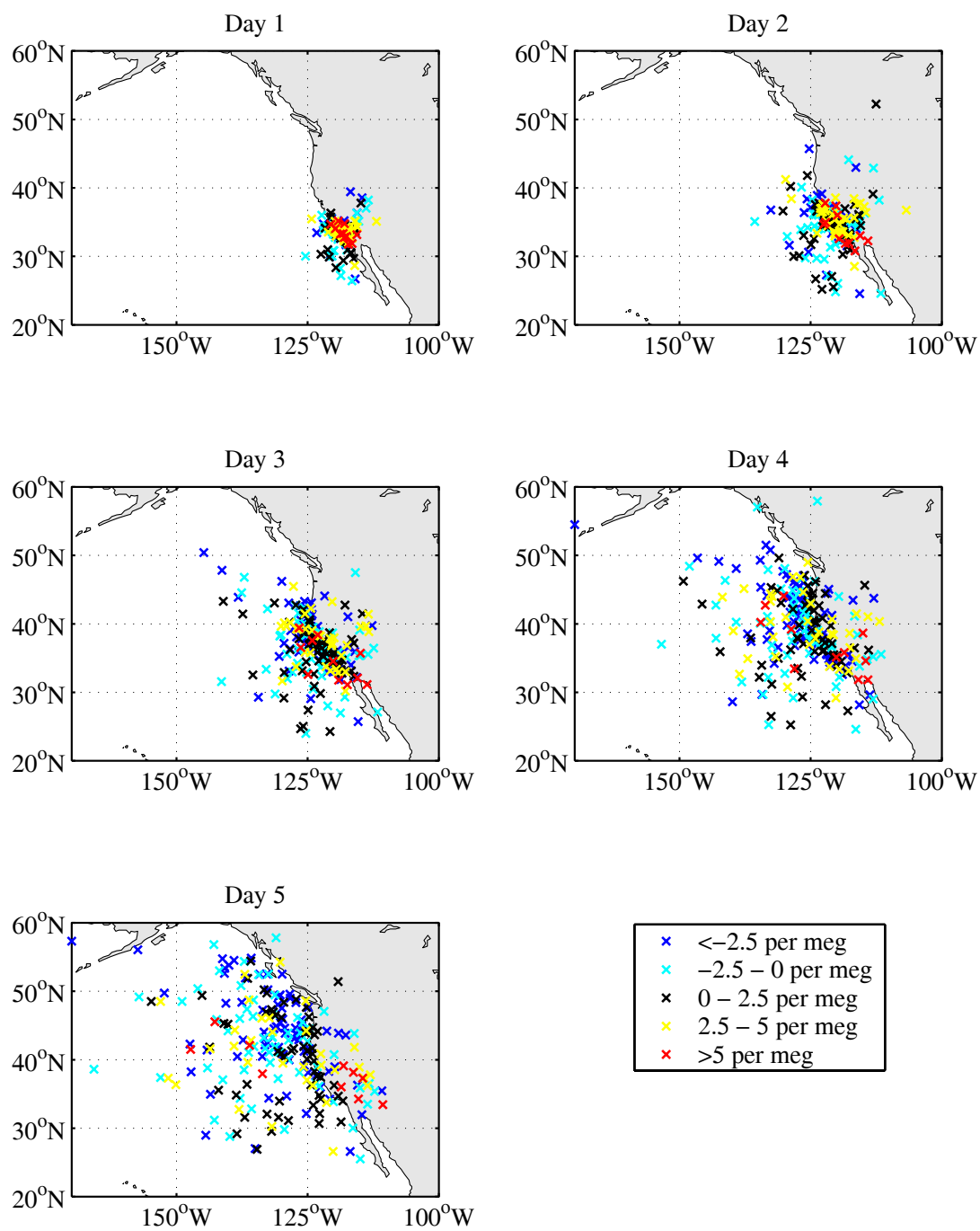
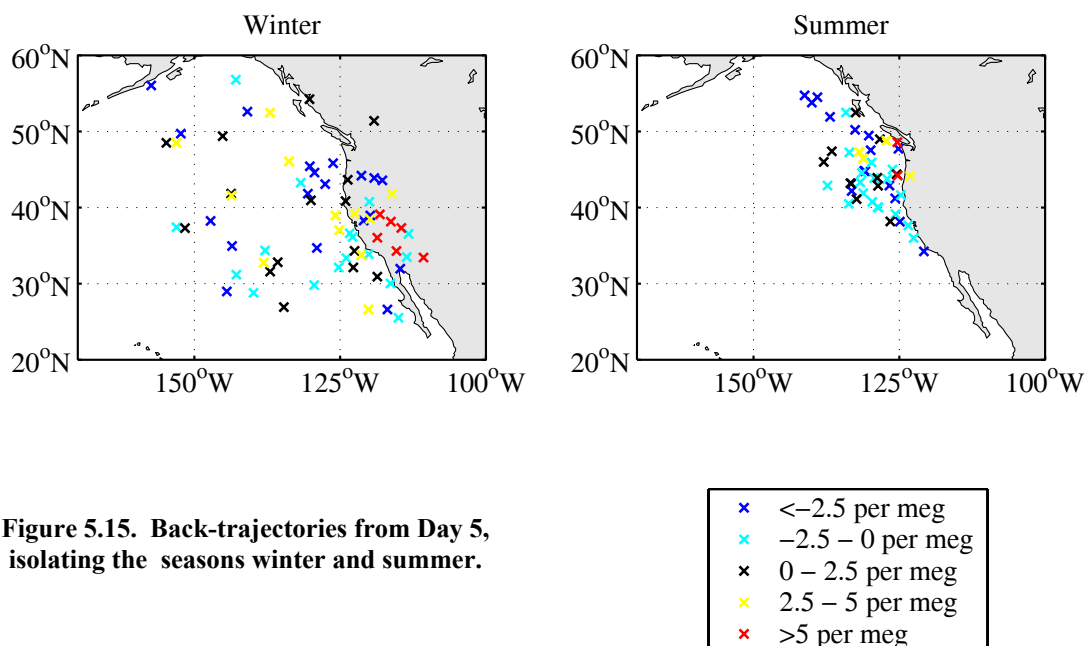


Figure 5.14. Location of air mass 1-5 days before reaching the La Jolla Scripps Pier station for all sample days, color-coded by the size of the anomaly.

along the California coast rather than being advected rapidly towards the station from other areas. Air coming from due south tends to have anomalies between -2.5 and 2.5 per meg but not high anomalies, whereas the air coming from the north and west shows both high and low anomalies.

The observation that the anomalies coming from the south tend to hover around zero is likely due to the smaller annual cycle expected in lower latitudes, as the air-sea heat flux cycle is also small. Any deviations due to variations in air-sea heat flux, the amount of solar radiation received, or air or water temperature is likely to be scaled accordingly. In contrast, air that is near the coast is probably exposed to areas with the largest fluctuations in local Ar/N₂ ratios, both because coastal upwelling causes changes in air-sea heat flux, but also because upwelling areas may cause unexpected changes in N₂ and Ar fluxes due to the origin of the water. As mentioned before, upwelling water tends to be high in nutrients and releases N₂O and N₂ to the atmosphere (Nevison et al. 2004). Upwelling water also has Ar and N₂ signatures of the place where that water initially downwelled, rather than being at equilibrium with local conditions. Just as oceans carry heat from low to high latitudes, they likely carry Ar and N₂. This flux should lead to a small zonal gradient in mean atmospheric $\delta(\text{Ar}/\text{N}_2)$ values whose size depends on the strength of the transport, with high values in equatorial areas and low values at high latitudes. Thus, the origin of local water masses near a station may be just as important as the origin of air masses arriving at the station in understanding both seasonal patterns and anomalies. Air masses that



have spent more time along the coast most likely reflect this variability in the pattern of anomalies.

When the back-trajectories are stratified for season (Fig. 5.15), one can quickly see the seasonal differences in air origin. Whereas the summertime data sample a clear jet of air along the California coast, the wintertime data show air origins from the south as well as the north, and inland as well as from the open ocean and coast. The summertime shows high anomalies from air originating near the Northwest coast and Canadian border. As this is a high upwelling area, it is possible that the anomalies represent supersaturation that comes from mixing (R. Weiss, pers. comm.). Because the slope of the dependence of solubility on temperature is larger for the Ar curve than for the N₂ curve (see Figure 3.1), supersaturation effects from mixing should cause $\delta(\text{Ar}/\text{N}_2)$ to rise.

The winter days with air origins from inland tend to have large positive anomalies. Representing stagnant air, these seven days have an average diurnal cycle of about 2.2 per meg (not shown), more than twice as large as the estimated diurnal cycle of about 1 per meg over the entire data set. Y. Adachi has shown night-time accumulation of Ar near the ground in the desert leading to fractionation of up to 200 per meg (Y. Adachi and R. Keeling, pers. comm.). It is possible that these days are measuring a pooling effect, in which a natural fractionation process over land leads to more Ar near the surface of the earth

5.5 Possible instrumental problems

Possible remaining instrumental problems were discussed in Chapter 4. It is probable that instrumental problems remain due to regular shutdown of the pierline on a weekly basis for use in other research. The mean of any given weekend run or given 24-hour period has a standard deviation of about 2 per meg; the difference between weekends can be much larger. The autocorrelation of the $\delta(\text{Ar}/\text{N}_2)$ residuals in Figure 5.11 supports the conclusion that stopping the instrument for several days is contributing to the jump in concentration: the autocorrelation drops on the order of 3-4 days, increasing again for 5-8 days. This dip corresponds to the average length of a weekend run before the instrument is shut off and is possibly caused by discrepancies in the $\delta(\text{Ar}/\text{N}_2)$ value between the end of one run and the start of the next.

5.6 Conclusions

A record of semi-continuous measurements of $\delta(\text{Ar}/\text{N}_2)$, along with contiguous measurements of $\delta(\text{O}_2/\text{N}_2)$ and CO_2 , now exists for 17 months at the Scripps Pier in La Jolla, CA. This record shows a clear annual cycle of $\delta(\text{Ar}/\text{N}_2)$ at this station, defined to within 0.1 per meg, with the annual mean defined to within 0.2 per meg. It also allows a close look at synoptic variability in the record. The lack of a good explanation for even the largest anomalies in the $\delta(\text{Ar}/\text{N}_2)$ record is a problem that will most likely be resolved with longer datasets and upgrading to a continuous (rather than semi-continuous) measurement system.. Regardless, this unique dataset will serve as a basis for comparison for any other upcoming continuous measurement system. It may also be important in analyzing results and continuing to make improvements in existing flask programs.

The size of the annual cycle in atmospheric $\delta(\text{Ar}/\text{N}_2)$ is within a range of values expected by comparison with estimates based on changes in solubility and seasonal air-sea heat flux estimates. Parallel measurements of CO_2 and $\delta(\text{O}_2/\text{N}_2)$ allow the annual $\delta(\text{O}_2/\text{N}_2)$ cycle to be broken into components due to air-sea heat flux, land biology, and changes in ocean biology and dynamics. Although the strength of these different components has been estimated in long-term records and in model results, no other data set exists where the comparative strength of these components can be broken down so clearly on a seasonal time scale.

In this dataset, the overall ratio between the part of the annual cycle due to ocean dynamics and the part due to air-sea heat transport is smaller than expected

given comparison with other research predicting this ratio. However, it is possible that these data demonstrate changes in the strength of different mechanisms on interannual time scales; in 2004-2005, the annual cycle of ocean heat storage was larger than the long-term mean. This observation may explain why the ratio is low over this period, as the part of the oxygen cycle attributable to air-sea heat flux may be large relative to the amount due to other ocean mechanisms. At this moment, any conclusions about atmospheric $\delta(\text{Ar}/\text{N}_2)$ based on this dataset are primarily restricted to seasonal time scales and anything on interannual time scales is speculative. However, these results give an indication of the importance of these measurements, especially in understanding the strength of different mechanisms on interannual time scales.

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Appendix 1

Determination of interference and nonlinearity correction factors

A1.1. Introduction

The measurements of a particular species in the mass spectrometer are not necessarily the actual concentration values, because of interferences from other gases or other effects. In order to develop fits between mass spectrometer measurements and the true values of the concentration of a species, named the S2 values, we bled gas of known mixtures of CO₂, O₂, and Ar into the working tank of the mass spectrometer and calculated linear relationships between the measured and expected concentrations of particular gases. We used 99% pure CO₂, a mixture of CO₂ and O₂, and a mixture of CO₂ and Ar, bled into two separate working tanks. The mixing ratios of the tanks used are listed in Table A1.1.

Table A1.1 Description of tanks used for bleed tests.

Tank Description	X _{N2}	X _{O2}	X _{Ar}	X _{CO2}
WT for pure CO2 bleeds	0.78084	0.20946	0.00934	0.00035468
WT for CO2:Ar and CO2:O2 bleeds	0.78084	0.20946	0.00934	0.00035348
PURE CO2	0	0	0	1
CO2:Ar MIXTURE	0	0	0.95	0.05
CO2:O2 MIXTURE	0	0.79059	0	20.94100

A1.2. Pure CO₂ bleed test

Using the pure CO₂ gas and measurements of CO₂ on both the mass spectrometer and the Siemens, we were able to look at the effect of CO₂ on the two other species, assuming a linear relationship. The jog heights for all mass spectrometer species as well as interferometer and Siemens measurements are listed in Table A1.2 for each jog associated with a different amount of bleed gas.

CO₂ concentrations are derived from a voltage change on the Siemens instrument which is corrected for changes in the span of the instrument. This span value is determined on a daily basis by comparison with a suite of reference tanks. In order to derive true CO₂ changes, it is necessary to apply a standard cubic correction to both the sample and working tank jogs:

$$CO_{2,S1} = CO_{2,WT} + CO_{2,SPAN} \cdot dv \quad (A1.1)$$

$$\Delta CO_{2,siemens} = poly(CO_{2,S1}) - poly(CO_{2,WT}), \quad (A1.2)$$

$$\text{where } poly(x) = -0.32331x + 0.00028439x^2 + 0.00000032872x^3,$$

and dv is the change in voltage, $CO_{2,SPAN}$ is the span value for the Siemens instrument, and $CO_{2,S1}$ and $CO_{2,WT}$ are intermediate values for the gas sample and working tank

Table A1.2. Jog results bleeding pure CO₂ gas.

Jog #	32/28 S0 per meg	44/28 S0 per meg	40/28 S0 per meg	Siemens volts	Interfer fringes
1	-7.5498	124420	-8.2439	2.3034	-21.5209
2	-5.3248	75690	-5.1026	1.6672	-16.3861
3	-11.2264	182250	-9.2601	3.3450	-31.8505
4	-14.0549	209460	-12.4318	3.8313	-38.5238
5	-15.8688	259670	-18.7736	4.6965	-46.8780
6	-1.8012	46500	-2.9895	0.8559	-7.1075
7	0	0	0	0	0

CO₂ concentrations, respectively, and $\Delta CO_{2,siemens}$ is the final value for the change in CO₂ in a sample as measured on the Siemens instrument.

In order to convert the interferometer O₂ fringe number to $\delta(O_2/N_2)$, it is necessary to account for changes in the span of the instrument as well as to account for interference from CO₂, as shown in the following equation:

$$\Delta(O_2/N_2)_{\text{interf}} = -O_{2,SPAN} \cdot df - 1.1156 \cdot [(CO_{2,WT} + CO_{2,SPAN} \cdot dv) - 363.39] \quad (\text{A1.3})$$

where df is the change in fringe number as measured by the interferometer and $O_{2,SPAN}$ is the interferometer span value.

The formulas for ΔCO_2 and $\Delta(O_2/N_2)$ were taken from the Access database used for the lab flask records. Values for the $CO_{2,SPAN}$ and $O_{2,SPAN}$ were taken from the database of reference tank runs (HILO tank runs) for the days on which the bleed tests were performed. Typical values are 22.7 and 2.73 respectively.

The raw jog heights from the mass spectrometer (labeled as “S0”) are initially corrected by a gain factor g , which accounts for day-to-day variations in span

Table A1.3. Final values bleeding pure CO₂ gas.

Jog #	$\delta(32/28)_{S1}$ (per meg)	$\delta(44/28)_{S1}$ (per meg)	$\delta(40/28)_{S1}$ (per meg)	$\Delta\text{CO}_{2,\text{siemens}}$ (ppm)	$\Delta(\text{O}_2/\text{N}_2)_{\text{interf}}$ (per meg)
1	-7.7008	126910	-8.4087	54.0826	0.3426
2	-5.4312	77200	-5.2046	38.7824	2.4516
3	-11.4509	185890	-9.4453	79.7472	2.1254
4	-14.3360	213640	-12.6804	91.9970	7.9954
5	-16.1862	264860	-19.1491	114.2298	8.8582
6	-1.8373	47430	-3.0493	19.6776	-2.2928
7	0	0	0	7	0

according to the observed differences in the span tank (OS) and the working tank (WT) in order to get what is labeled as the “*SI*” numbers:

$$\delta(44/28)_{S1} = g \cdot \delta(44/28)_{S0} \quad (\text{A1.4})$$

$$\delta(40/28)_{S1} = g \cdot \delta(40/28)_{S0} \quad (\text{A1.5})$$

$$\delta(32/28)_{S1} = g \cdot \delta(32/28)_{S0} \quad (\text{A1.6})$$

The final values (*S1* values for the mass spectrometer, ΔCO_2 for the Siemens, and $\Delta(\text{O}_2/\text{N}_2)$ for the interferometer) are shown in Table A1.3. Grayed values in all charts denote jogs that were eliminated later from the linear fits because they were obvious outliers.

It is expected that the interferometer $\Delta(\text{O}_2/\text{N}_2)$ numbers to be zero within a level of uncertainty because no O_2 was added. The systematic positive bias for this column can be largely explained by the fact that the formula above for CO_2

interference neglects the S1 to S2 correction for CO₂. If the cubic correction had been applied, these values would all be within ± 3 per meg of zero.

Independently of these calculations, I determined the expected $\Delta\delta$ values of the mass spectrometer species based on our knowledge of the composition of the gas in the main tank, the gas in the bleed tank, and the recorded Siemens CO₂ results. It is necessary to adjust for the dilution in other species as the amount of bleed gas introduced to the system varies. The following relationship was used (the full derivation is shown in Section A1.6):

$$\Delta\delta = \frac{f_2}{f_1} \frac{\chi_2}{\chi_1}, \quad (\text{A1.7})$$

where χ_1 and χ_2 are the mixing ratios of chosen species in the working tank and the bleed tank, respectively, and f_1 and f_2 are the volume flow rates for those tanks. The ratio (f_2/f_1) can be found using information on the Siemens CO₂ concentrations:

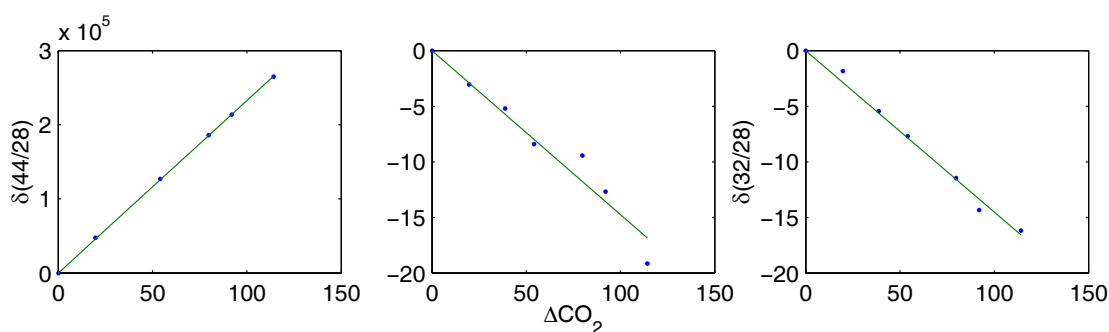
$$\frac{f_2}{f_1} = \frac{\chi_{\text{mix}} - \chi_1}{\chi_2 - \chi_{\text{mix}}}, \quad (\text{A1.8})$$

where χ_1 , χ_2 , and χ_{mix} are the CO₂ mixing ratios of the original tank, the bleed tank, and the resulting mixture as measured on the Siemens CO₂ analyzer. The expected amounts of the species measured on the mass spectrometer based on ΔCO_2 (i.e. $\chi_{\text{mix}} - \chi_1$) and the mixing ratios of the gases are listed in Table A1.4. Since only CO₂ was introduced in the bleed test, the numbers for $\delta(\text{O}_2/\text{N}_2)$ and $\delta(\text{Ar}/\text{N}_2)$ are zero.

I then plotted the relationship between the change in the Siemens CO₂ and the S1 values of $\delta(44/28)$, $\delta(32/28)$, and $\delta(40/28)$ (shown in Figure A1.1). These data

Table A1.4. Mixing ratio and expected values from the mass spectrometer.

Jog #	$\chi_{\text{mix}} - \chi_1$	$\Delta\delta(\text{O}_2/\text{N}_2)$ (per meg)	$\Delta\delta(\text{CO}_2/\text{N}_2)$ (per meg)	$\Delta\delta(\text{Ar}/\text{N}_2)$ (per meg)
1	54.0826	0	152540	0
2	38.7824	0	109390	0
3	79.7472	0	224940	0
4	91.9970	0	259490	0
5	114.2298	0	322210	0
6	19.6776	0	55500	0
7	0	0	0	0

**Figure A1.1. Relationship between the amount of CO₂ added and the values measured on the mass spectrometer.****Table A1.5. Slopes describing the relationship between amount of CO₂ added and the values measured on the mass spectrometer.**

Variable	Slope (per meg/ppm)	Error
m_1	2.3259E+03	2.1219E+01
m_2	-1.4760E-01	1.8200E-02
m_3	-1.4510E-01	1.2700E-02

show a strong linear relationship, with slopes listed in Table A1.5:

$$\delta(44/28)_{S1} = m_1 \cdot \Delta\text{CO}_2, \quad (\text{A1.9})$$

$$\delta(40/28)_{S1} = m_2 \cdot \Delta\text{CO}_2, \text{ and} \quad (\text{A1.10})$$

$$\delta(32/28)_{S1} = m_3 \cdot \Delta\text{CO}_2. \quad (\text{A1.11})$$

A1.3. CO₂ – O₂ bleed test

The initial part of the bleed test analysis remains the same as for the pure CO₂ bleed test. The raw jog heights for all mass spectrometer species as well as interferometer and Siemens measurements are listed in Table A1.6. The raw jog values were then converted to the mass spectrometer S1 values, Siemens CO₂, and interferometer $\delta(\text{O}_2/\text{N}_2)$ as in the first bleed test (Table A1.7).

For the mass spectrometer measurements, it is necessary to adjust for the effects of CO₂ added by the bleed gas in order to compute the change that would have been produced by the other gas (e.g. Ar or O₂) alone:

$$\delta(44/28)_{adj} = \delta(44/28)_{S1} - m_1 \cdot \Delta\text{CO}_2, \quad (\text{A1.12})$$

$$\delta(40/28)_{adj} = \delta(40/28)_{S1} - m_2 \cdot \Delta\text{CO}_2, \text{ and} \quad (\text{A1.13})$$

$$\delta(32/28)_{adj} = \delta(32/28)_{S1} - m_3 \cdot \Delta\text{CO}_2. \quad (\text{A1.14})$$

The adjusted values of the species are listed in the left columns of Table A1.7. Again, the expected values of each of these species were calculated from the Siemens CO₂ concentrations, using the same method as in the CO₂ bleed test (listed in Table A1.8).

Figure A1.2 shows the relationship between the expected amount of $\delta(\text{O}_2/\text{N}_2)$ and the S1 values of $\delta(44/28)$, $\delta(32/28)$, and $\delta(40/28)$. I fit the data with using a linear fit with an intercept of zero:

$$\delta(44/28)_{adj} = p_1 \cdot \delta(\text{O}_2/\text{N}_2)_{\text{expected}}, \quad (\text{A1.15})$$

$$\delta(40/28)_{adj} = p_2 \cdot \delta(\text{O}_2/\text{N}_2)_{\text{expected}}, \quad (\text{A1.16})$$

$$\delta(32/28)_{adj} = p_3 \cdot \delta(\text{O}_2/\text{N}_2)_{\text{expected}}, \quad (\text{A1.17})$$

Table A1.6. Jogs results bleeding the CO₂-O₂ gas mixture.

Jog #	32/28 S0 per meg	44/28 S0 per meg	40/28 S0 per meg	Siemens volts	Interfer fringes
1	41.5415	5388	47.3484	0.1072	-17.6059
2	83.1580	10553	93.5102	0.2139	-34.7129
3	138.2828	17593	28.8851	0.3593	-58.3172
4	191.0451	23847	7.9078	0.4877	-78.9500
5	245.2151	31035	-2.7764	0.6360	-105.0063
6	309.8225	38716	0.4858	0.7977	-132.0300
7	378.2273	46773	-0.9836	0.9704	-162.4443
8	447.3346	54901	-3.2858	1.1462	-190.2744
9	38.7902	5204	-2.6828	0.1038	-18.1004
10	0	0	0	0	0

Table A1.7. Final values and CO₂-adjusted values for bleeding the CO₂-O₂ gas mixture.

Jog #	$\delta(32/28)_{S1}$ (per meg)	$\delta(44/28)_{S1}$ (per meg)	$\delta(40/28)_{S1}$ (per meg)	$\Delta CO_{2, \text{siemens}}$ (ppm)	$\Delta(O_2/N_2)_{\text{interf}}$ (per meg)	$\delta(32/28)_{\text{adj}}$ (per meg)	$\delta(44/28)_{\text{adj}}$ (per meg)	$\delta(40/28)_{\text{adj}}$ (per meg)
1	42.3723	5496	48.2953	2.4650	45.3931	42.7318	-264	48.6608
2	84.8211	10764	95.3804	4.9255	89.4355	85.5393	-746	96.1107
3	141.0484	17945	29.4628	8.2898	150.2535	142.2573	-1427	30.6919
4	194.8660	24324	8.0659	11.2751	203.3790	196.5102	-2025	9.7376
5	250.1194	31656	-2.8319	14.7340	270.8266	252.2680	-2777	-0.6473
6	316.0190	39491	0.4956	18.5241	340.5751	318.7203	-3800	3.2422
7	385.7918	47709	-1.0033	22.5925	419.3115	389.0865	-5091	2.3467
8	456.2813	55999	-3.3516	26.7540	490.9042	460.1829	-6527	0.6155
9	39.5660	5308	-2.7365	2.3871	46.8318	39.9140	-271	-2.3825
10	0	0	0	0	0	0	0	0

Table A1.8. Mixing ratio and expected values from the mass spectrometer.

Jog #	$\chi_{\text{mix}} - \chi_1$	$\Delta\delta(O_2/N_2)$ (per meg)	$\Delta\delta(CO_2/N_2)$ (per meg)	$\Delta\delta(Ar/N_2)$ (per meg)
1	2.4646	44.5044	6985	0
2	4.9251	88.9302	13958	0
3	8.2894	149.6749	23493	0
4	11.2747	203.5770	31953	0
5	14.7336	266.0349	41757	0
6	18.5237	334.4729	52498	0
7	22.5921	407.9409	64030	0
8	26.7536	483.0932	75826	0
9	2.3867	43.0990	6765	0
10	0	0	0	0

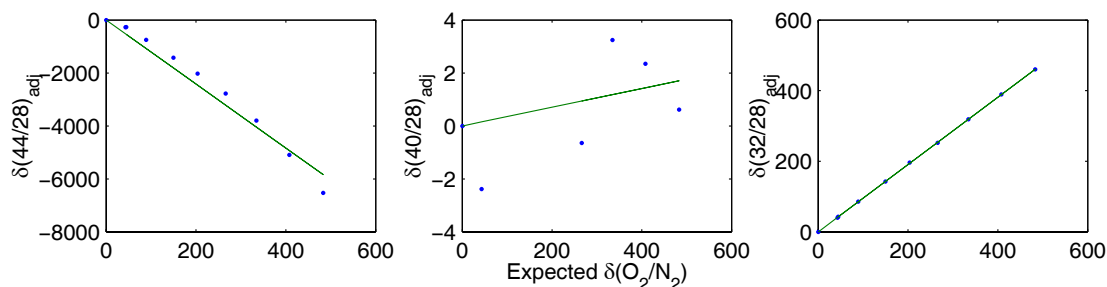


Figure A1.2. Relationship between the expected mass spectrometer measurement of the amount of $\delta(\text{O}_2/\text{N}_2)$ added and the values measured on the mass spectrometer.

Table A1.9. Slopes describing the relationship between the expected mass spectrometer measurement of the amount of $\delta(\text{O}_2/\text{N}_2)$ added and the values measured on the mass spectrometer.

Variable	Slope (per meg/ppm)	Error
p_1	-1.2089E+01	1.8713E+00
p_2	3.5000E-03	1.0600E-02
p_3	9.5330E-01	6.2000E-03

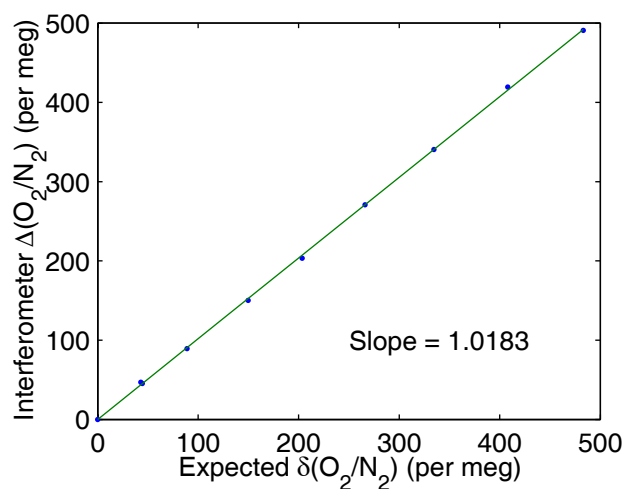


Figure A1.3. Linear fit between the expected $\delta(\text{O}_2/\text{N}_2)$ values and measured Interferometer $\delta(\text{O}_2/\text{N}_2)$ values testing the O_2 span calculations.

The values of the slopes are listed in Table A1.9.

This bleed test also provides a check on the O₂ span of the interferometer. A plot of the expected $\delta(\text{O}_2/\text{N}_2)$ against the interferometer values shows that the points are not quite exact. The fit (shown Figure A1.3) demonstrates a small discrepancy. The test thus confirms the interferometer span calibration to within 2%. It also confirms the interpretation of the Siemens jog heights to this level.

A1.4. CO₂ – Ar bleed test

The procedure for the CO₂ – Ar bleed test exactly follows the procedure for the CO₂ – O₂ bleed test. The raw jog heights for all mass spectrometer species as well as interferometer and Siemens measurements are listed in Table A1.10. The raw jog values were then converted to the mass spectrometer S1 values, Siemens CO₂, and interferometer $\delta(\text{O}_2/\text{N}_2)$ as in the first bleed test (Table A1.11). The mass spectrometer measurements were again adjusted for the effects of CO₂ added by the bleed gas, using Equations 12-14 (right columns of Table A1.11), and then the expected values were calculated using the same method as in the CO₂ bleed test (Table A1.12). I then fit the relationship between the expected amount of $\delta(\text{O}_2/\text{N}_2)$ and the S1 values of $\delta(44/28)$, $\delta(32/28)$, and $\delta(40/28)$ shown in Figure A1.4:

$$\delta(44/28)_{adj} = q_1 \cdot \delta(\text{Ar}/\text{N}_2)_{\text{expected}}, \quad (\text{A1.18})$$

$$\delta(40/28)_{adj} = q_2 \cdot \delta(\text{Ar}/\text{N}_2)_{\text{expected}}, \quad (\text{A1.19})$$

$$\delta(32/28)_{adj} = q_3 \cdot \delta(\text{Ar}/\text{N}_2)_{\text{expected}}, \quad (\text{A1.20})$$

The values of the slopes are listed in Table A1.13.

Table A1.10. Jog results bleeding the CO₂-Ar gas mixture.

Jog #	32/28 S0 per meg	44/28 S0 per meg	40/28 S0 per meg	Siemens volts	Interfer fringes
1	3.2800	8255	7158	-0.2531	39.0136
2	0.8941	12692	10965	-0.1635	52.8202
3	0.0508	5462	4760	-0.3086	23.1159
4	1.2740	1387	1180	0.0257	0.7525
5	-0.0913	2202	1928	0.0431	5.8219
6	-1.4722	3712	3297	0.0746	8.8072
7	1.9626	6768	5953	0.1360	14.7705
8	-1.6177	10674	9345	0.2144	21.2190
9	0	0	0	0	0

Table A1.11. Final values bleeding the CO₂-Ar gas mixture.

Jog #	$\delta(32/28)_{S1}$ (per meg)	$\delta(44/28)_{S1}$ (per meg)	$\delta(40/28)_{S1}$ (per meg)	$\Delta CO_{2,siemens}$ (ppm)	$\Delta(O_2/N_2)_{interf}$ (per meg)	$\delta(32/28)_{adj}$	$\delta(44/28)_{adj}$	$\delta(40/28)_{adj}$
1	3.3456	8420	7302	3.7950	-110.8891	3.9020	-497.0668	7302
2	0.9120	12946	11184	5.8629	-150.9297	1.7716	-830.4660	11185
3	0.0519	5571	4855	2.5162	-66.0026	0.4208	-340.9791	4856
4	1.2995	1415	1204	0.5895	-2.7144	1.3859	29.6647	1204
5	-0.0932	2246	1967	0.9898	17.0207	0.0519	-79.6142	1967
6	-1.5017	3786	3363	1.7132	-25.9879	-1.2505	-238.7079	3363
7	2.0019	6904	6072	3.1272	-43.8641	2.4604	-443.8446	6073
8	-1.6500	10888	9531	4.9378	-63.5034	-0.9261	-714.2203	9532
9	0	0	0	0	0	0	0	0

Table A1.12. Mixing ratio and expected values from the mass spectrometer.

Jog #	$\chi_{mix} - \chi_1$	$\Delta\delta(O_2/N_2)$ (per meg)	$\Delta\delta(CO_2/N_2)$ (per meg)	$\Delta\delta(Ar/N_2)$ (per meg)
1	3.7950	0	10813	7776
2	5.8629	0	16706	12013
3	2.5162	0	7169	5155
4	0.5895	0	1680	1208
5	0.9898	0	2820	2028
6	1.7132	0	4881	3510
7	3.1272	0	8911	6407
8	4.9378	0	14070	10117
9	0	0	0	0

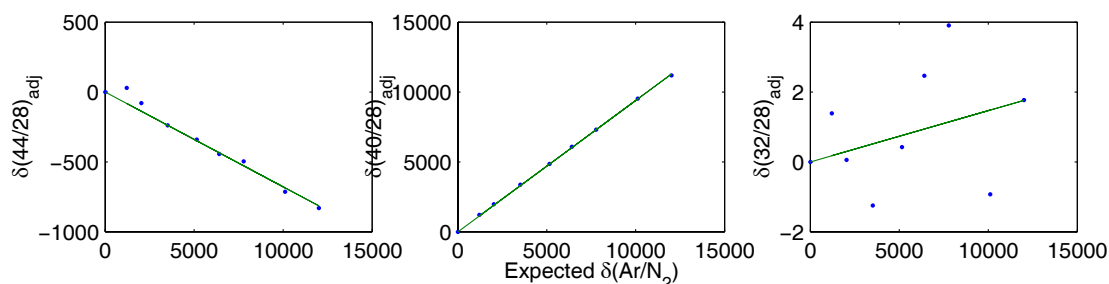


Figure A1.4. Relationship between the expected mass spectrometer measurement of the amount of $\delta(\text{Ar}/\text{N}_2)$ added and the values measured on the mass spectrometer.

Table A1.13. Slopes describing the relationship between the expected mass spectrometer measurement of the amount of $\delta(\text{Ar}/\text{N}_2)$ added and the values measured on the mass spectrometer.

Variable	Slope (per meg/ppm)	Error
q_1	-6.7800E-02	1.5600E-02
q_2	9.3920E-01	1.2700E-02
q_3	1.4664E-04	3.0000E-04

A1.5. Development of S2 calculations

We now have a matrix of 9 values that lets us adjust the mass spectrometer S1 values compute actual molecular abundances on the mass spectrometer, which we will refer to here as the S2 scale.

If we assume that the effects of $\delta(\text{O}_2/\text{N}_2)$ and $\delta(\text{Ar}/\text{N}_2)$ on $\delta(44/28)$ are actually not real (in other words, that the slopes p_3 and q_2 should in fact be zero), then the calculation of the S2 mass spectrometer values can be described by the following equations:

$$\delta(40/28)_{s2} = \left(\frac{1}{q_2} \right) \delta(40/28)_{s1} - \left(\frac{m_2}{q_2} \right) \Delta CO_2 \quad (\text{A1.21})$$

$$\delta(32/28)_{S2} = \left(\frac{1}{p_3}\right) \delta(32/28)_{S1} - \left(\frac{m_3}{p_3}\right) \Delta CO_2 \quad (A1.22)$$

This suggestion assumes that the gain factor is already included in the S1 values and therefore does not need to appear in the matrix. Relating the S2 values to ΔCO_2 is better than relating them to $\delta(CO_2/N_2)$ because there are long-term stability standards in CO_2 mole fraction but not in $\delta(CO_2/N_2)$.

A1.6. A note on the derivation of the expected Mass Spectrometer ratios

We calculated the expected values of the mass spectrometer species based on our knowledge of the composition of the gas in the main tank, the gas in the bleed tank, and the recorded Siemens CO_2 results. We had to adjust for the dilution in other species as the amount of bleed gas introduced to the system varies. The development of this relationship is given below.

The mixing ratio of a given species in the mixture of tank gas and bleed gas is the following:

$$\chi_{mix} = \frac{f_1 \chi_1 + f_2 \chi_2}{f_1 + f_2} = \frac{\chi_1 + \frac{f_2}{f_1} \chi_2}{1 + \frac{f_2}{f_1}}, \quad (A1.23)$$

where χ_1 , χ_2 , and χ_{mix} are the respective mixing ratios of a particular species of the tank gas, bleed gas, and resultant mixture, and f_1 and f_2 are the volume flows of the two gases. Assuming that we are introducing no nitrogen into the system through the

bleed gas, we can write the ratio of the mole fractions of a given species (such as argon) to N_2 as the following:

$$\begin{aligned}
 \left(\frac{Ar}{N_2} \right)_{mixture} &= \frac{\chi_{Ar}}{\chi_{N_2}} \\
 &= \frac{\chi_1(Ar) + \frac{f_2}{f_1} \chi_2(Ar)}{1 + \frac{f_2}{f_1}} \\
 &= \frac{\chi_1(N_2)}{\chi_1(N_2) + \frac{f_2}{f_1} \chi_2(N_2)} \\
 &= \left(\frac{Ar}{N_2} \right)_{initial} + \frac{f_2}{f_1} \frac{\chi_2(Ar)}{\chi_2(N_2)}
 \end{aligned} \tag{A1.24}$$

The change in the delta value δ of the species can be written as follows:

$$\Delta\delta = \frac{\left(\frac{Ar}{N_2} \right)_{mixture} - \left(\frac{Ar}{N_2} \right)_{initial}}{\left(\frac{Ar}{N_2} \right)_{initial}} = \frac{\frac{f_2}{f_1} \frac{\chi_2(Ar)}{\chi_2(N_2)}}{\left(\frac{Ar}{N_2} \right)_{initial}} = \frac{f_2}{f_1} \frac{\chi_2}{\chi_1}. \tag{A1.25}$$

We can solve for (f_2/f_1) from Equation (1) in terms of the CO_2 concentration measured on the interferometer:

$$\frac{f_2}{f_1} = \frac{\chi_{mix} - \chi_1}{\chi_2 - \chi_{mix}}, \tag{A1.26}$$

where χ_1 , χ_2 , and χ_{mix} are the CO_2 mixing ratios of the original tank, the bleed tank, and the resulting mixture as measured on the Siemens CO_2 analyzer.

Appendix 2

Timeline of instrument development

A2.1 Setup changes during development

1. Tests on roofline began 09/03. Described in lab notebook. Used ¼" Synflex tubing on a tower on the roof, snaked tubing down into interferometer room.
2. Pierline began 11/14/04. Assumed use of existing lines of ½" Synflex tubing. Intake located near east end (shore-side) of pier.
3. Stopped use of fridge on 12/15/2003. Subsequently relying only on -80°C chiller to get rid of water in the sample air.
4. Aspirator installed 1/20/04. Borrowed from Cayan's group.
5. Mass spec reference tank exhausted and replaced on 2/4/2004. No diptube on either old or new tank.
6. 3 ¼" Synflex tubing lines were installed between 3/8/04-3/12/04. Stopped using ½" lines for any pierline tests. Two dedicated lines for the pierline setup

lead into the interferometer lab, third line plumbed to go into Tim's equipment across the hall.

7. Mass Spec tuned on 5/5/04.
8. Hi Span exhausted and replaced on 5/7/04. No diptube in either old or new tank.
9. Moved cold traps to before pumps on 5/14/04. Was having significant problems with a failure rate of the pressure controller and the pumps associated with water and salt entering the system. In this setup, much of the water/particulates in the air freezes out before reaching the pump.
10. Swapped 1½" OD cold traps in for 1" OD cold traps on 5/21/04 in order to extend the length of time before cold traps need to be changed. The 1" OD traps were sometimes lasting only 22 hours before freezing up; the larger traps last almost twice as long.
11. Introduced first diptube pierline working tank on 5/24/05 when the last tank was exhausted and needed to be replaced. Diptube tanks described in Section 4.3.2.
12. Introduced two solenoid 3-port, 2 position valves and timer on 5/30/04 in order to switch automatically between cold traps in order to enhance trap lifetime. Using only one pierline, one valve was located before the two traps, one valve behind the traps. Both would switch automatically at the same time in order to switch the pierline from one trap to the other.

13. Phased out trap switch and returned to two-line system on 7/28/05, each line with its own dedicated trap. As of this date, the system looks like the description and schematic in Chapter 4. This system of two lines sampled every other hour has two advantages: can test changes in one line against the other (i.e. in testing a solar shield against the aspirator), and also can help recognize and diagnose problems in one line more rapidly.
14. Power failure on 11/15/04 18:30. Machine shut down, not fully operational again through the next day.
15. Mass spec reference tank exhausted and replaced on 12/10/04 12:00. Neither old nor new tank has a diptube.
16. Low span tank exhausted and replaced on 1/28/05. Old tank does not have diptube; new tank does have diptube. Note: Neither high nor oxspan tanks have diptubes.
17. Oxspan tank exhausted and replaced on 2/24/04. Neither old nor new tanks have diptubes. New working tanks for flask operation are installed; both have diptubes.

A2.2 Notes on particular tests

A2.2.1 Roofline tests

17-09-03 2 days LowWT leaks, failed HILO
 29-09-03 2 days LowWT leaks
 03-10-03 4 days LowWT
 24-10-03 2 days LowWT
 31-10-03 4 days LowWT
 07-11-03 4 days LowWT Have record of boiler switches during this time

