Chapter 4

Shipboard Atmospheric $O_2$ Measurements in the Equatorial Pacific
Abstract

I have used the VUV instrument described in Chapter 3 to measure atmospheric O$_2$ in the eastern equatorial Pacific between April 18 and May 20, 1998, aboard the NOAA ship Ka'imimoana. In this chapter, I present results from the atmospheric O$_2$ measurements and from concurrent atmospheric CO$_2$, dissolved O$_2$, and meteorological observations. The VUV measurements from this cruise agree with laboratory analyses of concurrent shipboard and background-station flask samples, and represent both the first successful field-based measurements of atmospheric O$_2$ and the first extensive measurements of atmospheric O$_2$ in the equatorial region. These measurements reveal a southward-increasing latitudinal trend and significant small-scale variability in atmospheric O$_2$. Variations in atmospheric O$_2$ near the Equator correlate with wind-direction, air-mass properties, and air-mass origins as determined by back-trajectory analyses. Thus, the observations in this region appear to predominantly reflect variable sampling across the relatively strong interhemispheric O$_2$ gradient rather than local variations in air-sea O$_2$ flux. On a regional scale, the observed O$_2$ concentrations are close to the predictions of the HAMOCC3.1-TM2 model, but are significantly lower than those of POBM-TM2 and LLOBM-TM2. The model-observation differences may result from errors in the amount of equatorial O$_2$ and CO$_2$ outgassing in these models, the lack of a seasonal marine O$_2$ rectifier in these models, or interannual variability in the observations associated with the large El Niño event during this cruise.
4.1 Introduction

The modeling results shown in Chapter 2 predict that the equatorial Pacific is a region of significant spatial variation in atmospheric O$_2$. As discussed in Section 2.2, the upwelling of DIC and preformed nutrients and the strong air-sea heat fluxes lead to a net outgassing of O$_2$ and CO$_2$ from this region. Two of the models, POBM-TM2 and LLOBM-TM2, predict peaks on the order of 10 per meg in the derived tracer APO between 20°N and 20°S, while the third model, HAMOCC3.1-TM2, predicts a smaller and southward-shifted APO peak (see Figure 2.5). In Chapter 2, I attributed much of the difference between models to the inclusion or exclusion of the marine O$_2$ rectifier, but also speculated that all of the models' equatorial predictions were sensitive to their overprediction of low-latitude deep-water upwelling. It is not possible to test models near the Equator using the available background O$_2$ flask data because of gaps in the sampling network. The measurements presented in this chapter represent a step toward filling in these gaps, and provide direct evidence of the controls on low-latitude atmospheric O$_2$ over a range of time and space scales.

The NOAA ship Ka'imimoana is dedicated to servicing the Tropical Atmosphere Ocean (TAO) array of moored buoys. These buoys are located within 8° of the Equator between 135°E and 95°W longitude in the Pacific (Figure 4.1), and provide temperature, salinity, current, and wind data that are critical to the prediction and observation of El Niño climate variability [McPhaden, 1999]. Ka'imimoana visits each of these buoys approximately twice a year, thus providing an excellent platform
Figure 4.1 Map showing the cruise track for Ka'imimoana leg GP2-98. The dark line shows the actual ship track, which diverted from the intended track (light line), to capture a drifting buoy. The circles represent the locations of the TAO array buoys. Figure obtained from http://rho.pmel.noaa.gov/atlasrt/kaimi.html.

for conducting repeatable geochemical surveys of this region. The data presented here are from leg GP2-98, which departed San Diego on April 18, 1998, included maintenance along the 125°W and 145°W buoy lines, and then returned to Honolulu on May 20. As the ship track in Figure 4.1 shows, after reaching 2°S, 125°W the ship diverted from its scheduled course to pursue a buoy that had broken free from its anchor and was steadily drifting westward. After capturing this buoy near 3°N, 147°E, the ship returned to 2°S, 140°W and continued north along the 140°W buoy line. The two southernmost turnaround points were within or just south of the
Intertropical Convergence Zone (ITCZ). Material presented in Section 4.4 below indicates that both the position of the ship relative to the ITCZ at these times, and the latitudinal history of the sampled air during the rest of the cruise had significant consequences for the measured O₂ concentrations.

I have combined these shipboard O₂ and CO₂ data, to calculate APO concentrations as for the flask data in Chapter 2. The resulting APO values for this particular region and time of year can be directly compared to coupled ocean-atmosphere models that explicitly resolve the seasonal cycle, such as HAMOCC3.1-TM2. Also, because the seasonal cycle in atmospheric O₂ is relatively small at low-latitudes, annual-mean APO values can be estimated from these observations and used to constrain aseasonal models. Material presented in Section 4.5 shows that these comparisons are relatively favorable for HAMOCC3.1-TM2, but that POBM-TM2 and LLOBM-TM2 appear to overpredict equatorial APO concentrations. This discrepancy could result from the presence of too much low-latitude outgassing of O₂ and CO₂, or the lack of seasonal rectification effects in these models. However, because all of the models represent climatologically average conditions, their comparisons to the observations may also be impacted by the large El Niño event that took place up to and during this cruise.

4.2 Atmospheric O₂ and CO₂ Data

The VUV instrument drew air from one of two sample lines: on a bow mast approximately 20 m above the water and at a high point on the aft control tower.
Figure 4.2  Hourly-mean concentrations of atmospheric O$_2$ and CO$_2$ plotted versus time. The O$_2$ and CO$_2$ vertical axes are scaled to be equivalent in moles. The ticks on the x-axis correspond to midnight local time and are labeled with the date of the following day. The large symbols represent 5-liter flask samples collected aboard the ship and analyzed on the Scripps interferometer. The O$_2$ values were determined as described in Section 3.4 from data similar to that in Figure 3.8. After April 30, the O$_2$ values have an uncertainty of $\pm$ 3 per meg. Prior to April 30, the O$_2$ values have been shifted down by 68 per meg to account for an independently-quantified fractionation effect and consequently have a higher uncertainty of $\pm$ 10 per meg (see Section 3.4.3). The overall accuracy of the CO$_2$ measurements is $\pm$ 0.4 ppm.

approximately 15 m above the water. I measured CO$_2$ in this same gas stream using a non-dispersive infrared gas analyzer, as described in Chapter 3. I manually switched between the fore and aft sample lines according to the prevailing winds to avoid sampling air from the engine exhaust stacks located amidships. However, it was still necessary to filter the data for times when exhaust air did occasionally get in the
sample lines, which were easily identifiable by strong O₂ and CO₂ excursions. I show the resulting O₂ and CO₂ data, averaged over hourly periods and plotted versus time, in Figure 4.2. I have adjusted the O₂ data before April 30 to account for fractionation effects, as described in Section 3.4.3. The gaps in this figure correspond to times when I was modifying and testing the instrument to quantify and eliminate these effects.

The large symbols in Figure 4.2 represent six 5-liter flask samples that I collected on the ship, and which were analyzed by E. McEvoy on the Scripps O₂ laboratory interferometer. The flask sample taken on May 12 is 8 per meg higher than the adjacent VUV O₂ values. However, because the O₂:CO₂ ratio in this flask sample is also anomalous (see Figure 4.6 below), it is likely that a problem during flask collection or storage, rather than VUV instrument error, is the cause of this discrepancy. The other three flasks that overlap VUV data give O₂ values that are in good agreement with the in situ measurements, and do not reveal any consistent offsets. The differences of ± 2-3 per meg are within the combined errors for these two techniques. One of these flasks overlaps the early fractionation-adjusted VUV data, however I calculated this adjustment independent of the flask result. The two flask samples taken when continuous data are not available give O₂ values that appear reasonable in comparison to the nearby VUV data and trends.

Figure 4.3 shows the same continuous data plotted versus latitude. Together, Figures 4.2 and 4.3 show coherent O₂ variations on time scales of hours to weeks and space scales of tens to hundreds of kilometers. I will briefly describe these variations
Figure 4.3 Hourly-mean shipboard O₂ and CO₂ plotted versus latitude. Data is the same as in Figure 4.2 for (a) O₂ concentrations and (b) CO₂ concentrations. The diamonds represent measurements on flask trios collected on April 23rd and May 6th at La Jolla (LJO), on May 4th and 19th at Samoa Observatory (SMO), and on May 12th and 26th at Cape Kumukahi (KUM).

Here then discuss their likely causes in more detail in the following sections. For the first several days steaming south from San Diego, O₂ concentrations increased by ~10 per meg and CO₂ concentrations decreased by ~2 ppm. However, at around 25°N these trends shifted as CO₂ leveled off and O₂ began a slight decrease (Figure 4.3). Then, on the morning of April 23 near 14°N, these trends underwent another larger shift as O₂ concentrations began a steady climb, and CO₂ a steady decline, that continued all the way to the Equator. On the first pass across the Equator along...
125°W, O₂ concentrations increased by a total of ~10 per meg and CO₂ decreased by ~1 ppm as indicated by the flask sample taken at 2°S on April 29 (Figure 4.2). I observed a much larger jump across the Equator on the second pass just over a week later and 15 degrees further west, when O₂ increased by ~30 per meg and CO₂ decreased by ~3 ppm. These concentration excursions along 145°W longitude actually diminished by a factor of 2 by the time the ship reached its southernmost point at 2°S. From this point to the end of the cruise in Honolulu, I observed the reverse of the general trends seen earlier from San Diego to the Equator. Again at
around 14°N I observed a leveling-off of CO₂ and a shift to slightly increasing O₂ concentrations.

The overall latitudinal gradients shown in Figure 4.3 are consistent with the larger scale interhemispheric differences in O₂ and CO₂ at this time of year. I have also included points in this figure representing background-station flask trios collected near the beginning of the cruise at La Jolla, California (LJO), near the middle of the cruise at American Samoa (SMO), and near the end of the cruise at Cape Kumukahi, Hawaii (KUM). The LJO and KUM measurements agree well with the adjacent continuous values, and the southward trends are generally in line with the SMO concentrations at 14°S. Figure 4.4 compares the shipboard O₂ and CO₂ data to flask data from SMO and LJO over the past 5 years. This figure shows that the interhemispheric O₂ and CO₂ gradients reverse every summer and winter, and that this cruise happened to take place at the time of year with the greatest interhemispheric O₂ and CO₂ differences.

The observed latitudinal CO₂ gradient resulted from a combination of terrestrial respiration occurring during the boreal winter preceding this cruise and the large industrial source in the northern hemisphere. The observed latitudinal O₂ gradient was oppositely affected by the corresponding industrial and terrestrial O₂ sinks in the north. In addition, the O₂ gradient was steepened by oceanic outgassing in the southern hemisphere resulting from net productivity, and by oceanic ingassing in the northern hemisphere resulting from enhanced vertical mixing of O₂-depleted waters, which occurred throughout the boreal winter.
An indication of the relative terrestrial and oceanic contributions to the latitudinal gradients presented here can be obtained by directly comparing the O\textsubscript{2} and CO\textsubscript{2} data. Figure 4.5 shows a plot of the observed O\textsubscript{2} versus CO\textsubscript{2} concentrations. These data correlate well, with an average slope of -2.3 mol O\textsubscript{2}:mol CO\textsubscript{2}. By comparison, fossil fuel burning alone would produce a slope of around -1.4 mol O\textsubscript{2}:mol CO\textsubscript{2} [Keeling, 1988], and terrestrial exchange would produce a slope of around -1.1 mol O\textsubscript{2}:mol CO\textsubscript{2} [Keeling, 1988; Severinghaus, 1995]. The more negative observed slope reflects the influence of oceanic O\textsubscript{2} exchange, which has very little
Figure 4.5 Hourly-mean shipboard O₂ versus CO₂ concentrations. The line and reported slope are from a least squares fit to the shipboard data. The O₂ and CO₂ vertical axes are scaled to be equivalent in moles.

corresponding CO₂ flux. The value of -2.3 mol O₂:mol CO₂ is consistent with approximately equal oceanic and terrestrial influences on the interhemispheric O₂ gradient at this time.

The tight relationship between the shipboard O₂ and CO₂ observations is further illustrated in Figure 4.6. The one time when O₂ does not closely track CO₂ at a consistent ratio is from April 20 to around April 24, as the ship steamed from 25°N to 13°N near 120°W longitude. During this period, O₂ dropped by ~10 per meg while CO₂ remained fairly constant. Although instrument error must be considered for this
period of known fractionation problems, the O₂ values determined from the adjusted VUV signal on April 23 are very close to the independently determined flask concentration. An alternative explanation is that this O₂ divergence represents the influence of northern oceanic O₂ uptake, as discussed below in Section 4.4.

4.3 Dissolved O₂ Data

In addition to atmospheric O₂ and CO₂, I also measured the dissolved oxygen concentration of surface waters. I collected water samples four times per day from the
Figure 4.7 Dissolved O$_2$ measurements made using the Winkler titration method. Samples were collected from the underway sample line and from surface CTD bottles. Plotted versus (a) time and (b) latitude.

...ship's underway sampling system, and from the surface bottle on every CTD cast. The purpose of these samples was to explore possible regional correlations between surface-water and atmospheric O$_2$, and to aid in the interpretation of the atmospheric measurements with respect to interannual variability in the equatorial Pacific. Resolving correlations between atmospheric O$_2$ and diurnal or sharp-frontal surface O$_2$ variations, if they existed, would require a much higher dissolved-O$_2$ sampling frequency. I analyzed the water samples using a Winkler titration apparatus [Carpenter, 1965] obtained from the Scripps Oceanographic Data Facility, which has a
potential precision of 0.01 ml l⁻¹. Of 125 underway samples and 26 CTD samples collected, I have discarded 23 either because bubbles were inadvertently introduced during pickling or storage, or because of problems with sampling from the underway line while the ship was on station. The dissolved O₂ concentrations for the remaining 128 samples are shown in Figure 4.7.

The agreement between the underway line and the CTD samples appears good, and as expected the O₂ concentration is less in warmer water, where O₂ is less soluble. Figure 4.8 shows the dissolved O₂ saturation anomaly (ΔO₂). These data reveal a moderate amount of scatter that appears to increase close to the Equator. More
Figure 4.8 Dissolved O$_2$ anomaly (ΔO$_2$) plotted versus (a) time and (b) latitude.

importantly, they indicate that the eastern equatorial Pacific was consistently supersaturated during the time of this cruise. This is not normally the case. Figure 4.9 compares the ΔO$_2$ measurements from this cruise to those made by NOAA scientists along 125°W and 140°W during the US JGOFS Equatorial Pacific Process Study (EQPAC) cruises [Wanninkhof et al., 1995] in the boreal spring and fall of 1992, and to monthly ΔO$_2$ values for this region from the climatology of Najjar and Keeling [1997]. The fall EQPAC measurements were made during post-El Niño conditions, and show a strong understaturation in O$_2$ along the Equator that reflects local upwelling produced by Ekman divergence in this region. In contrast, the spring
EQPAC measurements were made during a moderate El Niño, when this upwelling was shut off. Similar to my observations, these spring El Niño data lack a strong undersaturation at the Equator.

However, the 1992 El Niño $\Delta O_2$ values are still lower than I observed, possibly reflecting the fact that the 1997-98 El Niño event was much larger than the one in 1992 (see Section 4.6 below). Overall, these previous measurements indicate that the variability in my dissolved $O_2$ data is not uncommon. As illustrated by Feely et al. [1994] and Murray et al. [1994], such variability can be produced by the passage of tropical instability waves. The climatology of Najjar and Keeling [1997] is based on
Figure 4.9  Dissolved O$_2$ anomaly (ΔO$_2$) compared to measurements during the 1992 EQPAC cruises [Wanninkhof et al., 1995] and the climatology of Najjar and Keeling [1997]. The spring EQPAC measurements were made during a moderate El Niño, while the fall measurements were made during non-El Niño conditions.

Over 90 years of observations, and thus smooths over these waves and any interannual variability. This climatology predicts a general undersaturation of O$_2$ near the Equator, indicating either that the equatorial dip during non-El Niño times is on average more persistent than the supersaturation during El Niños, or an aliasing of non-El Niño periods during generation of the climatology. The saturation levels observed during this cruise along 125°W are closer to the climatology values for
140°W, again possibly reflecting the vast amount of warm, O$_2$-rich waters pushed eastward during the 1997-98 El Niño.

The coherent dip in ∆O$_2$ observed on May 1$^{st}$ corresponds to a northward pass across the Equator and may be a sign of a small amount of renewed local upwelling. However, it is not possible to find any correspondence between the small-scale ∆O$_2$ variations in Figure 4.8 and the atmospheric O$_2$ variations in Figures 4.2 and 4.3. It is clear that at least during this cruise, the equatorial O$_2$ source was too homogenous relative to the interhemispheric atmospheric gradient to imprint strong signals on the atmosphere.

### 4.4 Origin of Sampled Air

Manning and Keeling [1994] found that the aliasing of meridional gradients at MLO was a significant source of observed O$_2$ variability, and predicted that this effect would be greater at lower latitudes. The indication from Figures 4.3-4.5, that selective sampling across the strong interhemispheric gradient was the dominant source of variability in these measurements, confirms their prediction and is borne out by further meteorological analyses. To help identify the origin of the sampled air, I have calculated 72-hour back-trajectories for daily ship locations using the HYbrid Single-Particle Lagrangian Integrated Trajectory model version 4 (HYSPLIT4), developed by the NOAA Air Resources Laboratory [HYSPLIT4, 1997; Draxler and Hess, 1998]. For input fields, this model uses 1° meteorological analyses from the National Centers for Environmental Prediction. These analyses are based on a global set of
Figure 4.10 Back-trajectories calculated using the HYSPLIT4 model [HYSPLIT4, 1997; Draxler and Hess, 1998]. Trajectories were run for 72 hours, and the symbols are plotted every 12 hours UT. The end points for the trajectories (stars) correspond to actual ship positions, and are labeled in local time to facilitate comparison to the other figures.

observations, which over the ocean consist of satellite scatterometer winds and direct observations from ships, including observations made on Ka'imimoana during this cruise. The HYSPLIT4 back-trajectories (Figure 4.10) predict that the VUV instrument sampled air almost exclusively of northern hemisphere origin, but that there were significant variations in the origin of the air within the eastern Pacific
Figure 4.11 Hourly-mean shipboard meteorological data. The VUV O$_2$ data is the same as in Figure 4.2. This plot also includes wind speed, wind direction, northward wind component ($v$), air temperature, and relative humidity (RH). Vertical reference lines are plotted every 5 days at local midnight, and at 0112 local time on May 7$^{th}$.
basin. These variations correspond to variations in the measured O$_2$ and CO$_2$ concentrations.

Figure 4.11 shows the O$_2$ data of Figure 4.6 along with concurrent measurements of wind speed, wind direction, northward wind component (v), air temperature, and relative humidity. As Figures 4.10 and 4.11 show, the air sampled near the Equator was primarily delivered by the northeasterly trades, with a few exceptions at the southern extensions of the cruise track. By the turnaround point at 2°S, 125°W, where only a flask sample is available, the winds had shifted to a northwesterly direction (Figure 4.10). This point also appears to have been a temporal peak in O$_2$. The GOES-9 satellite image in Figure 4.12a indicates that the ITCZ was relatively indistinct at this time. However the ship was directly under a thin line of high clouds that did exist, suggesting that it was sampling a convergent mixture of northern and southern air.

On the return back across the Equator, the winds shifted back to the northeast and O$_2$ decreased (Figure 4.11). During the transect to capture the drifting buoy, the ship's latitude remained relatively constant, yet on May 3rd I observed a +10 per meg and -1 ppm step in O$_2$ and CO$_2$ respectively. The back trajectories for this longitudinal transect (not shown) indicate that the observed concentration shifts correspond to a change in the origin of the air from the northeast to the east. At the end of this transect on May 6th, before the ship turned to the south, the winds increased in speed and returned to the northeast while O$_2$ and CO$_2$ returned to values close to those observed 20° to the west (Figure 4.11). Variations in the efficiency of
Figure 4.12 GOES-9 infrared satellite images. Selected images corresponding to (a) 1300 local time on April 29th, close to the ships furthest extent south along 125°W, (b) 1200 local time on May 7th, corresponding to the O₂ maximum measured while the ship was on its way south towards 2°S 140°W and (c) 0000 local time on May 9th, corresponding to relatively lower O₂ concentrations while the ship was near 2°S 140°W. The ship position is marked in each image by a black dot with a white hatch. Images obtained from the Canadian Meteorological Centre archives.
Figure 4.12 (continued)
Figure 4.12 (continued)
atmospheric transport from the north appears to have produced these changes in the observed concentrations, with more efficient southward transport corresponding to low O\textsubscript{2} and high CO\textsubscript{2}.

The sharpest observed change in O\textsubscript{2} and CO\textsubscript{2} occurred on May 7\textsuperscript{th} as the ship headed south across the Equator. This change was coincident with a sharp slackening of the winds, a shift to a less northerly wind direction, a decrease in relative humidity, an increase in air temperature, and a change from almost complete cloud cover to mostly clear skies (Figures 4.11 and 4.12). The GOES-9 satellite image in Figure 4.12b shows that the ITCZ was relatively distinct at this time, and that the ship had just penetrated south of the main line of high clouds centered near 5\textdegree N. The ship remained under the patch of clear sky between this and a southern branch of clouds throughout most of May 8\textsuperscript{th}. The O\textsubscript{2} and CO\textsubscript{2} concentrations observed aboard the ship on this day are close to those from a flask sample taken on May 5\textsuperscript{th} at SMO (see Figure 4.3), suggesting that the ship was in fact sampling air primarily of southern hemisphere origin. The HYSPLIT4 model predicts that the sampled air at this time ultimately originated to the north (not shown), but this may be a model artifact resulting from the limited observations in this region. The lack of clouds could indicate descending air conditions, and it is possible that the high-O\textsubscript{2}, low-CO\textsubscript{2} air moved north at a higher altitude before descending upon the ship.

The easterly back-trajectory at 2\textdegree S, 140\textdegree W in Figure 4.10 actually corresponds to a time when the O\textsubscript{2} and CO\textsubscript{2} concentrations were closer to their more northerly values (Figure 4.3). By the time the ship reached this point, the winds had
shifted back to the north, relative humidity and cloud cover had increased, and
temperature had decreased (Figure 4.11). Satellite imagery from early on May 9th
(Figure 4.12c) shows that the band of high clouds had shifted southwards by ~ 5° and
were now effectively surrounding the ship. This combination of meteorological
observations suggest that the O₂ and CO₂ concentrations observed near the Equator
were highly sensitive to the position of the ship relative to the ITCZ and local synoptic
weather systems. These observations highlight the difficulty of measuring seasonal
and interannual variations in low-latitude O₂ using background-station or shipboard
flask measurements. Discrete samples taken at biweekly or longer intervals could
alias synoptic variations such as those presented here. Further evidence of this
atmospheric transport uncertainty can be seen in Figure 4.4, which shows that the
greatest O₂ and CO₂ variability in the SMO flask data occurs when the
interhemispheric gradients are largest.

The HYSPLIT4 back-trajectories shown in Figure 4.10 may also provide clues
as to the source of the observed O₂ variations at higher latitudes. The higher O₂ and
lower CO₂ concentrations at the beginning and end of the cruise are as expected
associated with sampling air from further north. However, as previously mentioned
the variations near the beginning of the cruise are anomalous with respect to their
O₂:CO₂ ratio. The back-trajectories show that during this period the sampled air was
travelling from far to the north along the coast of California. The northern Pacific and
California coast are both regions of relatively strong vertical mixing at this time of
year, which delivers a greater O₂-deficit to the surface than local productivity can
accommodate. The resulting O₂ uptake in these regions might explain the observed drop in O₂ with constant CO₂ from April 20th to the 23rd. In support of this hypothesis, when the ship began sampling air from much further south and off the coast on the 23rd the atmospheric O₂ concentrations began a steady climb.

4.5 Comparison to Model Estimates

While the O₂ and CO₂ variations discussed thus far appear to be consistent with interhemispheric mixing superimposed by synoptic variability, with little influence from local air-sea gas exchange, I have yet to address the broader implications of the average concentrations. Considering the large disparity among the equatorial O₂ patterns predicted by the three models in Chapter 2 (Figure 2.4) these VUV measurements have the potential to shed some light on the actual air-sea O₂ exchange in this region. To compare the observations to model estimates, I have calculated atmospheric potential oxygen concentrations according to

\[ \text{APO (per meg)} = \delta(O_2/N_2) + (CO_2 - 363.29) \times 1.1 / X_{O_2} \]  

(4.1)

This equation differs from Equation 2.4 in that it does not include CO or CH₄ corrections, and it establishes an arbitrary reference point that corresponds to the reference cylinders used to define zero on the Scripps O₂/N₂ scale. The resulting latitudinal APO variations observed during this cruise are shown in Figure 4.13.

The southwards-increasing gradient in APO results from the industrial and seasonal-oceanic influences discussed in Section 4.2 above. In addition, the APO values between 10°N and 20°N in Figure 4.13 reveal a longitudinal/temporal
**Figure 4.13** Hourly-mean shipboard concentrations of the derived tracer APO compared to HAMOCC3.1-TM2. The flask samples from SMO, LJO, and KUM are the same as in Figure 4.3. The model prediction corresponds to a mean from April 18th to May 20th, interpolated along the track in Figure 7.1, and adjusted vertically to optimize its fit to the background sites.

A difference of 5-10 per meg that is larger than that for O₂ or CO₂ alone. The temporal nature of this difference is consistent with the rapidly increasing APO concentrations in the northern hemisphere at this time of year (see Figure 2.8). However, it may also include an oceanic signal resulting from greater uptake, or less release, of O₂ and CO₂ in the eastern Pacific, and in fact HAMOCC3.1-TM2 predicts a longitudinal APO gradient of 2.5 per meg for this time and these locations. Of the models used in Chapter 2, only HAMOCC3.1-TM2 has seasonal variations that can be directly
compared to these measurements. LLOBM has a seasonal cycle, but because its biological parameterization does not accurately reproduce seasonal air-sea O\textsubscript{2} flux variations (see discussion in Section 2.4) I have only used its annual mean fluxes here.

The curve in Figure 4.13 represents the predictions of HAMOCC3.1-TM2 averaged over the time of year of the cruise, along a track from SMO to KUM passing through the Equator near the area of this cruise (see Figure 7.1). There are two features of low-latitude atmospheric O\textsubscript{2} that should be matched by such a model: the absolute difference across the Equator as measured between locations such as SMO and KUM or LJO, and the curvature of the gradient between these points. The absolute low-latitude interhemispheric O\textsubscript{2} difference is likely determined by processes outside the tropics, while the local curvature of the gradient should be sensitive to Equatorial outgassing or ingassing.

The HAMOCC3.1-TM2 model is unable to reproduce the total LJO-SMO difference at this time (Figure 4.13), or for the long-term mean (see Table 2.2), thus making it difficult to compare the predicted curvature. However, if I shift the model-predicted gradient to minimize the total error at these two stations, its predictions at the Equator are in fairly good agreement with the shipboard observations. It does not produce an APO minimum as observed near 15°N, but it does predict a large jump in APO at the Equator, as observed.

Although seasonal predictions are not available from the other two models used in Chapter 2, it is possible to derive an annual mean estimate from the measurements. The seasonal data shown in Figure 2.8 indicate that APO at low
latitudes has a relatively small seasonal cycle and that at this time of year it is close to its annual-mean value. To avoid having to make large seasonal corrections, I have excluded the clearly trending APO values south of the Equator and north of 8°N (see Figure 4.13) and have simply averaged the observations between these two latitudes. I have also excluded observations before the fractionation problem was resolved, and thus include only data from April 30th - May 15th. The resulting mean value is -210.8 per meg.

The HAMOC3.1-TM2 model, which is successful at reproducing the seasonal cycles in Figure 2.8, predicts that in this region APO has a seasonal peak-to-peak amplitude of 15 per meg, and that at this time its value is only 1.1 per meg above the annual mean. I have therefore subtracted 1.1 per meg from the calculated average, and obtain a value of -211.9 per meg at a mean position of 2° 56' N, 137° 42' W. I have calculated an error of ± 5.0 per meg for this annual mean estimate by geometrically summing the statistical error from averaging 213 hourly observations (± 3.3 per meg), the absolute accuracy estimate from Chapter 3 (± 3 per meg), and a value equal to 200% of the seasonal adjustment (± 2.2 per meg). As in Chapter 2, I have not attempted to estimate the uncertainty due to interannual variability, however as discussed in the next section it may be significant.

Figure 4.14 compares the annual-mean equatorial estimate to the model predictions along the track in Figure 7.1. I have also included annual means from SMO and KUM centered on May 1, 1998 in this figure, and have adjusted the model gradients to minimize their error relative to these two background-station values.
Figure 4.14 Annual-mean APO estimate compared to HAMOCC3.1-TM2, POBM-TM2, LLOBM-TM2 predictions. The flask-station values for SMO, KUM are annual means centered on the time of the cruise. The model predictions have been interpolated along the track in Figure 7.1 and vertically adjusted to optimize their fits to the background sites.

Similar to the direct comparison in Figure 4.13, HAMOCC3.1-TM2 underpredicts the overall gradient but gets the relative position of the equatorial value approximately correct. The other two models, POBM-TM2 and LLOBM-TM2, predict a large equatorial APO peak that is not supported by these in situ observations. It is apparent from Figure 2.3d, that the HAMOCC3.1 model predicts less equatorial outgassing of O₂ than the other two models. Although not as apparent in Figure 2.3c, this is also the case for CO₂. These differences in annual mean O₂ and CO₂ outgassing could explain
much of the gap between the models' equatorial APO predictions, as well as the POBM-TM2 and LLOBM-TM2 discrepancies with the observations of 5-6 per meg (Figure 4.14).

Another factor that may be involved is the seasonal marine O$_2$ rectifier, which I have hypothesized (Section 2.7) could cause equatorial surface stations to preferentially see air from the winter hemisphere. The two aseasonal models, POBM-TM2 and LLOBM-TM2, can not account for such an effect. Because the ship was primarily sampling air from the northern hemisphere that carried a strong winter signal, the lack of seasonal resolution in these models may explain some of their disagreement with the observations and with HAMOCC3.1-TM2. However, the TM2 curve in Figure 2.6 indicates that adding the predicted marine O$_2$ rectifier to the other models would degrade their prediction of the SMO-KUM difference by 2 per meg while only improving their equatorial predictions relative to these two background stations by 3 per meg. Although large uncertainties still exist with respect to the numerical representation of rectifier effects, this limited analysis suggests that other effects must contribute to the discrepancies in Figure 4.14.

4.6 The Effect of El Niño

Because the predictions of the three models in Figure 4.14 represent climatological means, interannual variability such as that associated with El Niño events could affect their success at matching observations. This month-long cruise coincided with the end of the largest El Niño event on record. At the midpoint of the
cruise the sea surface temperature (SST) on the Equator at 140°W was 3°C above average, at the end of the cruise it was average, and two weeks later it was 3°C below average (Figure 4.15). This sudden collapse of the El Niño event requires a certain amount of caution in interpreting coincident equatorial Pacific measurements. However, if the response of atmospheric gas concentrations to oceanic perturbations were slower than ~ one week, these measurements would represent close to full El Niño conditions.

Feely et al. [1994], Murray et al. [1994], Feely et al. [1995], and Wanninkhof et al. [1995] provide in-depth discussions of the marine biogeochemical responses to El Niño, as characterized by their EQPAC measurements during and after the moderate 1991-1992 El Niño event. This study found O₂ undersaturation anomalies along the Equator at 125°W as large as -0.75 ml l⁻¹ during the boreal autumn post-El Niño period compared to smaller than -0.2 ml l⁻¹ during the spring El Niño period [Wanninkhof et al., 1995] (Figure 4.9). In addition, these scientists found surface pCO₂ levels that were 15 to 55 µatm lower during El Niño conditions than during
post-El Niño conditions, and inferred a reduction in the annual sea-air CO₂ flux from this region of 0.5-0.7 Gt C [Feely et al., 1995]. They attributed these marked changes to the advection of CO₂-depleted, O₂-enriched water from the west and the locally reduced upwelling of CO₂-enriched, O₂-depleted water.

The ΔO₂ measurements (Figure 4.9) from this cruise clearly show that these effects were present and probably greater in magnitude than for the 1991-1992 El Niño. The implications of the combined O₂ and CO₂ effects for APO fluxes are complex. During the initial stages of an El Niño a local O₂ outgassing, or reduced ingassing, may result from the decreased upwelling of O₂-depleted waters, followed at a slightly longer response time by an associated CO₂ ingassing signal. Eventually however, as the broader equatorial Pacific region comes into equilibrium with the reduced input of preformed nutrients from below, an O₂ ingassing signal will result (see discussion in Section 2.2). Furthermore, the reduced air-sea heat flux in this region during El Niño will result in less outgassing of both O₂ and CO₂. Le Quéré et al. [1999] have investigated these effects using a version of the Océan Parallélisé (OPA) model that has high equatorial resolution and is forced by meteorological and oceanic observations over the period January 1979 through December 1997. This model qualitatively reproduces the timing of events outlined above for CO₂ [Le Quéré et al., 1999] and O₂ (C. Le Quere, personal communication, 1999). The net effect of El Niño on APO in this model is an ingassing signal that lags the Southern Oscillation Index by approximately one year.
I have used these results to get an indication of the potential sensitivity of the observations to El Niño variability. By extrapolating the OPA model predictions, I obtained an estimate for an anomalous APO sink at the time of this cruise of $1.0 \pm 0.5$ mol m$^{-2}$ yr$^{-1}$ from $15^\circ$S to $15^\circ$N in the Pacific. I have not included the effect of thermal N$_2$ fluxes in this estimate, which would have a small compensating effect on the apparent APO flux. Using this flux estimate as a lower boundary condition for the TM2 atmospheric transport model (S. Piper, personal communication, 1999) produces a steady-state APO concentration at the Equator that is 3 per meg lower than at SMO and KUM. This implies that the shipboard observations might be an underestimate of the climatological values represented by the models. However, the O$_2$ ingassing prediction of the OPA model requires that dissolved O$_2$ concentrations be lower than average. In contrast, the observations (Figure 4.9) from this cruise suggest that they were significantly higher than average. This suggests an anomalous APO outgassing, which would imply that the shipboard observations were actually an overestimate of climatological conditions.

Another potentially significant El Niño influence on these observations is through altered wind patterns. The winds on the Equator at $140^\circ$W were much more northerly and much less easterly during the 1997-98 El Niño event, which at the time of year of this cruise would have led to anomalously low APO concentrations. However, by the time of the cruise the wind had already returned to close to its normal velocity and direction, in advance of the SST shift [McPhaden, 1999; TAO, 1999].
Many of these issues could be resolved by future equatorial Pacific O$_2$ measurements during non-El Niño conditions.

4.7 Conclusion

In this chapter, I have presented the first field-based measurements of atmospheric O$_2$ variations and the first extensive measurements of atmospheric O$_2$ in the equatorial region. Comparisons between these measurements and concurrent shipboard and background-station flask measurements demonstrate that a shipboard VUV instrument is capable of accurately detecting meaningful changes in atmospheric O$_2$ on time scales of hours to weeks and on space scales of tens to hundreds of kilometers. Comparisons with atmospheric CO$_2$, dissolved O$_2$, and meteorological measurements from this cruise show that equatorial atmospheric O$_2$ concentrations at this time of year are strongly influenced by atmospheric mixing processes. As a result of the strong oceanic, terrestrial, and industrial influences on the latitudinal gradients, O$_2$ concentrations were lower and CO$_2$ concentrations higher when the ship sampled air from further north. Likewise, I observed the highest O$_2$ and lowest CO$_2$ concentrations when the ship briefly sampled air that was primarily of southern hemisphere origin.

The dissolved O$_2$ measurements from this cruise indicate that the equatorial surface was consistently supersaturated with respect to O$_2$, an anomalous condition tied to the large El Niño event at this time. The uncertainties associated with the effect of El Niño on equatorial atmospheric O$_2$ and CO$_2$ somewhat limit the ability of these
measurements to constrain climatological-mean model simulations. Nonetheless, I have made preliminary comparisons between these measurements and the predictions of three chemically-coupled atmosphere-ocean carbon cycle models, based on the derived tracer APO. These comparisons suggest that both the amount of equatorial outgassing of O\textsubscript{2} and the representation of the marine O\textsubscript{2} rectifier are important to predictions of low-latitude meridional atmospheric O\textsubscript{2} gradients.

These comparisons also provide a framework for using future measurements to investigate the seasonal and interannual controls on equatorial atmospheric O\textsubscript{2}. Because atmospheric O\textsubscript{2} is more sensitive to oceanic perturbations than is atmospheric CO\textsubscript{2}, equatorial O\textsubscript{2} measurements have the potential to significantly improve our understanding of the response of the ocean carbon cycle to natural and anthropogenic climate perturbations. Initially resolving the influence of rectification effects on annual-mean concentrations will require repeated measurements at several different times of year. Then, rigidly constraining the amount of equatorial O\textsubscript{2} outgassing in models, and quantifying its interannual variability, will require repeated measurements over several years.

Recently M. Bender has undertaken a Pacific atmospheric O\textsubscript{2} measurement program based on flask samples collected from a north-south transecting commercial ship. This program promises many insights into global biogeochemical cycling. However, as noted above, the flask samples taken near the Equator during spring and fall are likely to be highly variable due to selective sampling across the interhemispheric gradient. High-resolution continuous field-based measurements,
such as the VUV measurements presented here, can provide additional information on
the sources of O₂ variability and improved estimates of mean concentrations. The
NOAA ship Ka'imimoana is an advantageous platform for future VUV O₂
measurements because of its repeatable transects over a wide range of longitudes, and
the extended periods of time spent near the Equator.
4.8 References


