2.8. AIR-SEA GAS EXCHANGE

There are several strong incentives to improve the understanding of the process of air-sea gas exchange. The strongest oceanic data constraint on the uptake of CO_2 by the oceans is a decadal one, namely the rate of increase of the ocean inventories as measured by World Ocean Circulation Experiment/Joint Global Ocean Flux Study (WOCE/JGOFS), Geochemical Ocean Sections (GEOSECS), etc. [e.g., *Gruber et al.*, 1996]. An independent estimate is obtained from measurements of ΔpCO_2 (the difference in partial pressure of CO_2 between the water and the air) at the surface of the oceans, as compiled by *Takahashi et al.* [1997]. In order to convert that information into a flux, the map of ΔpCO_2 needs to be multiplied by the space- and time-dependent air-sea transfer coefficient, which has traditionally been modeled as a function of wind speed. The currently most-often used relationship is that proposed by *Wanninkhof* [1992], in which the transfer velocity increases quadratically with wind speed. There is a large amount of scatter in the measurements that suggest there are factors other than wind speed influencing gas transfer.

Because there is not a satisfactory physical explanation of the gas exchange velocity, we cannot be very sure of fluxes derived with this relationship from observed ΔpCO_2 values. The global flux estimate is sensitive to the relative rates of gas exchange at high and low wind speeds. Low wind speeds are more prevalent at low latitudes that tend to have positive ΔpCO_2 (outgassing), whereas high wind speeds occur more often at high latitudes that tend to take up CO_2 because of negative ΔpCO_2 values. The net global uptake is the balance between these two opposing tendencies at low and high latitudes.

The first combined use of the large scale north-south gradient of atmospheric CO_2 with oceanic ΔpCO_2 data led to the hypothesis of a large terrestrial sink of CO_2 at northern midlatitudes [*Tans et al.*, 1990]. The north-south gradient determines, with the use of an atmospheric transport model, the balance of all sources and sinks of CO_2 as a function of latitude. The partitioning between land and ocean at each latitude zone depends on ΔpCO_2 data and the air-sea gas exchange velocity. The recent paper by *Fan et al.* [1998] also had to employ independent estimates of net air-sea exchange to arrive at its conclusion of unexpectedly large CO_2 uptake in North America. The lesson is that atmospheric inverse models, used to derive sources and sinks from atmospheric gradients, would gain significantly in value and power as our understanding of air-sea gas exchange is improved. Not only would terrestrial estimates be improved, but regional oceanic uptake or loss would be much better quantified based on atmospheric gradients. This is especially true over the southern oceans where the atmospheric constraint would attain serious weight.

Furthermore the $^{13}C/^{12}C$ ratio of CO_2 provides us with a tool to distinguish between terrestrial and oceanic influences on

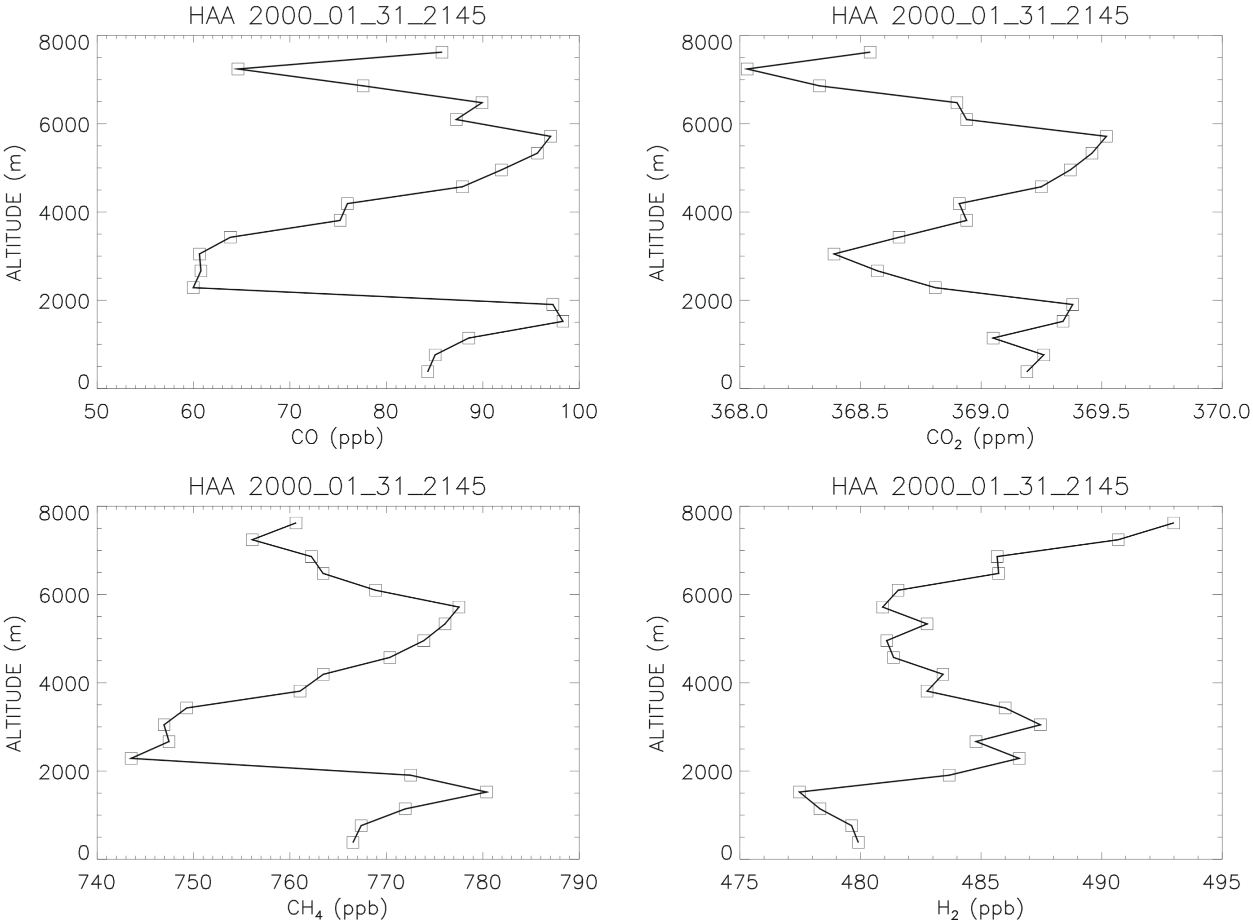

Fig. 2.24. Example of vertical profile results collected as part of the MOPITT calibration program at Molokai, Hawaii, on January 31, 2000. CO has been corrected to the 1999 gravimetric scale (section 2.4.2).

atmospheric CO_2. Unfortunately the largest term in the ^{13}C atmospheric budget, fossil fuel emissions, is followed *not* by the net uptake of CO_2 by terrestrial ecosystems, but by two-way "gross" isotopic exchange between the atmosphere and the oceans unrelated to net uptake. Also the global effect here is a balance between high latitudes that tend to decrease atmospheric $\delta^{13}C$ and low latitudes that tend to increase $\delta^{13}C$. The functional form of the gas exchange parameterization has a major effect on the use of $^{13}C/^{12}C$ to apportion carbon between the oceans and the continents.

The atmosphere, with its rapid mixing, gives us the best tool to keep track of seasonal and interannual variations of the carbon cycle on large spatial scales. The relatively large interannual variations that are being measured [e.g., *Conway et al.*, 1994] give us an opportunity to validate process models. Once such variations are mostly understood, it will be much easier to discern underlying trends in the atmospheric CO_2 burden. At present there appears to be a conflict between deductions purely from atmospheric data [*Francey et al*., 1995] about the variability of ocean uptake, and an oceanographic approach using pCO_2 data combined with observed wind speed and temperature [*Lee et al*., 1998]. The latter approach depends on the gas exchange velocity.

CCGG participated in a measurement campaign aboard the NOAA ship *Ronald H. Brown* from the late spring to the early summer of 1998 to specifically study gas exchange (GASEX98). Three different methods were employed to measure the CO_2 flux: on leg 2 in a cold core eddy with large negative ΔpCO_2 values north of the Azores, the small vertical CO_2 gradient created above the water by the flux was measured, and on leg 3 during the return to Miami, the flux was measured by the eddy covariance and eddy accumulation methods. An important zero bias of the eddy covariance method that affects, to a greater or lesser degree, all other such measurements that have been made to date with a rotating optical chopper wheel in the CO_2 analyzer was discovered. The motion of the ship produces a torque on the chopper that affects the analyzer response. This false signal component of the analyzer is multiplied with the ship-motion corrected vertical wind that still has a residual error. The residual error is coherent with the false analyzer signal, and multiplication leads, therefore, to an apparent CO_2 flux.

On leg 2 vertical concentration differences above the water that were significantly different from zero were measured. Several tests for potential systematic biases gave zero results. The observed concentration differences had to be converted into fluxes with the help of meteorological data and similarity theory. When the derived gas exchange velocities are plotted as a function of wind speed, two features stand out. There is a finite gas exchange velocity at low wind speeds ($U < 6$ m s^{-1}) that appears to be independent of wind speed. It is likely that the gas exchange in this regime is controlled by thermally driven overturning of the thin skin layer of the water. At intermediate wind speeds (6 m s^{-1} $< U <$ 11 m s^{-1}) the gas exchange velocity seems to increase linearly with wind speed. In this range CMDL results appear to agree well with the often used relationship between gas exchange velocity and the square of the wind speed [*Wanninkhof*, 1992], but our results are significantly higher at the lower wind speeds. CMDL data do not extend into the higher wind speed range.