

Figure 1 Scientist from the University of Hawaii have visited Station ALOHA 163 times since October, 1988 to measure a broad spectrum of physical and biogeochemical phenomena. Each blue dot represents a HOT cruise.

Methods of Measurement

All measurements of CO_2 equilibria parameters closely follow recommendations of the Department of Energy's (DOE) Carbon Dioxide Survey Science Team. Detailed standard operating procedures are found in their publication:

DOE (1994) *Handbook of methods for the analysis of the various parameters of the carbon dioxide system in sea water*. Version 2, A. G. Dickson & C. Goyet, eds. ORNL/CDIAC-74

The handbook is available on the web at:

<http://andrew.ucsd.edu/co2qc/handbook.html>

Dissolved Inorganic Carbon

The total dissolved inorganic carbon (DIC) is defined as the sum of carbon found as dissolved carbon dioxide, bicarbonate ion and carbonate ion. DIC samples are collected directly into combusted glass bottles, fixed with mercuric chloride to inhibit biological activity and returned to our shore based laboratory. Analyses are performed by automated coulometry using a computer controlled single-operator multiparameter metabolic analyzer (SOMMA) system and UIC model 5011 coulometer.

Total Alkalinity

The total alkalinity (TA) of a sample of seawater is defined as the quantity of hydrogen ion required to neutralize bases formed from weak acids with dissociation constants greater than $10^{-4.5}$ in one kilogram of seawater. TA is measured in our shore based laboratory from the same samples collected for DIC. Subsamples of approximately 75 ml are measured gravimetrically and titrated with coulometrically standardized hydrochloric acid using an automated potentiometric titration system. Total alkalinity is calculated using a Gran plot corrected for interference from bisulfate and hydrogen fluoride.

pH

The activity of hydrogen ion (pH) is determined spectrophotometrically on the total hydrogen concentration scale. Samples are collected directly into spectrophotometer cells and analyzed immediately at-sea by adding m-cresol purple dye and measuring the absorbance maxima.

Quality Control

Quality control of HOT CO_2 measurement is maintained using certified reference materials obtained from Andrew Dickson at the Oceanic Carbon Dioxide Quality Control Research Group (<http://andrew.ucsd.edu/co2qc/rms.html>). Precision for measurement of DIC is better than $1 \mu\text{mol/kg}$ and for TA it is better than $2 \mu\text{mol/kg}$. Precision of pH measurements is 0.001 pH units with an estimated accuracy of 0.004 pH units .

	1989	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004
DIC	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
TA	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
pH			*	*	*	*	*	*	*	*	*	*	*	*	*	*
pCO ₂								*	*	*						

Table 1 Yearly history of CO_2 parameter measurements.

HOT CO_2 on the Web

For all things HOT: Programs, Schedules, Reports

<http://hahana.soest.hawaii.edu>

HOT-DOGS: Program Data

(Hawaii Ocean Time-series Data Organization & Graphical System)

<http://hahana.soest.hawaii.edu/hot/hot-dogs/interface.html>

Publications from HOT Program:

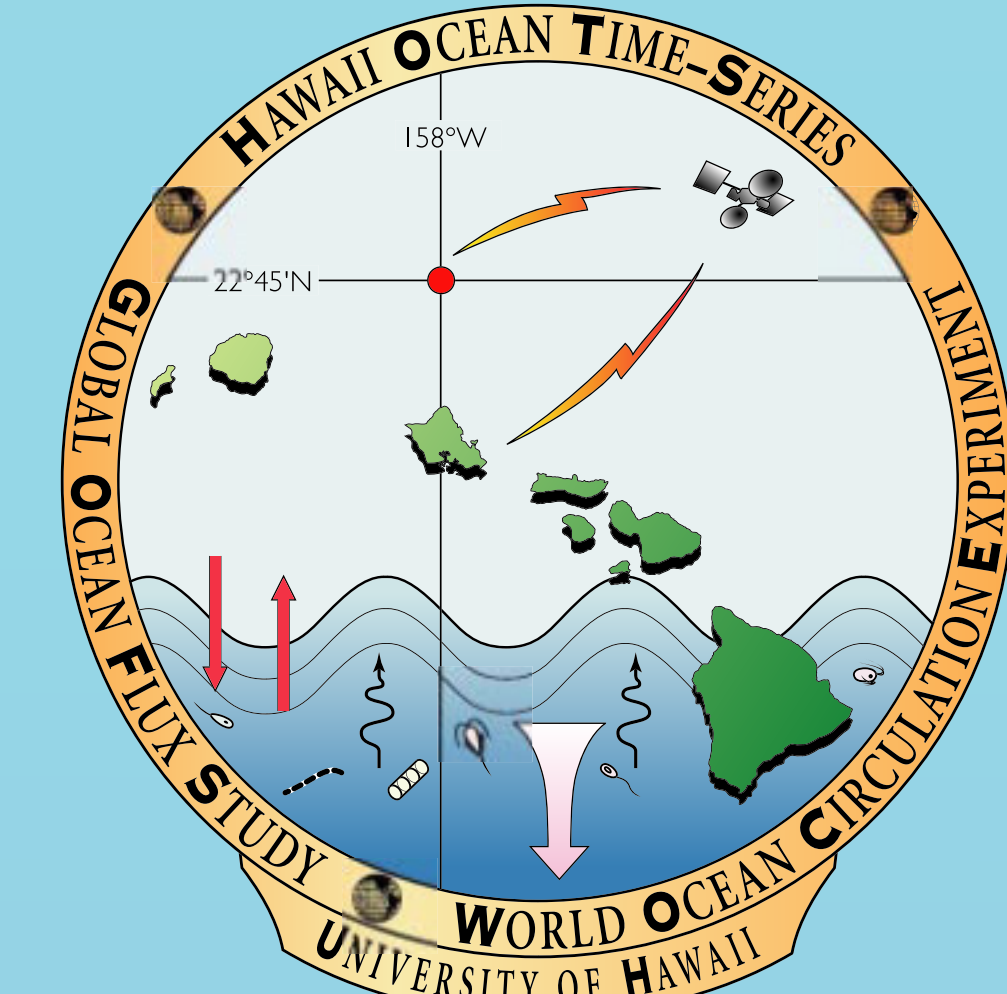
<http://hahana.soest.hawaii.edu/hot/hotpub.html>

CO_2 is HOT: 15 Years Quantifying Carbon Dioxide in the Subtropical Pacific Ocean

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Current and former members of the HOT CO_2 Team have made invaluable contributions both at sea and on shore. Many others have also done their part in supporting the collection, analysis and distribution of this high quality data set.

Ancillary Investigations

Charles D. Keeling and Peter Guenther

Scripps Institute of Oceanography

DIC, TA and stable carbon isotopes of surface waters.

Paul Quay and Johnny Stutsman

University of Washington

Stable carbon isotopes throughout the water column.

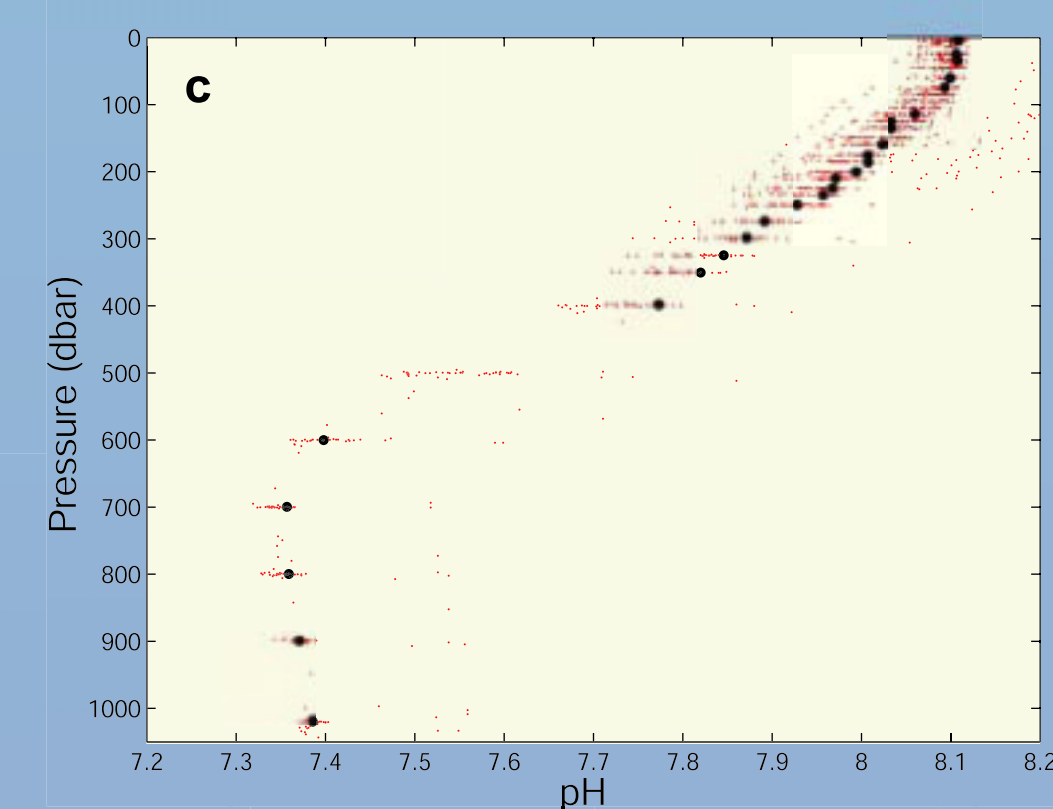
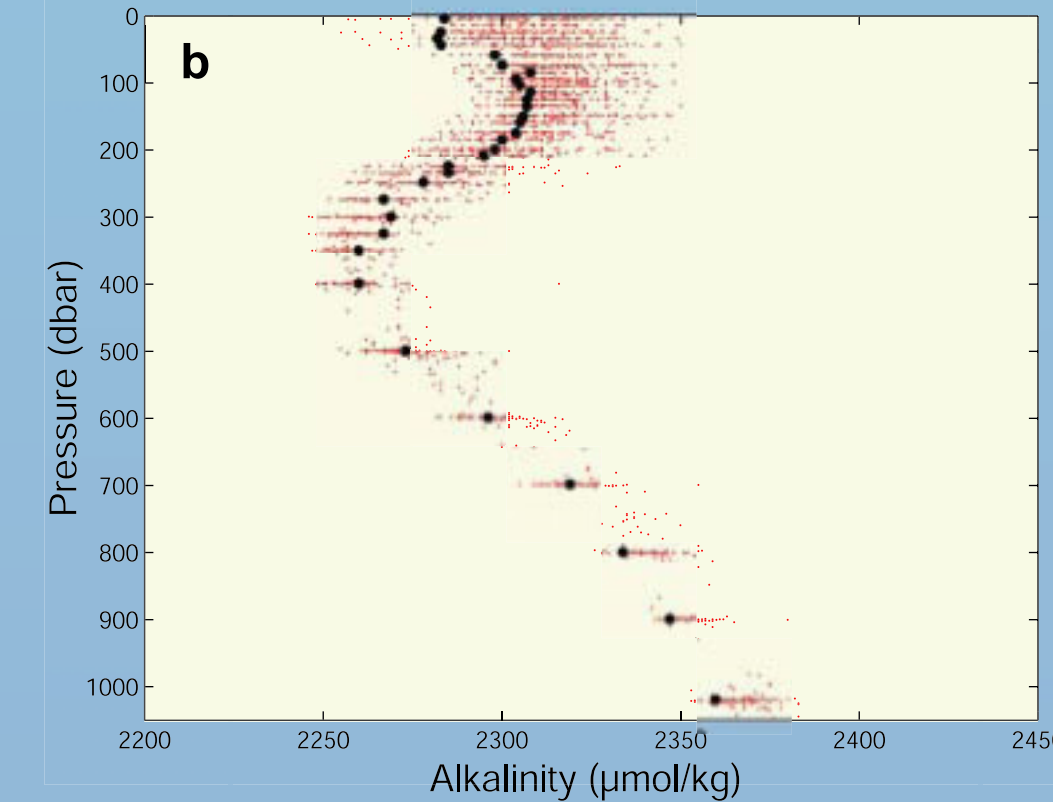
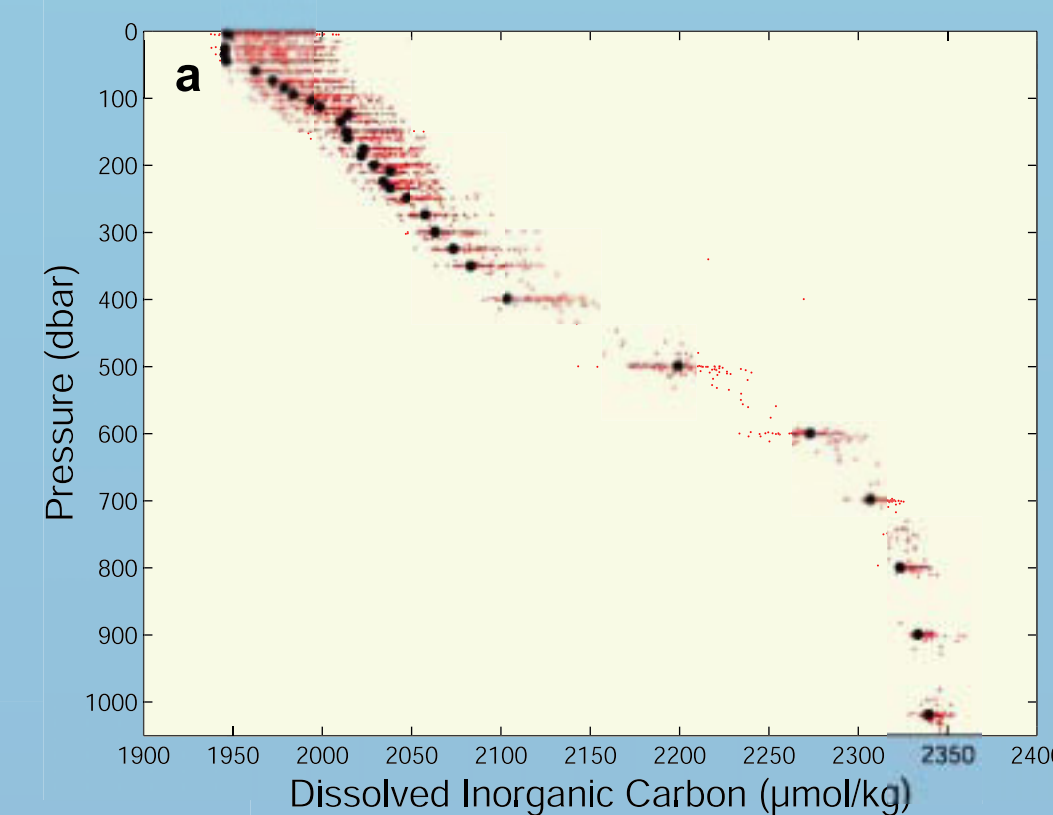


Figure 3 Profiles of **a**, DIC, **b**, TA and **c**, pH. Measurements from samples collected at Station ALOHA in August, 1996 are shown by black circles. The historical data set is denoted by red points. The physical and biogeochemical processes controlling the distribution of these properties are discussed by Sabine et al., 1994.

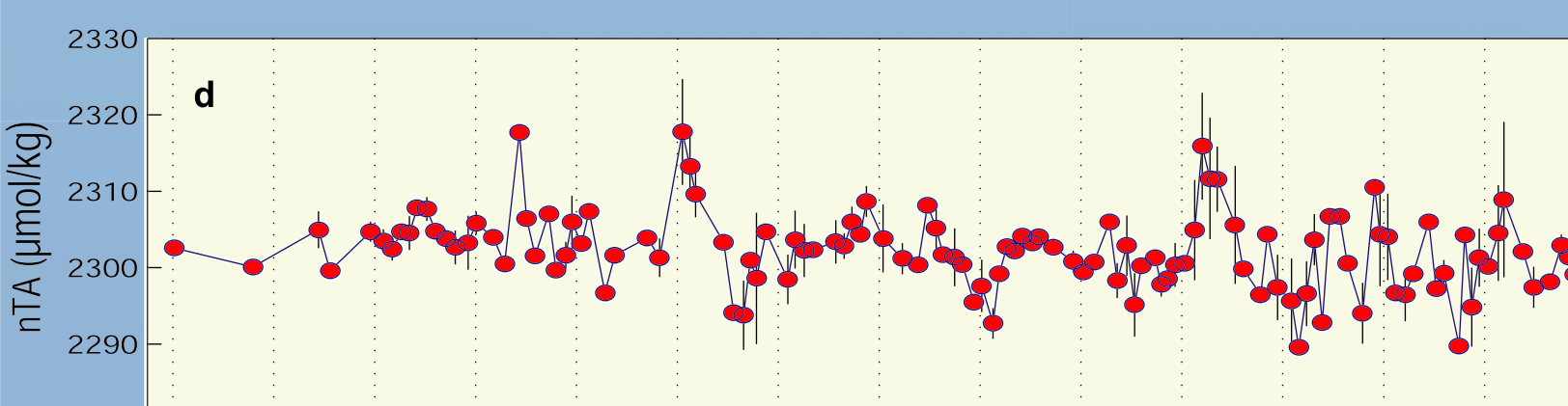
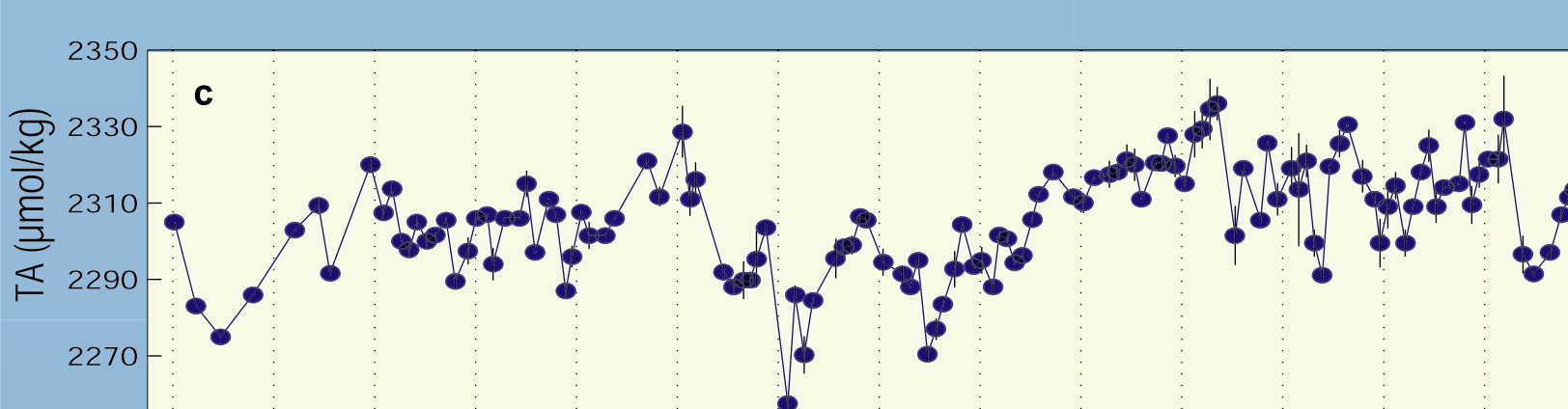
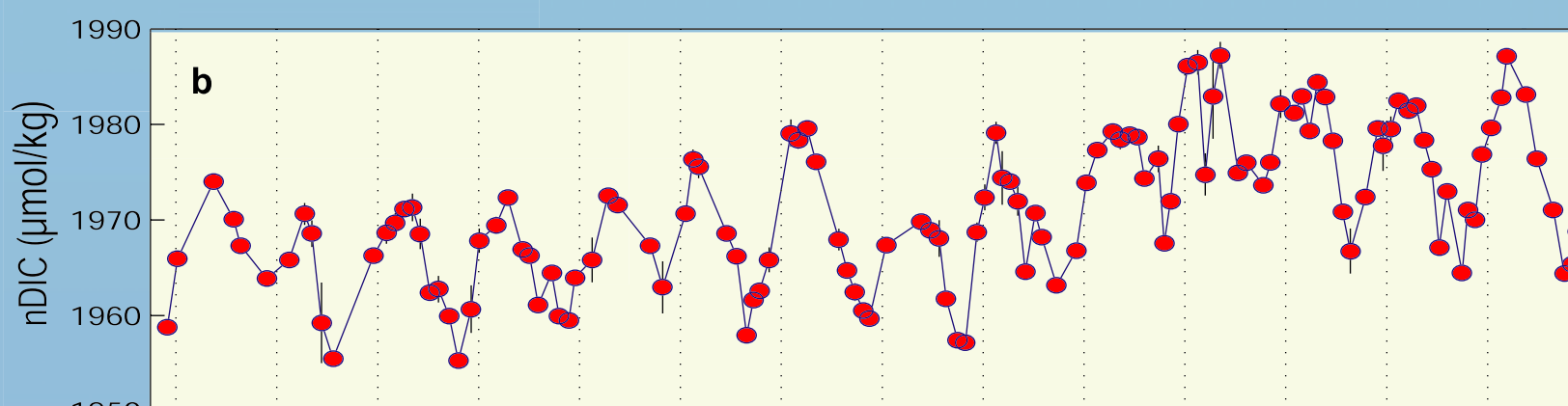
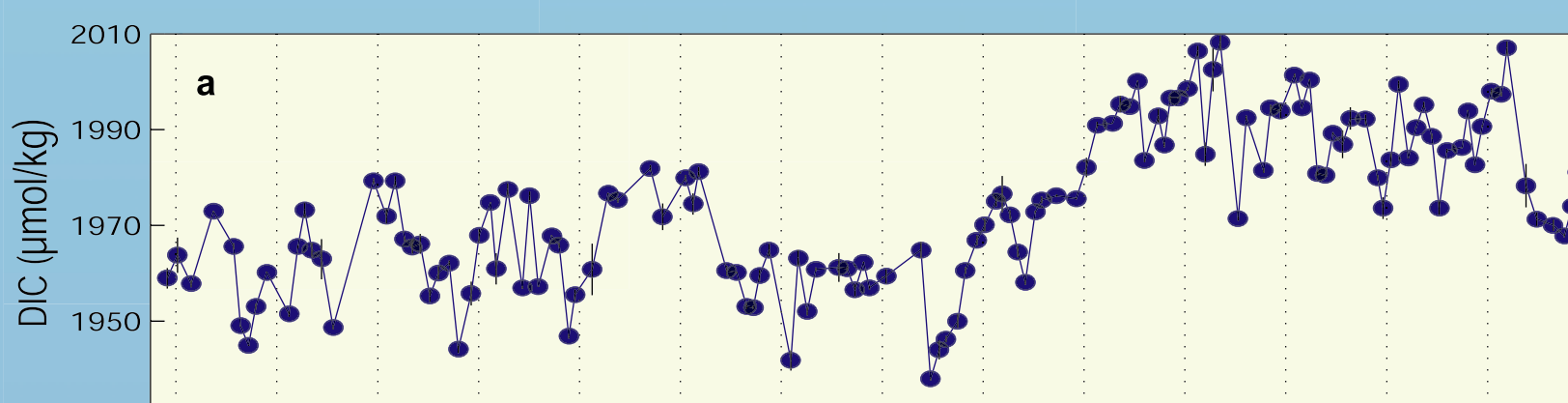


Figure 4 Time-series of DIC and TA Station ALOHA for waters between 0-30 m. The blue circles show mean values of DIC (**a**) and TA (**c**), while the red circles indicate the same data normalized to a salinity of 35, nDIC (**b**) and nTA (**d**). Since 1996, an increase in the salinity of surface waters due to lower than normal precipitation is evident when comparing DIC to nDIC and TA to nTA. Once the salinity effect is removed, nDIC demonstrates an annual signal and increasing trend. This data has been used to show that the waters around Hawaii are a net sink for CO_2 and accumulate DIC consistent with the rise in atmospheric CO_2 . (Winn et al., 1998, Dore et al., 2003, Keeling et al., 2004)

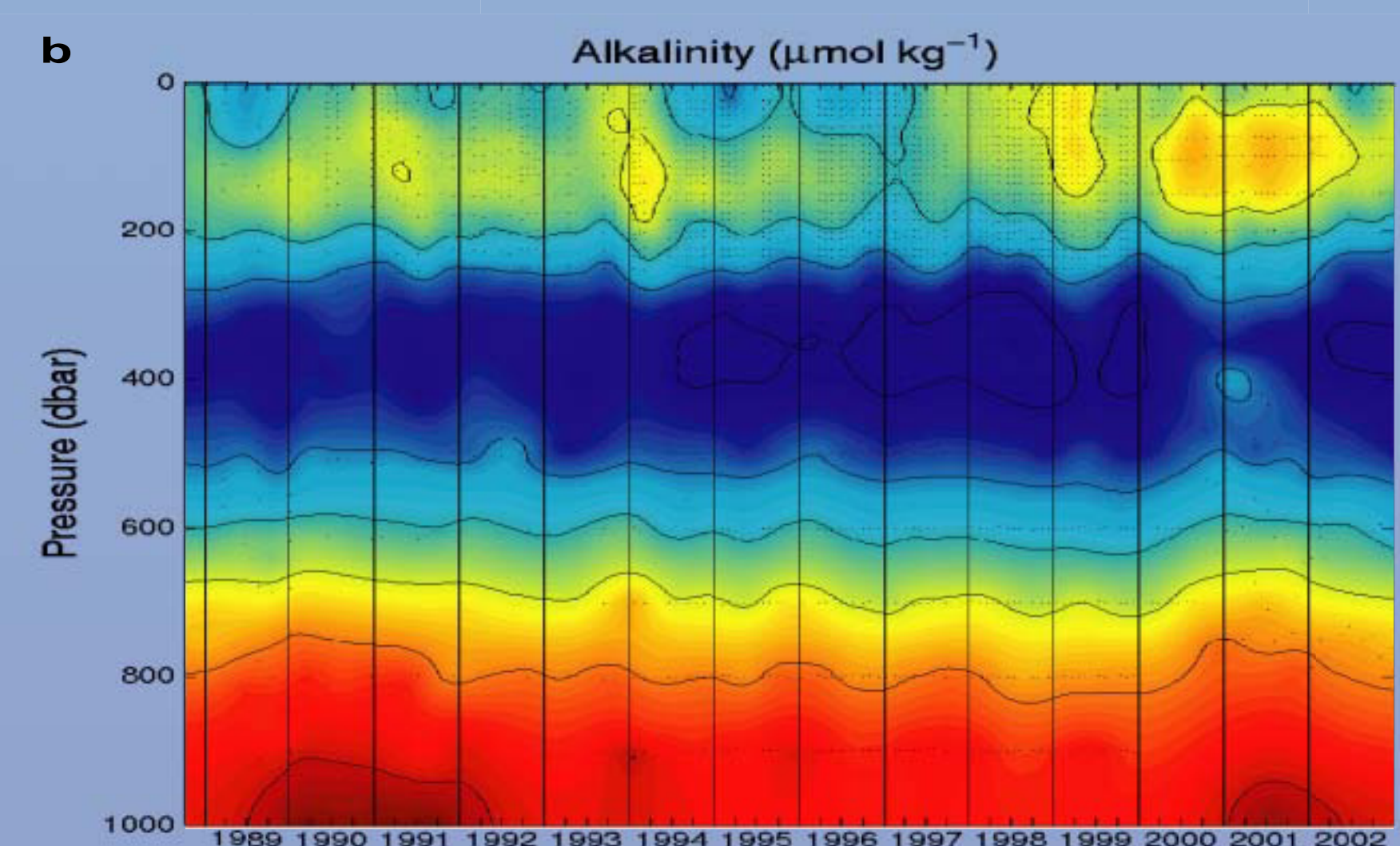
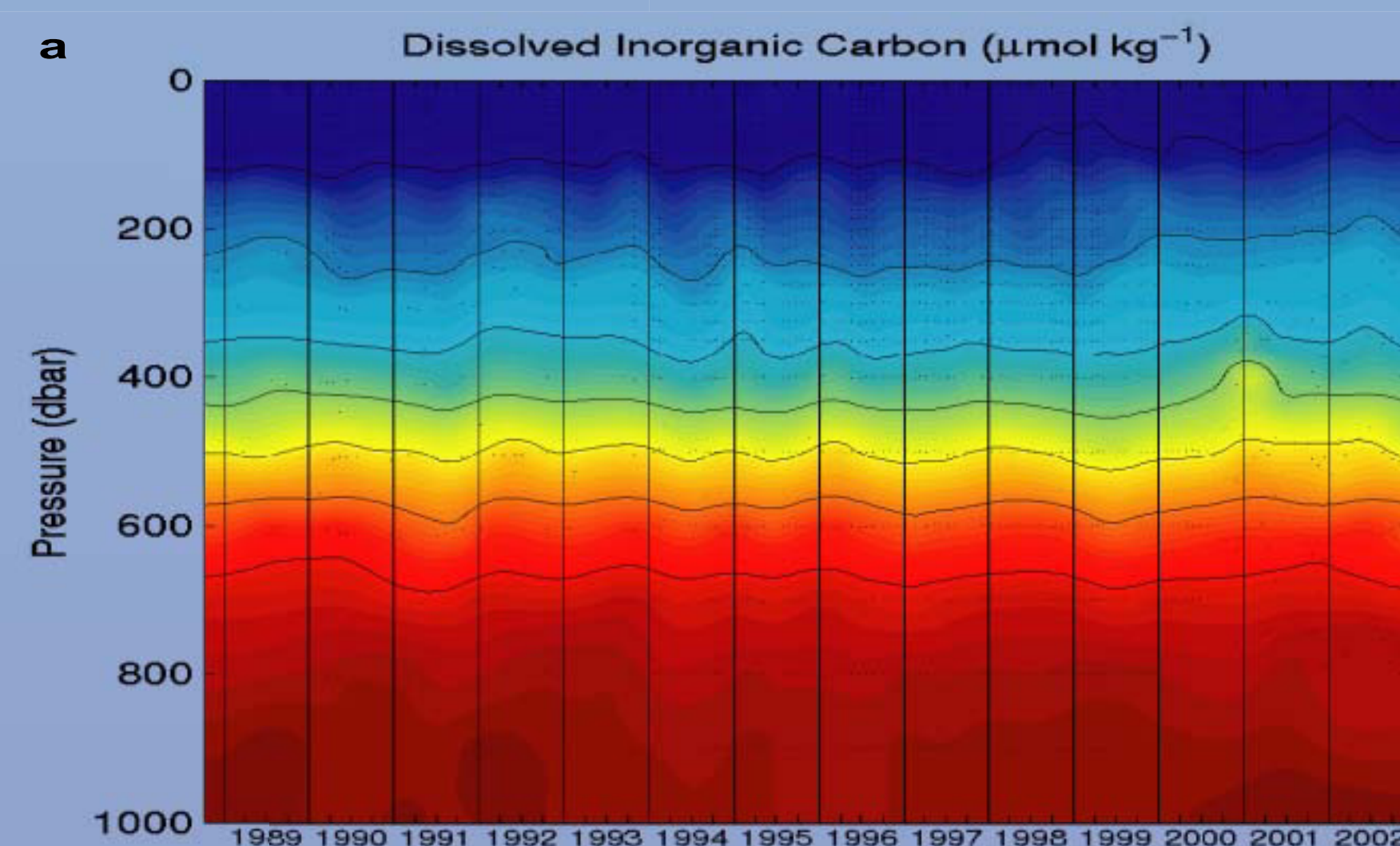


Figure 2 Countours of DIC (**a**) and TA (**b**) for the upper 1000 m at Station ALOHA. A black point denotes the location in the water column for each sample was collected.

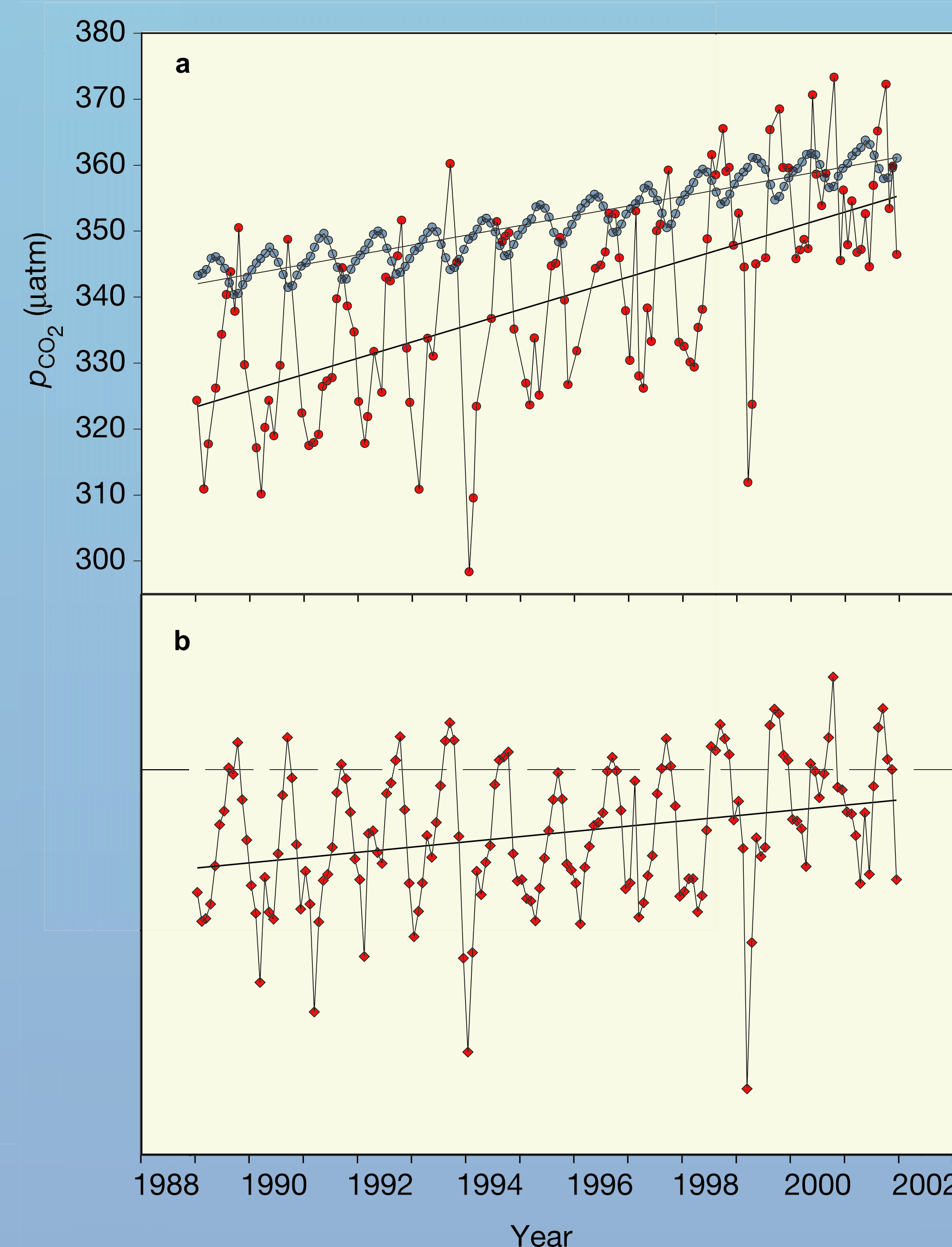


Figure 3 Interannual variability and trends in pCO_2 and the sea-air flux of CO_2 at Station ALOHA. **a**, Cruise mean values and linear trend in pCO_2 . The blue circles indicate atmospheric data while the red circles represent oceanic surface water concentrations calculated from DIC and TA. **b**, Monthly flux of CO_2 from ocean to atmosphere. The red diamonds represent the flux interpolated to the fifteenth day of each month and the solid black line indicates the linear trend in flux. Extrapolating the converging trend lines suggest the region will cease acting as a sink for atmospheric CO_2 by 2008. This figure is reproduced from Dore, et al. 2004.

pCO₂ at ALOHA and Beyond ...



An underway pCO_2 system is scheduled to be installed aboard the R/V Kilo Moana in 2005. This will provide continuous measurements of surface water pCO_2 and atmospheric pCO_2 as the ship operates throughout the Pacific.

A moored pCO_2 instrument has been installed on the MOSEAN HALE-ALOHA buoy to provide a nearly continuous stream of surface water and atmospheric pCO_2 . Based on a MBARI design, the system is operated by the NOAA PMEL CO_2 group. Measurements are made every 3 hours and transmitted to shore daily via an Iridium satellite link. Data and additional information can be found at:

www.pmel.noaa.gov/co2/moorings/hot/hot_main.htm



Selected Publications:

KEELING, C.D., H. BRIX, and N. GRUBER. Seasonal and long-term dynamics of the upper ocean carbon cycle at station ALOHA near Hawaii, *Global Biogeochem. Cycles*, 18(4), GB4006, doi:10.1029/2004GB002227, 2004.

DORE, J. E., R. LUKAS, D. W. SADLER and D. M. KARL. Climate-driven changes to the atmospheric CO_2 sink in the subtropical North Pacific Ocean. *Nature*, 424: 754-757, 2003.

KARL, D. M., N. R. BATES, S. EMERSON, P. J. HARRISON, C. JEANDEL, O. LLINAS, K.-K. LIU, J.-C. MARTY, A. F. MICHAELS, J. C. MIQUEL, S. NEUER, Y. NORJI and C. S. WONG. Temporal studies of biogeochemical processes determined from ocean time-series observations during the JGOFS era. In: M. J. R. Fasham (ed.), *Ocean Biogeochemistry: The Role of the Ocean Carbon Cycle in Global Change*, Springer, New York, pp. 239-267, 2003.

KARL, D. M., J. E. DORE, R. LUKAS, A. F. MICHAELS, N. R. BATES and A. KNAP. Building the long-term picture: The U.S. JGOFS time-series programs. *Oceanography Magazine*, 14: 6-17, 2001.

EMERSON, S. and D. M. KARL. The biological carbon pump in the subtropical Pacific Ocean: Nutrient limitations and CO_2 fluxes. In Y. Norji (ed.), *Proceedings of the 2nd International Symposium on CO_2 in the Oceans*, NIES, Tsukuba, Japan, pp. 317-323, 1999.

WINN, C. D., Y.-H. LI, F. T. MACKENZIE and D. M. KARL. Rising surface ocean dissolved inorganic carbon at the Hawaii Ocean Time-series site. *Marine Chemistry* 60: 33-47, 1998.

KARL, D. M. and R. LUKAS. The Hawaii Ocean Time-series (HOT) Program: Background, rationale and field implementation. *Deep-Sea Research (part II)* 43: 129-156, 1996.

SABINE, C. L., F. T. MACKENZIE, C. WINN and D. M. KARL. Geochemistry of carbon dioxide in seawater at the Hawaii Ocean Time-series station, ALOHA. *Global Biogeochemical Cycles* 9: 637-651, 1995.

WINN, C. D., F. T. MACKENZIE, C. J. CARRILLO, C. L. SABINE and D. M. KARL. Air-sea carbon dioxide exchange in the North Pacific subtropical gyre: Implications for the global carbon budget. *Global Biogeochemical Cycles* 8: 157-163, 1994.

KARL, D. M. and C. D. WINN. A sea of change: Monitoring the ocean's carbon cycle. *Environmental Science and Technology*, 25: 1976-1981, 1991.



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