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Final Technical Report

Measurements of Surface Ocean Carbon Dioxide

Partial Pressure During WOCE

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Final Technical Report

All of the technical goals of the World Ocean Circulation Experiment (WOCE) field program which were supported under the Department of Energy research grant "Measurements of Surface Ocean Carbon Dioxide Partial Pressure During WOCE" (DE-FG03-90ER60981) have been met. This has included the measurement of the partial pressures of carbon dioxide (CO_2) and nitrous oxide (N_2O) in both the surface ocean and the atmosphere on 24 separate shipboard expedition legs of the WOCE Hydrographic Programme. These measurements were made in the Pacific, Indian and Atlantic Oceans over a six-and-a-half year period, and over a distance of nearly 200,000 kilometers of ship track. The total number of measurements, including ocean measurements, air measurements and standard gas measurements, is about 136,000 for each gas, or about 34,000 measurements of each gas in the ocean and in the air.

This global survey effort is directed at obtaining a better understanding of the role of the oceans in the global atmospheric budgets of two important natural and anthropogenic modulators of climate through the "greenhouse effect", CO_2 and N_2O , and an important natural and anthropogenic modulator of the Earth's protective ozone layer through catalytic processes in the stratosphere, N_2O . For both of these compounds, the oceans play a major role in their global budgets. In the case of CO_2 , roughly half of the anthropogenic production through the combustion of fossil fuels has been absorbed by the world's oceans. In the case of N_2O , roughly a third of the natural flux to the atmosphere originates in the oceans. As the interpretation of the variability in the oceanic distributions of these compounds improves, measurements such as those supported by this research project are playing an increasingly important role in improving our understanding of natural and anthropogenic influences on climate and ozone.

The methods used to carry out these observations have been reported previously (Weiss, 1981; Weiss *et al.*, 1992). Briefly, surface ocean waters are pumped from the bow of the research vessel to the shipboard laboratory, where they are equilibrated with a gas headspace that is vented to atmospheric pressure using a 2-stage "equilibrator". Samples of this gas space, and of clean air pumped to the laboratory, are analyzed by an automated gas chromatograph. CO_2 is detected by flame ionization after high-temperature catalytic conversion to methane in a stream of hydrogen. N_2O is detected by electron capture. Unknown sample injections are alternated with injections of high- and low-concentration gas standards. The chromatographic analysis time is 7.5 minutes. Since four gases are analyzed in sequence, a total of 48 samples of equilibrated gas and of air are measured each day. The results for both gases are calibrated against secondary air standards prepared at the Scripps Institution of Oceanography by C. D. Keeling for CO_2 and by R. F. Weiss for N_2O . The equilibrator measurements are corrected for slight warming by the ship's pumping system. The results are reported for both the equilibrated gas and the air measurements as dry gas mole fractions, $x\text{CO}_2$ and $x\text{N}_2\text{O}$. These can be converted to partial pressures, $p\text{CO}_2$ and $p\text{N}_2\text{O}$, using the ancillary measurements of barometric pressure and water temperature (the latter for determining the water vapor pressure).

Improvements in the measurement technique included the use of modern analog-to-digital and computer techniques to record complete chromatograms and ancillary data, and enlargement of the sample size used to measure N_2O from 1 cm^3 to 3 cm^3 .

This work also represented the first time that we have relied heavily on personnel from other laboratories to tend the equipment at sea. After some initial difficulties, and with a heavy reliance on training and on support via satellite communication, this has become a reliable way to operate the measurement program at reduced cost.

The 24 expedition legs of the US WOCE program on which underway CO₂ and N₂O measurements were made are listed in the following tables:

WOCE Pacific Ocean Expeditions

WOCE Line	Dates	Ports	Ship	Operator
Transit	5/31/91- 6/1/91	San Diego- Port San Luis	R/V <i>Washington</i>	F. A. Van Woy SIO
P-17C (Tunes Leg 1)	6/1/91- 7/11/91	Port San Luis- Papeete	R/V <i>Washington</i>	K. Sullivan U. Miami
P-16S/P-17S (Tunes Leg 2)	7/17/91- 8/25/91	Papeete- Papeete	R/V <i>Washington</i>	G. Mathieu LDEO
P-16C (Tunes Leg 3)	9/3/91- 10/1/91	Papeete- Honolulu	R/V <i>Washington</i>	D. Wisegarver PMEL/NOAA
P-6C	5/30/92- 7/6/92	Easter Island- Auckland	R/V <i>Knorr</i>	F. A. Van Woy SIO
P-6W	7/13/92- 7/29/92	Auckland- Sydney	R/V <i>Knorr</i>	M. J. Warner UW
P-14C	9/1/92- 9/13/92	Auckland- Suva	R/V <i>Knorr</i>	M. J. Warner UW
P-16S/P-17S (Juno Leg 9)	10/6/92- 11/26/92	Papeete- Papeete	R/V <i>Knorr</i>	F. A. Van Woy SIO
P-17S/P-19S (Juno Leg 10)	12/3/92- 1/22/93	Papeete- Punta Arenas	R/V <i>Knorr</i>	P. K. Salameh SIO
P-19N	2/22/93- 4/13/93	Punta Arenas- Panama	R/V <i>Knorr</i>	K. Sullivan U. Miami

WOCE Indian Ocean Expeditions

WOCE Line	Dates	Ports	Ship	Operator
I-8S/I-9S	12/01/94- 1/19/95	Fremantle- Fremantle	R/V <i>Knorr</i>	K. Hargreaves PMEL/NOAA
I-9N	1/24/95- 3/06/95	Fremantle- Colombo	R/V <i>Knorr</i>	K. Sullivan U. Miami
I-8N/I-5E	3/10/95- 4/16/95	Colombo- Fremantle	R/V <i>Knorr</i>	R. Schottle SIO
I-3	4/20/95- 6/07/95	Fremantle- Mauritius	R/V <i>Knorr</i>	F. A. Van Woy SIO
I-5W/I-4	6/11/95- 7/11/95	Mauritius- Mauritius	R/V <i>Knorr</i>	K. Maillat U. Miami
I-7N	7/15/95- 8/24/95	Mauritius- Matrah	R/V <i>Knorr</i>	K. Sullivan U. Miami
I-1	8/29/95- 10/18/95	Matrah- Singapore	R/V <i>Knorr</i>	S. Covey UW
I-10	11/06/95- 11/24/95	Singapore- Singapore	R/V <i>Knorr</i>	K. Sullivan U. Miami
I-2	11/28/95- 1/19/96	Singapore- Mombasa	R/V <i>Knorr</i>	R. Schottle SIO

WOCE Atlantic Ocean Expeditions

WOCE Line	Dates	Ports	Ship	Operator
Transit	5/19/97- 5/29/97	Woods Hole- Azores	R/V <i>Knorr</i>	F. A. Van Woy SIO
A-24	5/29/97- 7/04/97	Azores- Halifax	R/V <i>Knorr</i>	F. A. Van Woy SIO
A-20	7/17/97- 8/10/97	Halifax- Trinidad	R/V <i>Knorr</i>	C. Sabine Princeton
A-22	8/15/97- 9/03/97	Trinidad- Woods Hole	R/V <i>Knorr</i>	R. Rotter Princeton
AR-24	10/05/97- 11/19/97	Woods Hole- Woods Hole	R/V <i>Knorr</i>	G. Eischeid WHOI

The results from these measurements are presented graphically in the following figures, which show the cruise tracks and the equilibrator and atmospheric results in the same format and with the same Gaussian smoothing procedures as were used by Weiss *et al.* (1992). The data plots are largely self-explanatory, and provide a very considerable improvement in the geographic coverage of $p\text{CO}_2$ and $p\text{N}_2\text{O}$ data in the vast South Pacific and Indian Oceans, as well as providing important repeat observations in the North Atlantic Ocean. Beyond this simple descriptive presentation, it is the subject of future research to interpret these results in the context of the global CO_2 and N_2O budgets and the processes that control them. It is also worth noting that the data reported here bring the total length of ship track measurements carried out by our laboratory using this technique to about 529,000 kilometers over a period of 20 years.

Finally, all of these data will be reported to the Carbon Dioxide Information Analysis Center (CDIAC) in the form of a data report similar to Weiss *et al.* (1992). The data are close to their final form, except that the detailed IMET underway position and temperature data for the most recent WOCE North Atlantic expedition legs have yet to be merged with our data set. With the understanding that the support for the DOE CO_2 program was being terminated, we decided to use the funds that were available to us to complete the shipboard measurement program in the North Atlantic, rather than to complete the reporting of the earlier data to CDIAC and fail to complete the WOCE measurements. We nevertheless expect to complete this reporting requirement within two years of the completion of the expedition work. Until then, all the completed data are available directly from us over the Internet via "ftp" (Unix File Transfer Protocol).

References

- Weiss, R. F. Determinations of carbon dioxide and methane by dual catalyst flame ionization chromatography and nitrous oxide by electron capture chromatography, *J. Chromatographic Science*, 19, 611-616 (1981).
- Weiss, R. F., F. A. Van Woy, and P. K. Salameh. *Surface Water and Atmospheric Carbon Dioxide and Nitrous Oxide Observations by Shipboard Automated Gas Chromatography: Results from Expeditions between 1977 and 1990*. Scripps Institution of Oceanography Reference 92-11. ORNL/CDIAC-59, NDP-044. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 144 pp. (1992)

SIO Underway CO₂ and N₂O Measurements During WOCE

WOCE P17C

WOCE P16S-P17S

WOCE P16S-P17S, Papeete to Papeete, 17 Jul 91 to 25 Aug 91

WOCE P16C

WOCE P6C

WOCE P6C, Easter Is. to Auckland, 20 May 92 to 6 Jul 92

WOCE P6W, Auckland to Sydney, 13 Jul 92 to 29 Jul 92

WOCE P14C

WOCE P14C, Auckland to Suva, 1 to 13 Sep 92

WOCE P16S-P17S

WOCE P16S-P17S, Papeete to Papeete, 6 Oct 92 to 26 Nov 92

WOCE P17S-P19S

WOCE P17S-P19S, Papeete to Punta Arenas, 3 Dec 92 to 22 Jan 93

WOCE P19N

WOCE P19N, Punta Arenas to Panama, 22 Feb 93 to 13 Apr 93

WOCE I8S-I9S, Fremantle to Fremantle, 1 Dec 94 to 19 Jan 95

WOCE I9N

WOCE 19N, Fremantle to Colombo, 24 Jan 95 to 6 Mar 95

WOCE I8N-15E

WOCE I8N-15E, Colombo to Fremantle, 10 Mar 95 to 16 Apr 95

WOCE I3, Fremantle to Mauritius, 20 Apr 95 to 7 Jun 95

WOCE 15W-14, Mauritius to Mauritius, 11 Jun 95 to 11 Jul 95

WOCE I7N

WOCE I7N, Mauritius to Matruh, 15 Jul 95 to 24 Aug 95

WOCE I1, Matrah to Singapore, 29 Aug 95 to 18 Oct 95

WOCE 110

WOCE I2, Singapore to Mombasa, 4 Dec 95 to 21 Jan 96

WOCE A24, Woods Hole to Halifax, 19 May 97 to 4 Jul 97

WOCE A22, Trinidad to Woods Hole, 15 Aug 97 to 3 Sep 97

WOCE AR24, Woods Hole to Woods Hole, 5 Oct 97 to 19 Nov 97