WOCE PACIFIC OCEAN RADIOCARBON PROGRAM

ROBERT M. KEY

Ocean Tracer Laboratory, Atmospheric and Oceanic Sciences Program, Department of Geosciences, Princeton University, Princeton, New Jersey 08610 USA

ABSTRACT. Fieldwork for the World Ocean Circulation Experiment (WOCE) radiocarbon program was recently completed. *Ca.* 9000 samples were collected for analysis using both conventional β -counting techniques and the newer AMS technique. The mean uncertainty for the β analyses is 3%; for AMS analyses, *ca.* 4.5%.

INTRODUCTION

The World Ocean Circulation Experiment (WOCE) has been an unprecedented effort to study largescale ocean circulation, with fieldwork by scientists from more than 30 countries making many thousands of measurements. The overall goal of the program is to obtain a detailed description of the physical properties and circulation of the global ocean. These data will be used to determine the role of ocean circulation in global climate change and to help develop models that can be used to predict those changes.

A major component of WOCE was the "one-time survey". This phase of the fieldwork was conducted along both zonal and meridional hydrographic lines, on which stations were occupied with a nominal horizontal spacing of 30 nautical miles (~56 km, or ~0.5° latitude or longitude). At each station, discrete water samples (small-volume samples (SV)) were collected over the entire water column using a CTD equipped with a 24- to 36-place Rosette sampler. At some of the stations in the Pacific, the deep and bottom waters also were sampled using 250-liter stainless steel Gerard barrels to collect large-volume (LV) samples. Each small-volume sample was measured for pressure, temperature, salinity, oxygen, nitrate, nitrite, silicate and phosphate. Significant subsets of the SV samples were measured for chlorofluorocarbons, ³H, ³He, ¹³C and ¹⁴C. Through a collaborative effort with the Joint Global Ocean Flux Study (JGOFS) many of the SV samples were also measured for carbon species (generally TCO₂ and alkalinity). Pressure, temperature, salinity, silicate and ¹⁴C were measured on all of the LV samples.

This paper gives an overview of the U.S. WOCE radiocarbon measurement program for the Pacific Ocean. All of the planned U.S. Pacific Ocean fieldwork has been completed. Table 1 summarizes the legs that were sampled for ¹⁴C. For each entry, the table lists the cruise leg, the common cruise name (AKA, "also known as") and the official WOCE designation, the chief scientist for that leg, the dates of the cruise, the principal investigator (PI) responsible for ¹⁴C collection and interpretation and the lab(s) responsible for the actual sample measurements. The Pacific Ocean stations that were sampled for ¹⁴C are shown in Figure 1. Over 9000 samples were collected for ¹⁴C analysis during this effort. Some of the apparent gaps in Figure 1 were filled by the sampling programs of other countries (primarily Australia, New Zealand and Japan). Some of the early results from these measurements are presented in this issue (Key *et al.* 1996; Stuiver *et al.* 1996).

METHODS

The goal of the WOCE Pacific radiocarbon program was to generate a data set of sufficient density and precision that the distribution could be described with reasonable accuracy in three dimensions. The GEOSECS survey of the Pacific deep and bottom waters (depths > ~1000m) clearly demonstrated that the meridional Δ^{14} C gradients were small (Östlund and Stuiver 1980). While no zonal





• · · · · · · · · · · · · · · · · · · ·	АКА				Analytical lab
Cruise	WOCE name	Chief scientist	Cruise dates	¹⁴ C PI	AMS*/LV-β†
P17N‡	CGC-91 Leg 1 31DSCGC91/1	D.Weisgarver	2/16-2/28/1991	R. Key	NOSAMS ¹ M. Stuiver
P16N	CGC-91 Leg 2 31DSCGC91/2	J. Bullister	3/7-4/8/1991	R. Key	NOSAMS ² G. Östlund ³ M. Stuiver ⁴
P17C	TUNES-1 31WTTUNES/1	M. Tsuchiya	5/31–7/11/1991	R. Key	NOSAMS ⁵ G. Östlund ⁶
P16S17S	TUNES-2 31WTTUNES/2	J. Swift	7/16-8/25/1991	R. Key	NOSAMS ⁷ G. Östlund ⁸ M. Stuiver ⁹
P16C	TUNES-3 31WTTUNES/3	L. Talley	8/31–10/1/1991	P. Quay	NOSAMS ¹⁰ M. Stuiver ¹¹
S4P	RUKDIOFFE6/1	Koshlyakov	2/14-4/6/1992	P. Schlosser	NOSAMS
P6E	316N138/3	H. Bryden	5/2-5/26/1992	R. Key	NOSAMS ¹²
P6C	316N138/4	M. McCartney	5/30-6/7/1992	R. Key	NOSAMS ¹³
P6W	316N138/4	J. Toole	6/13-6/30/92	R. Key	NOSAMS ¹⁴
P14C	316N138/7	D. Roemmich	9/1-9/15/1992	R. Key	NOSAMS
P13N	CGC-92 Leg 1 3220CGC92/1	J. Bullister	8/3-9/10/1992	P. Quay	NOSAMS
P16A17A	Juno-1 316N138/9	J. Reid	10/6–11/26/1992	R. Key	NOSAMS ¹⁵ G. Östlund ¹⁶
P17E19A	Juno-2 316N138/10	J. Swift	12/4/92-1/22/1993	R. Key	NOSAMS G. Östlund ¹⁷
P19C	316N138/12	L. Talley	2/22-4/13/1993	R. Key	NOSAMS G. Östlund ¹⁸
P17N	325021/1	D. Musgrave	5/15-6/26/1993	P. Quay R. Key	NOSAMS M. Stuiver
P10	3250TN026/1	M. Hall	10/5–11/10/1993	R. Key	NOSAMS M. Stuiver
P18S	31DSCGC94/2	B. Taft	2/22-3/2/1994	P. Quay	NOSAMS
P18N	31DSCGC94/3	G. Johnson	3/27-4/27/1994	P. Quay	NOSAMS

TABLE 1. WOCE Pacific Cruise Summary

*NOSAMS determined δ^{13} C for all AMS¹⁴C measurements except for legs on which P. Quay was PI. †M. Stuiver determined δ^{13} C for all LV samples

‡Not an official WOCE cruise

¹NOSAMS 1994a; ²NOSAMS 1994a; ³Östlund 1992a; ⁴Stuiver 1994; ⁵NOSAMS 1994c; ⁶Östlund 1992b, 1994; ⁷NOSAMS 1995a, 1996; ⁸Östlund 1994, 1995; ⁹Stuiver 1994; ¹⁰NOSAMS 1996; ¹¹Stuiver 1994; ¹²NOSAMS 1995b; ¹³NOSAMS 1994; ¹⁴NOSAMS 1995b; ¹⁵NOSAMS 1995c; ¹⁶Östlund 1995; ¹⁷Östlund 1994, 1995; ¹⁸Östlund 1994, 1995

section was collected during GEOSECS, the data were sufficient to indicate that deep zonal Δ^{14} C gradients would be even smaller.

During the planning phase of WOCE, the accelerator mass spectrometry (AMS) technique for measuring ¹⁴C was still relatively new in the United States. The general procedures had been worked out, but no lab was prepared to handle the large number of samples expected from the WOCE program,

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nor had it been demonstrated that the AMS technique could deliver the required precision on a routine basis. The National Ocean Sciences AMS Facility (NOSAMS) at Woods Hole Oceanographic Institution was established in 1989 to serve this purpose. In planning the WOCE Pacific fieldwork, it was recognized that sample collection would begin well before NOSAMS could deliver the high precision offered by conventional β -counting techniques. Therefore, both techniques were utilized.

On those legs which included both LV and SV sampling, the LV stations were spaced at an average interval of 5° (~300 nautical miles = ~555 km). LV stations normally included two casts of nine Gerard barrels each covering the water column from ~1000 m to the bottom. The upper kilometer of a LV station was covered by 16 SV samples taken from the CTD/Rosette cast. The legs that included both sample types are the ones that have more than one entry in the rightmost column of Table 1 and are indicated in Figure 1 by a * in the legend. One to three SV stations were placed between each LV station. On SV stations only the upper thermocline region was sampled, using 16 SV samples.

¹⁴C was extracted from the LV samples at sea as ¹⁴CO₂, absorbed on excess NaOH and returned to shore in well-sealed glass bottles using a modification of the technique described by Fonselius and Östlund (1959) (Key 1991; Key *et al.* 1991). Once ashore, the samples were sent to one of two labs for analysis: Tritium Laboratory, University of Miami, Miami, Florida (G. Östlund, director); or Quaternary Isotope Laboratory, University of Washington, Seattle (M. Stuiver, director). A short description of the measurement procedure and a cross-check between these two labs is available in Stuiver *et al.* (1974). Stuiver reports an error estimate for each analysis ranging from 2.5 to 4.0%; Östlund reports a uniform sample error of 4‰. In both cases, the reported uncertainty is primarily counting error and does not include any error due to sample collection. All δ^{13} C measurements for the LV samples were made by Stuiver.

All SV ¹⁴C samples were collected from standard CTD/Rosette casts into 500-ml glass bottles fitted with high-quality ground glass stoppers. The samples were poisoned with HgCl₂ immediately after collection, then returned to the U.S. for extraction and analysis at NOSAMS. Details of the extraction, counting, *etc.* are available from Key (1991), McNichol and Jones (1991), Gagnon and Jones (1993), Cohen *et al.* (1994), McNichol *et al.* (1994), Osborne *et al.* (1994), Schneider *et al.* (1994) and Séguin *et al.* (1994). All δ^{13} C analyses, except for the samples collected by Quay (who extracted and measured his own δ^{13} C values), were performed at NOSAMS.

The standards for the ¹⁴C measurements were NBS oxalic acid standards (Östlund, RM 49 and SRM 4990C; Stuiver, RM 49 and SRM 4990C; NOSAMS, SRM 4990 and SRM 4990C). All results are reported as Δ^{14} C, which is the deviation in per mil (‰) from unity of the sample to standard activity ratio, isotope-corrected to a sample δ^{13} C value of -25%. (For more information on standards and calculation methods, see Broecker and Olson (1961), Stuiver and Robinson (1974) and Stuiver (1980).) As measurements were completed, the results were communicated from the analytical lab to the PI responsible for the cruise *via* periodic data reports (see footnotes to Table 1). R. Key gathered the Δ^{14} C data from the PI, merged it with hydrographic data supplied either by the chief scientist or by the WOCE Hydrographic Office (WHPO), added WOCE quality-control flags, and finally submitted the data to WHPO along with a final report for each leg (Key 1994, 1995, 1996a–i; Key and Quay 1996). All of the LV samples collected in the Pacific will be completed by 1997 and the Pacific SV samples by 1998.

DATA QUALITY

The precision of the LV technique was established during the GEOSECS program to be 2-4%. This precision is primarily a function of sample counting time and has held constant throughout the succeeding large-scale ocean survey programs. What was unknown at the beginning of WOCE was the

ultimate precision of the AMS technique and whether or not the AMS and LV data would be totally compatible, *i.e.*, no systematic errors would be found in either data set.

NOSAMS is currently running water samples with a mean "external" precision of 3.6%. This precision is indicative of the AMS target preparation and counting and does not include any uncertainty due to sample collection, storage or stripping. A better estimate of the sample precision can be obtained by comparing the results from duplicate samples. A summary all of the true WOCE duplicates (*i.e.*, two different sample bottles rather than two analyses from the same bottle) analyzed at NOSAMS showed that the average of the standard deviation for each pair was 4.6%. The reason for the difference between this number and the external precision estimate (3.6%) is currently unknown, but must involve either sample collection or sample processing prior to counting. A reproducibility of 3% is needed for the AMS technique to be equivalent to the average uncertainty for the LV technique. Sample storage experiments at NOSAMS and other facilities have so far indicated that this is not a source of error.

Once all of the Pacific samples are completed, sufficient data will exist to make statistically significant comparisons between AMS and LV sampling. For now, the best that can be done is to graphically compare WOCE stations where the two techniques overlap, and to compare WOCE results in deepwater to GEOSECS results. Figure 2 shows results from TUNES-2 (P16S17S) station 179, Juno-1 (P16A17A) station 119 and P6C station 100 taken at ca. 33°S, 135°W. The TUNES station includes both LV and SV samples and was occupied on 7/1991. Stuiver analyzed the LV samples from this station. The Juno occupation was on 11/1992 at the same location as the TUNES station. Östlund measured the LV samples from Juno-1. The P6 station was ca. 250 nautical miles away (463 km) and was occupied on 7/1992. Each datum is shown with 2- σ error bars. At this scale, the agreement between the techniques appears to be good. The only possible systematic difference is in the upper thermocline, with the TUNES samples being slightly lower than those from Juno and P6. This apparent offset may be due to a real difference in the water column structure. A better place to compare the results is in the deepwater. The insert in the lower right portion of Figure 2 shows the data from the bottom 2 km on a greatly expanded scale. The pressure scale for the insert is aligned and scaled to match the pressure scale of the main figure. There is some structure in the Δ^{14} C signal, but there is no apparent systematic difference between the measurement techniques. This plot clearly demonstrates the need for very high-precision data in the deep and bottom waters.

Another data test can be made by comparing the new AMS data to existing historical data. Figure 3 shows a plot of WOCE P6 station 148 (32.5°S, 163.6°W; 6/1992) AMS results (NOSAMS 1994b) with GEOSECS station 306 (32.5°S, 165.2°W; 3/1974) LV results (Östlund and Stuiver 1980). The invasion of bomb ¹⁴C into the thermocline is clearly evident. The deep- and bottom-water data are shown on an expanded scale in the insert in the lower right portion of the figure. The deepwater data (2500–4500 m) from the two stations appear to be the same. Below 4500 m the AMS Δ^{14} C results are slightly higher than the GEOSECS results. At this point it is difficult to determine if this difference is a measurement difference or a small bomb-produced ¹⁴C signal that has been introduced into the bottom waters since the time of GEOSECS. The meaning of differences this small will require a careful statistical analysis of the full WOCE data set.

CONCLUSION

The Pacific Ocean WOCE program has generated a new high-quality data set for analyzing the distribution of ¹⁴C. Comparison using currently available data indicates that measurements using the



Fig. 2. Comparison of AMS and LV results for three stations in the south-central Pacific Ocean. The TUNES-2 station 179 data and the Juno-1 station 119 data were collected at the same location (33°S, 135°W), but 14 months apart (7/1991 and 11/1992, respectively). The P6 station 100 data (7/1992) were collected *ca*. 250 nautical miles (463 km) away (32.5°S, 130°W). The insert shows data from the bottom 2500 dB on an expanded scale. Both LV and AMS techniques were employed on the TUNES and Juno cruises while only AMS was used on P6. No systematic difference in techniques is evident for these data.



Fig. 3. Comparison of WOCE AMS (P6 station 148, 32.5° S, 163.6° W, 6/1992) results with GEOSECS (station 306, 32.5° S, 165.2° W, 3/1974) LV results. (Error bars represent the 2- σ range). Data from the 3000–6000 dB range is shown on an expanded scale in the insert. The invasion of bomb-produced ¹⁴C during the time interval between the expeditions is clearly evident in the 250–1250 dB range. The deepwater values for the two stations appear to be the same. A statistical analysis of the entire WOCE data set will be required to determine if the slight difference *ca.* 5500 dB. is significant. If real, the direction of the bottom water difference is consistent with a very small addition of bomb-produced ¹⁴C over the time interval.

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newer AMS technique are comparable to the WOCE LV data as well as to the historical data. The combined WOCE data set is approximately an order of magnitude larger than all prior measurements in the Pacific combined.

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