Final Technical Report

Measurements of Surface Ocean Carbon Dioxide Partial Pressure During WOCE

U. S. Department of Energy
Grant Number DE-FG03-90ER60981
1 June 1990 — 31 May 1998

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DISCLAIMER

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 steam 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, xCO_2 and xN_2O. These can be converted to partial pressures, pCO_2 and pN_2O, 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 CO_2 and N_2O 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 *Washington*	F. A. Van Woy SIO
P-17C (Tunes Leg 1)	6/1/91-7/11/91	Port San Luis-Papeete	R/V *Washington*	K. Sullivan U. Miami
P-16S/P-17S (Tunes Leg 2)	7/17/91-8/25/91	Papeete-Papeete	R/V *Washington*	G. Mathieu LDEO
P-16C (Tunes Leg 3)	9/3/91-10/1/91	Papeete-Honolulu	R/V *Washington*	D. Wisegarver PMEL/NOAA
P-6C	5/30/92-7/6/92	Easter Island-Auckland	R/V *Knorr*	F. A. Van Woy SIO
P-6W	7/13/92-7/29/92	Auckland-Sydney	R/V *Knorr*	M. J. Warner UW
P-14C	9/1/92-9/13/92	Auckland-Suva	R/V *Knorr*	M. J. Warner UW
P-16S/P-17S (Juno Leg 9)	10/6/92-11/26/92	Papeete-Papeete	R/V *Knorr*	F. A. Van Woy SIO
P-17S/P-19S (Juno Leg 10)	12/3/92-1/22/93	Papeete-Punta Arenas	R/V *Knorr*	P. K. Salameh SIO
P-19N	2/22/93-4/13/93	Punta Arenas-Panama	R/V *Knorr*	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 *Knorr*	K. Hargreaves PMEL/NOAA
I-9N	1/24/95-3/06/95	Fremantle-Colombo	R/V *Knorr*	K. Sullivan U. Miami
I-8N/I-5E	3/10/95-4/16/95	Colombo-Fremantle	R/V *Knorr*	R. Schottle SIO
I-3	4/20/95-6/07/95	Fremantle-Mauritius	R/V *Knorr*	F. A. Van Woy SIO
I-5W/I-4	6/11/95-7/11/95	Mauritius-Mauritius	R/V *Knorr*	K. Maillet U. Miami
I-7N	7/15/95-8/24/95	Mauritius-Mattrah	R/V *Knorr*	K. Sullivan U. Miami
I-1	8/29/95-10/18/95	Mattrah-Singapore	R/V *Knorr*	S. Covey UW
I-10	11/06/95-11/24/95	Singapore-Singapore	R/V *Knorr*	K. Sullivan U. Miami
I-2	11/28/95-1/19/96	Singapore-Mombasa	R/V *Knorr*	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 *Knorr*	F. A. Van Woy SIO
A-24	5/29/97-7/04/97	Azores-Halifax	R/V *Knorr*	F. A. Van Woy SIO
A-20	7/17/97-8/10/97	Halifax-Trinidad	R/V *Knorr*	C. Sabine Princeton
A-22	8/15/97-9/03/97	Trinidad-Woods Hole	R/V *Knorr*	R. Rotter Princeton
AR-24	10/05/97-11/19/97	Woods Hole-Woods Hole	R/V *Knorr*	G. Eischeid WHOI

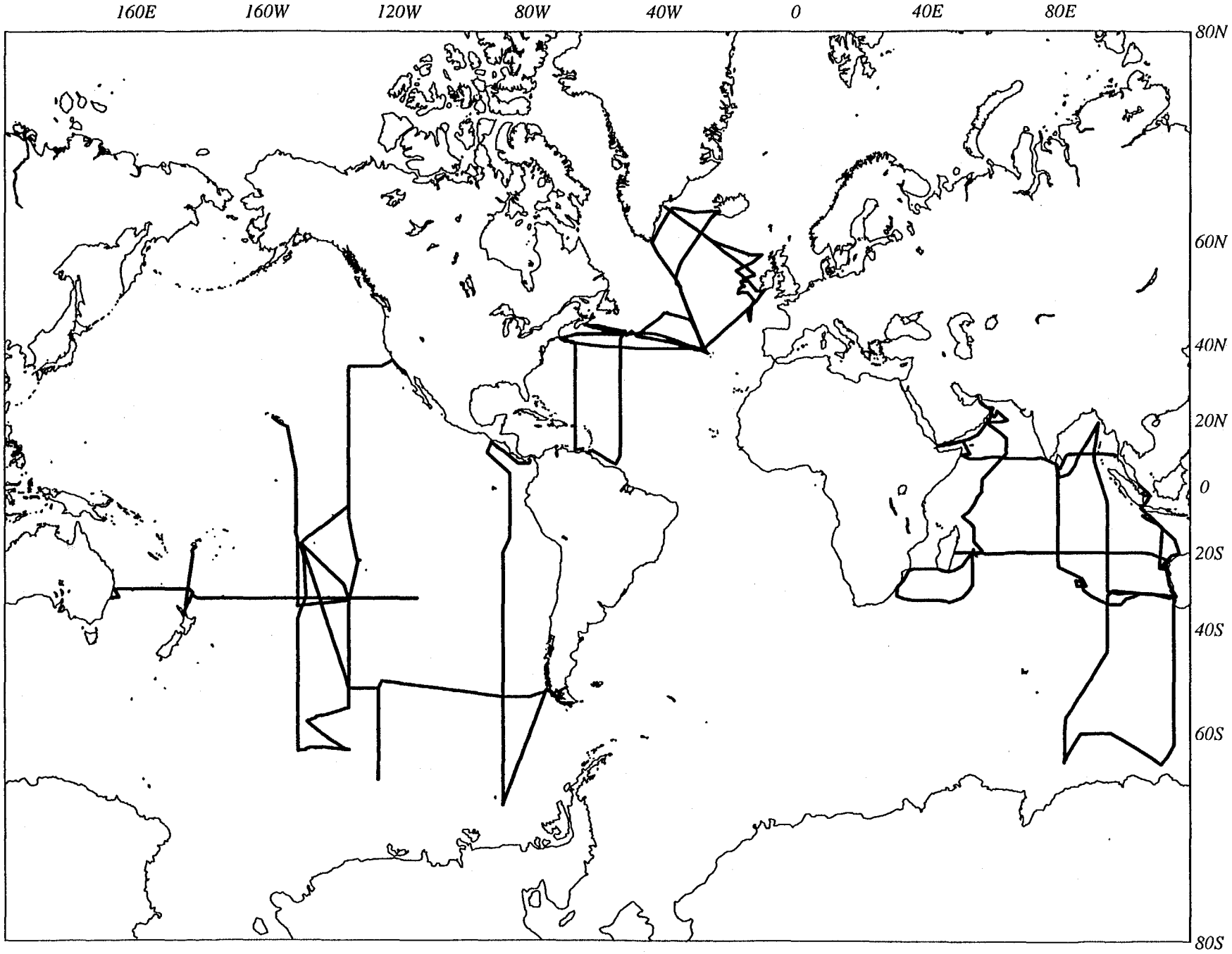
The results from these measurements are presented graphically in the following figures, which show the cruise tracks and the equilibrator and atmospheric results in the same format and with the same Gaussian smoothing procedures as were used by Weiss *et al.* (1992). The data plots are largely self-explanatory, and provide a very considerable improvement in the geographic coverage of pCO_2 and pN_2O 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).

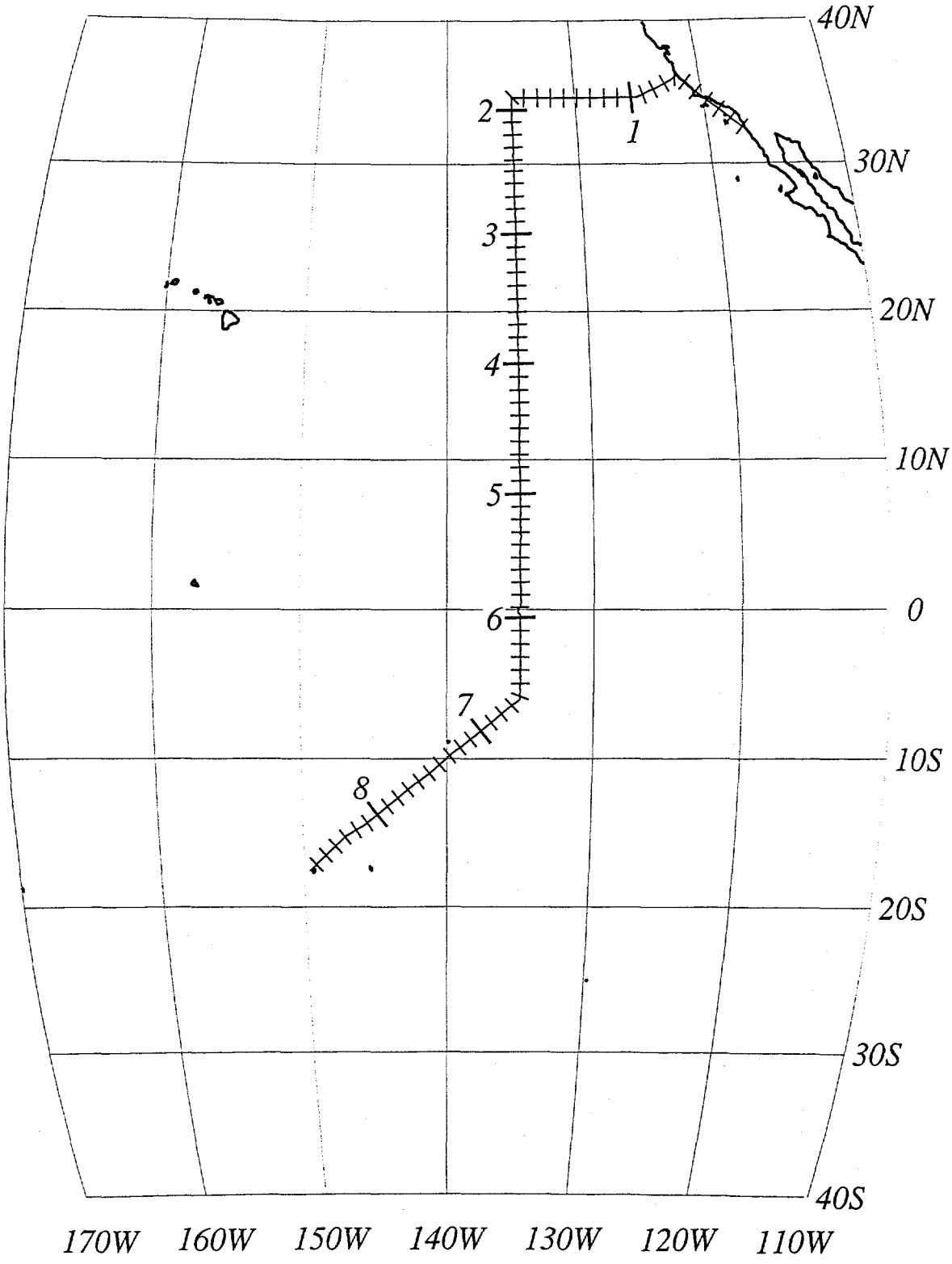
References

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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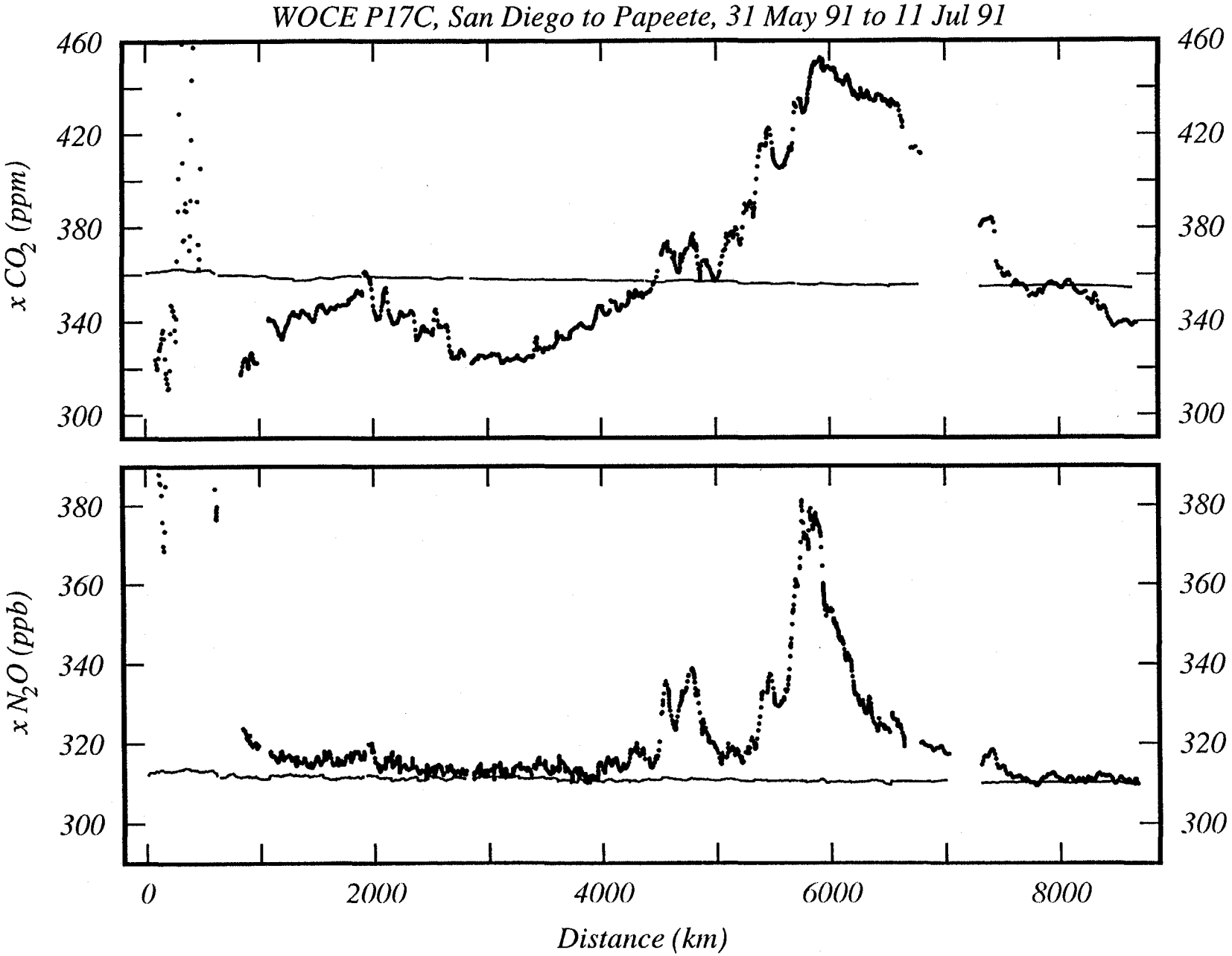
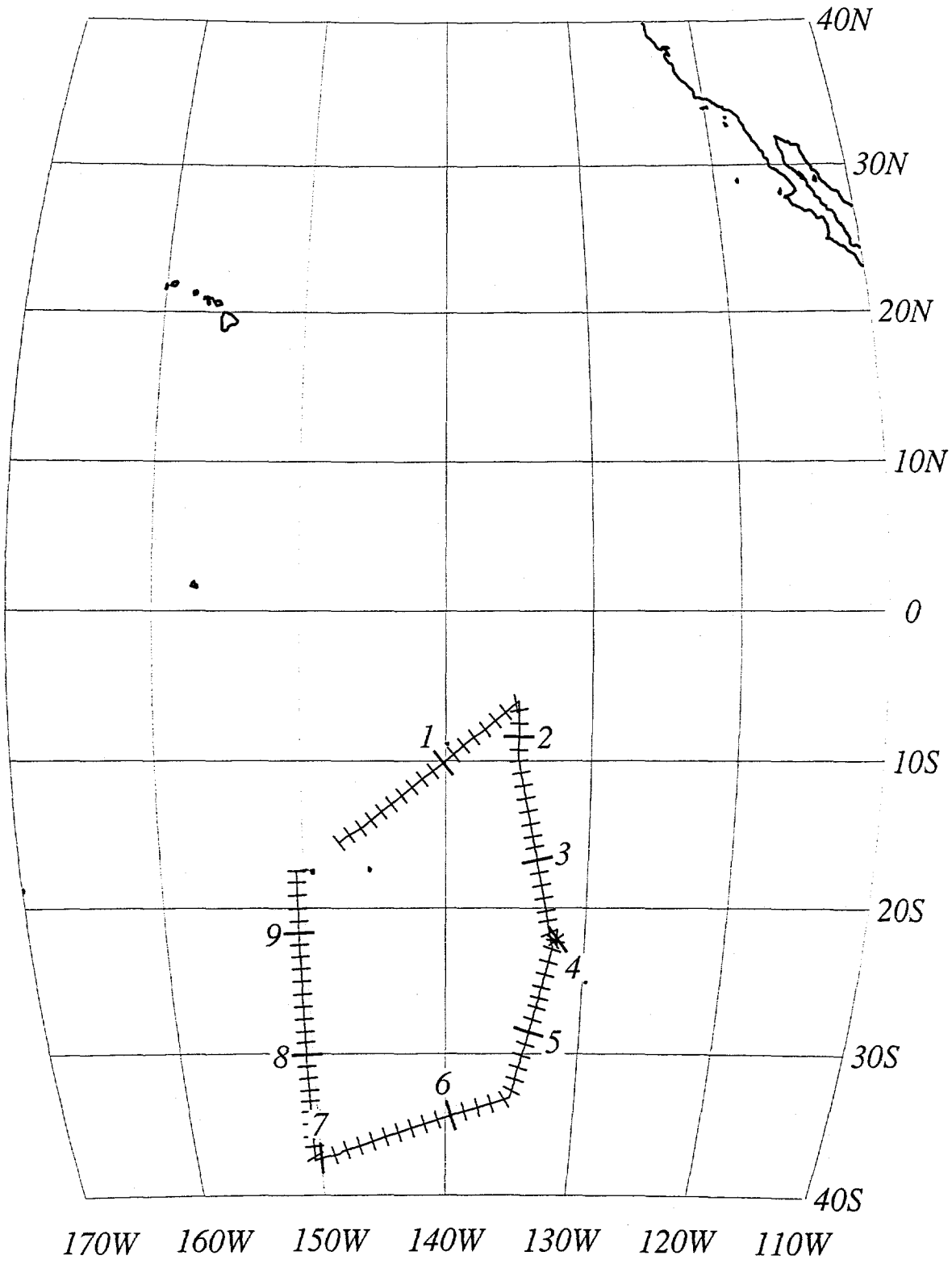
30N
20N
10N
0
10S
20S
30S
40S
1
2
3
4
5
6
7
8
170W
160W
150W
140W
130W
120W
110W

WOCE P17C


WOCE P17C, San Diego to Papeete, 31 May 91 to 11 Jul 91
x CO2 (ppm)
460
420
380
340
300
x N2O (ppb)
380
360
340
320
300
0
2000
4000
6000
8000
Distance (km)



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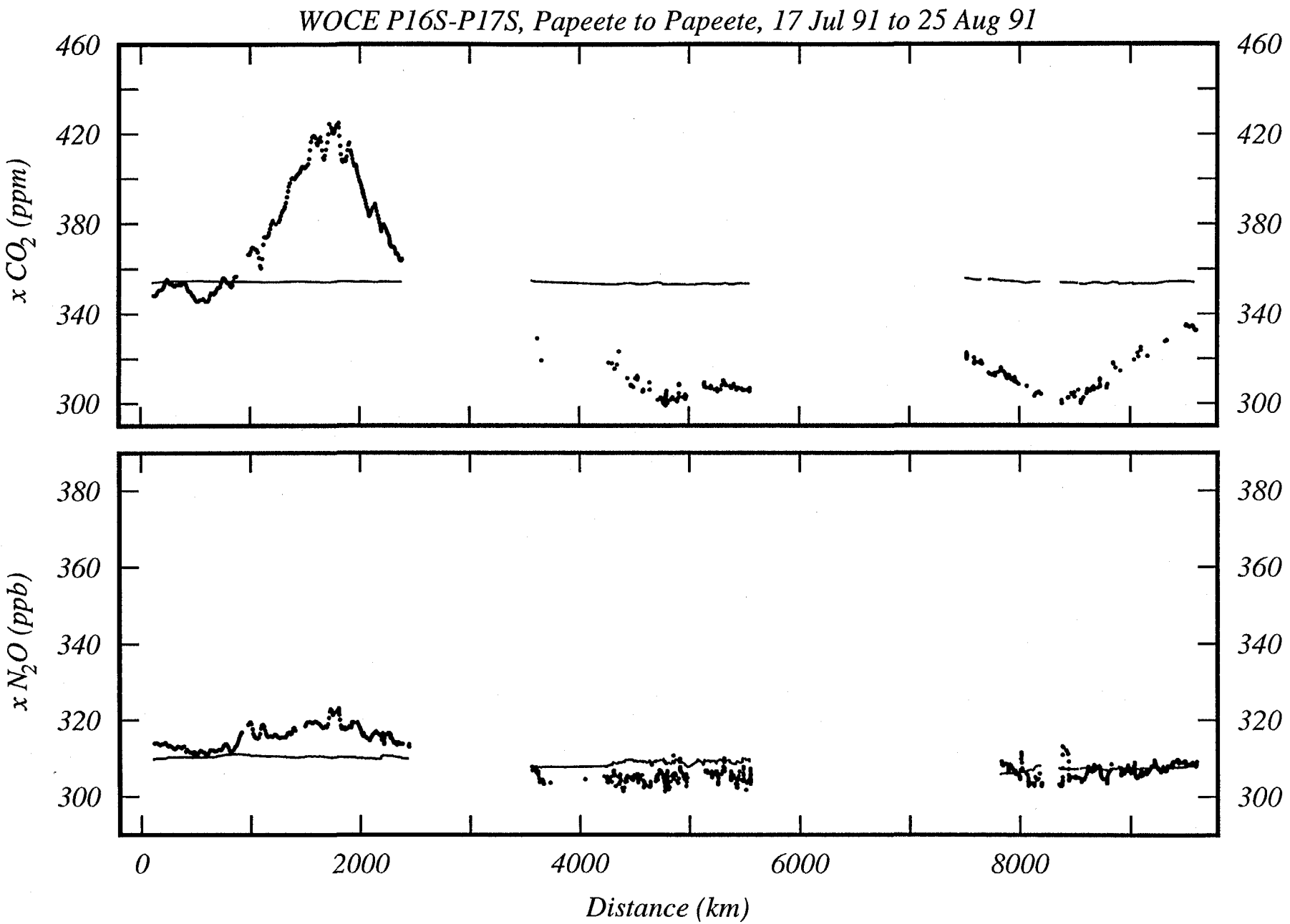
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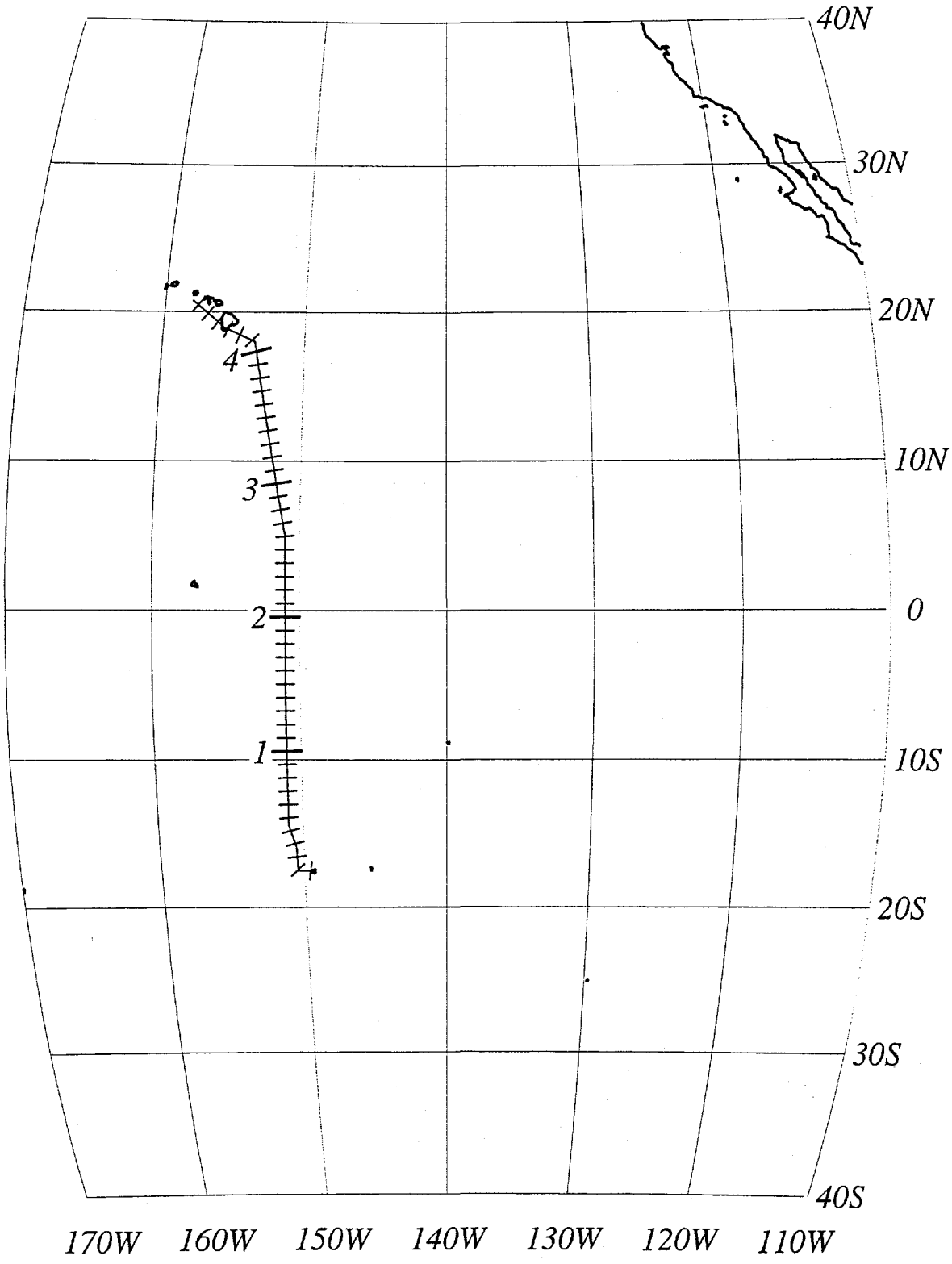
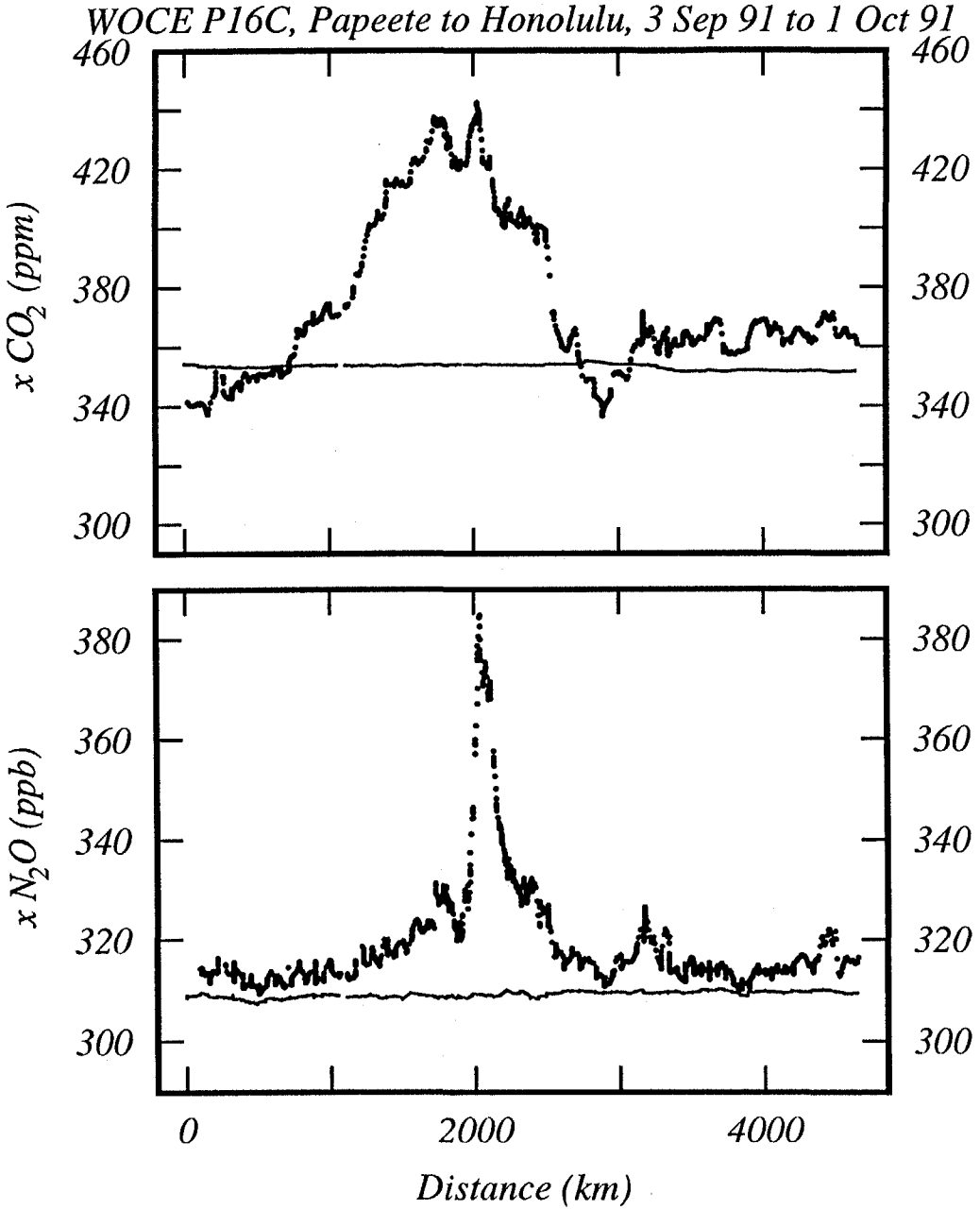
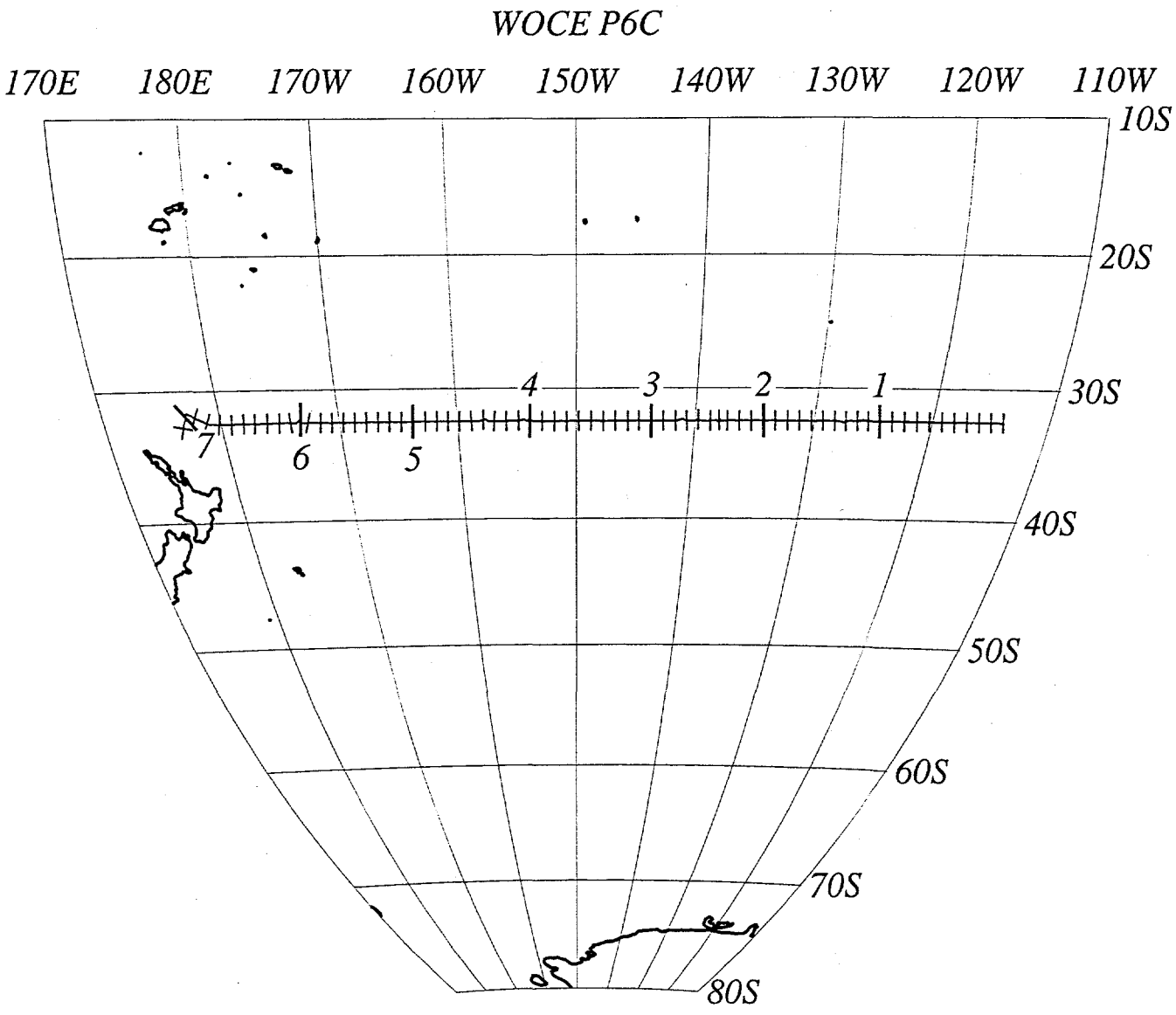
460
420
380
340
300
x CO2 (ppm)
380
360
340
320
300
x N2O (ppb)
0
2000
4000
6000
8000
Distance (km)


40N
30N
20N
10N
0
10S
20S
30S
40S
170W
160W
150W
140W
130W
120W
110W
4
3
2
1

WOCE P16C


WOCE P16C, Papeete to Honolulu, 3 Sep 91 to 1 Oct 91
460
420
380
340
300
x CO_2 (ppm)
380
360
340
320
300
x N_2O (ppb)
0
2000
4000
Distance (km)


WOCE P6C
170E
180E
170W
160W
150W
140W
130W
120W
110W
10S
20S
30S
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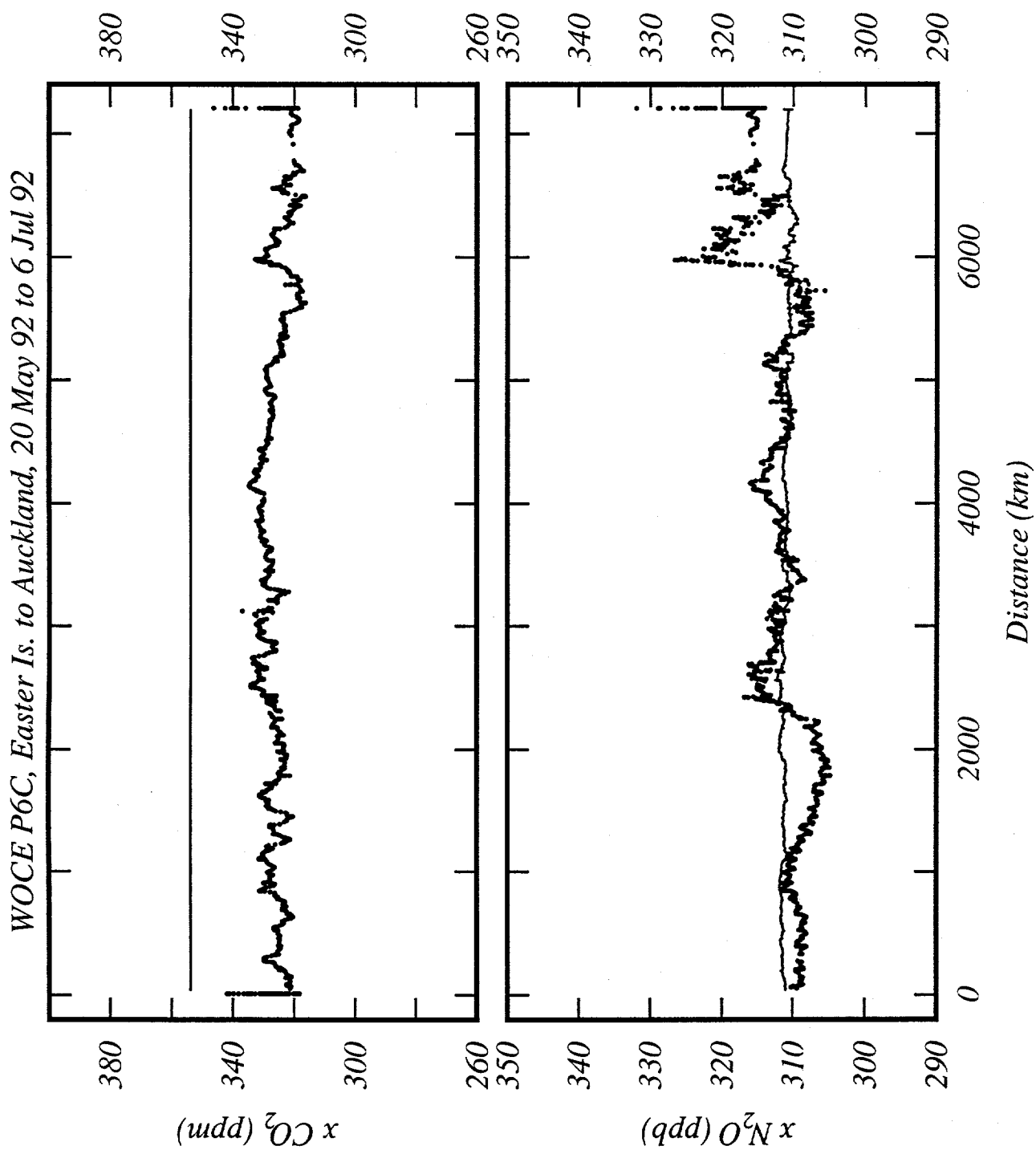
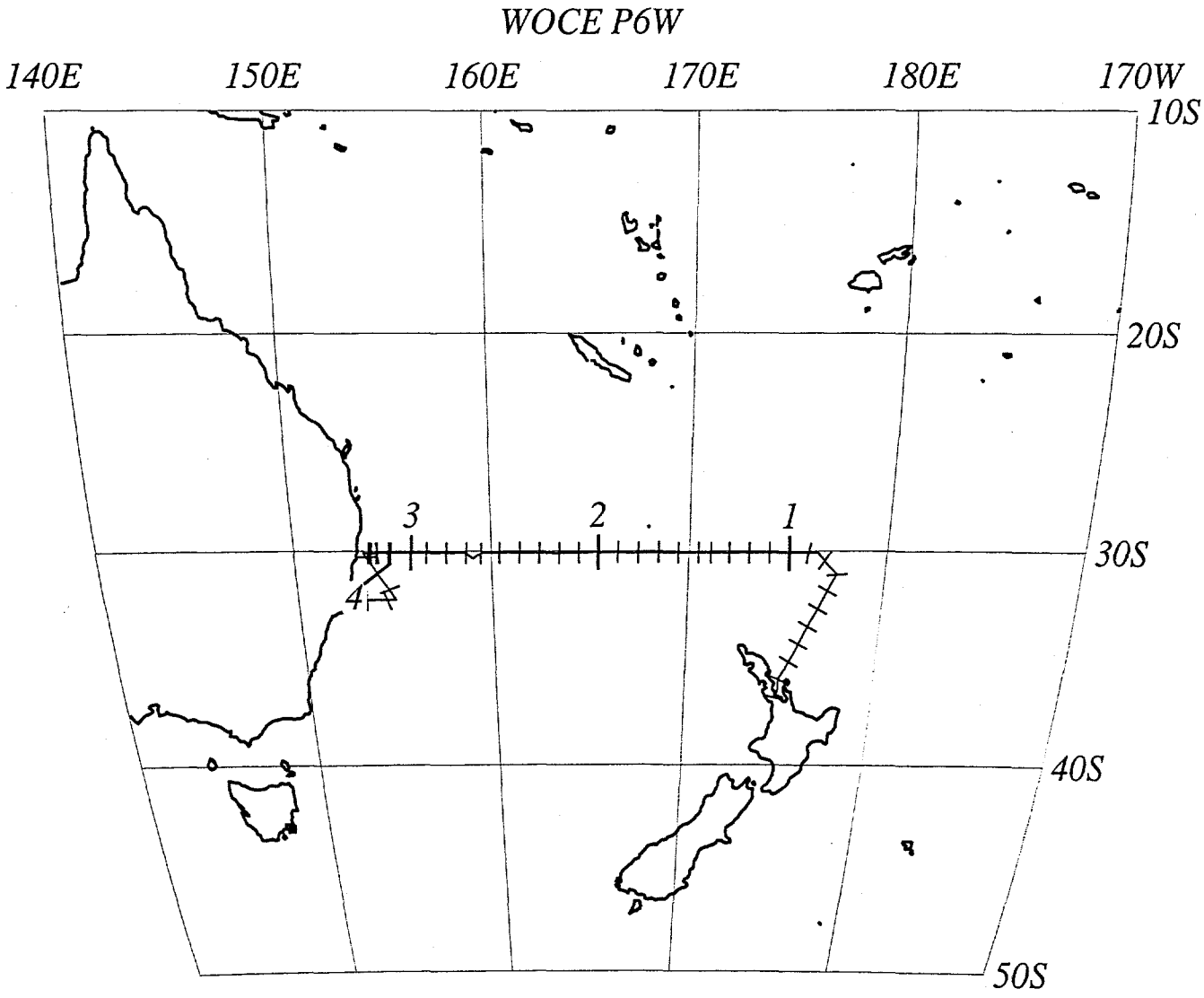
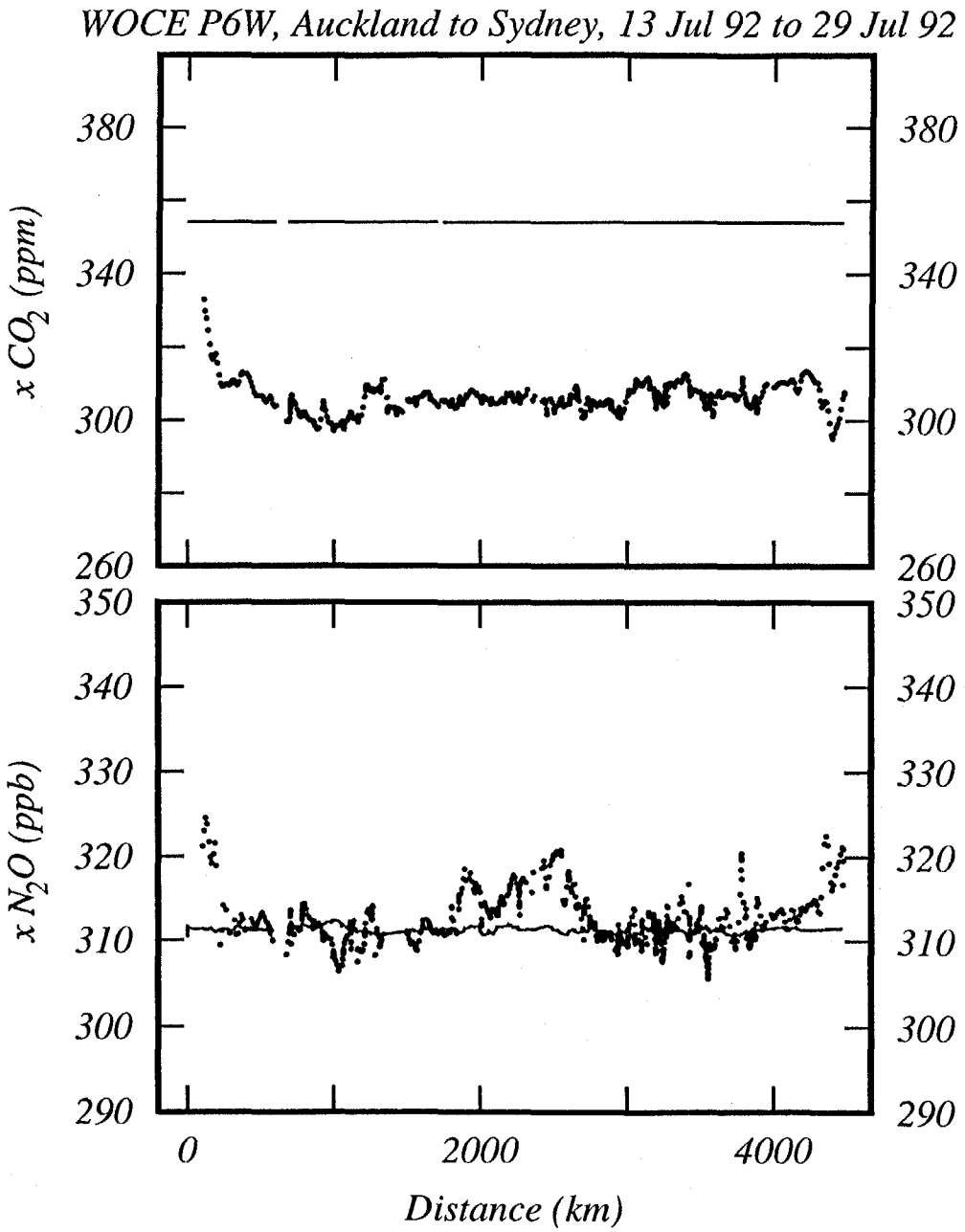
60S
70S
80S
1
2
3
4
5
6
7


WOCE P6C, Easter Is. to Auckland, 20 May 92 to 6 Jul 92
x CO2 (ppm)
x N2O (ppb)
Distance (km)
0
2000
4000
6000
380
340
300
260
350
330
320
310
290


WOCE P6W
140E
150E
160E
170E
180E
170W
10S
20S
30S
40S
50S
1
2
3
4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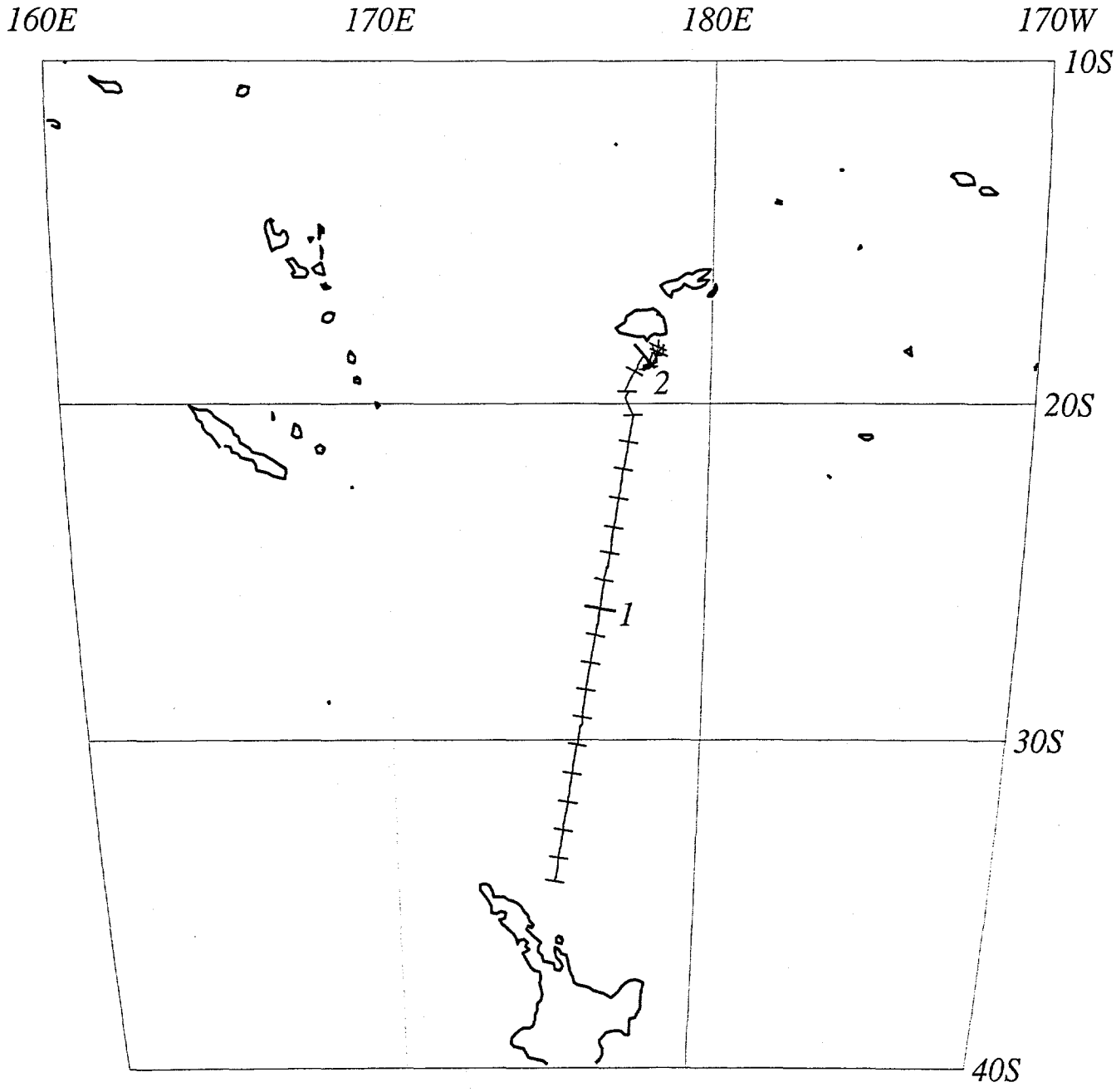
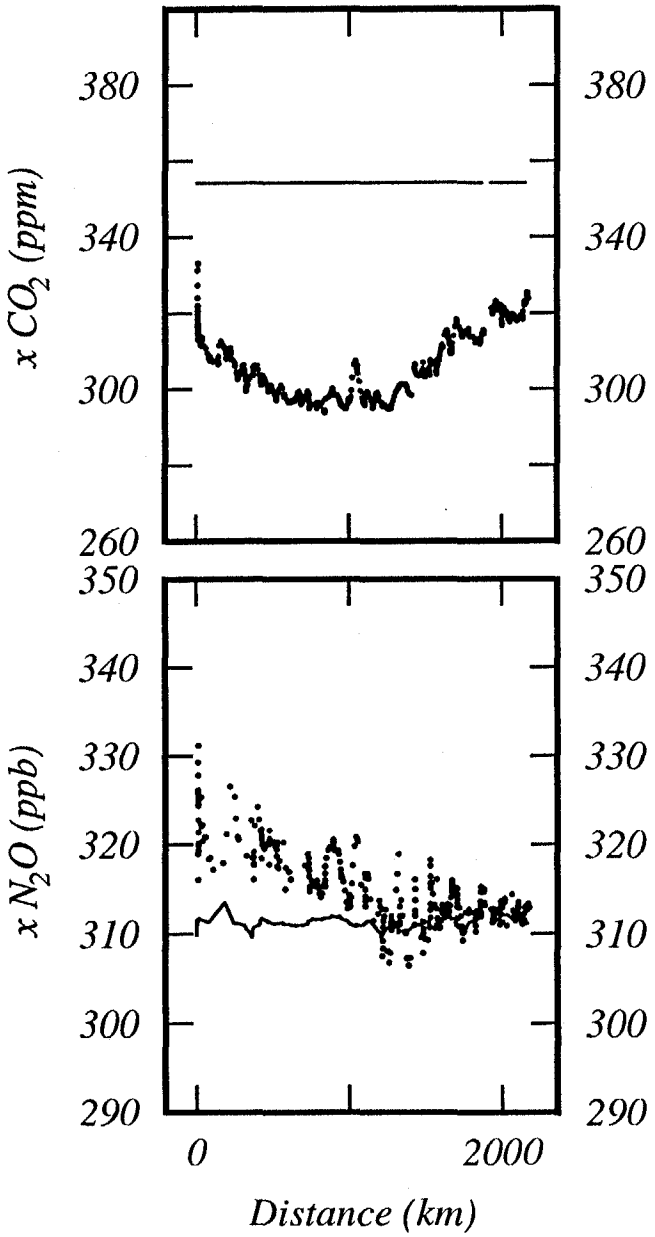
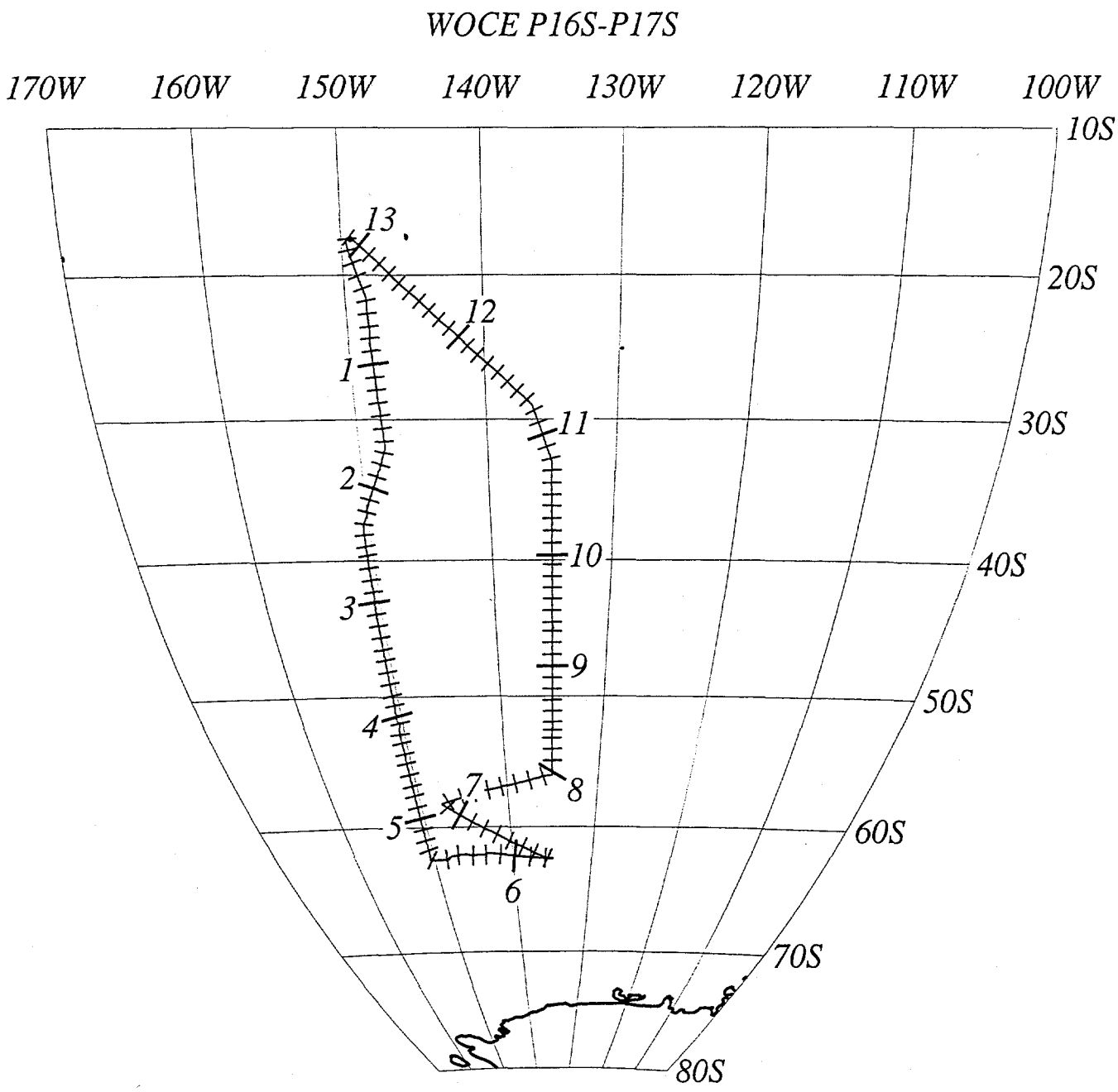
x CO2 (ppm)
380
340
300
260
x N2O (ppb)
350
340
330
320
310
300
290
0
2000
4000
Distance (km)

WOCE P14C



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




WOCE P16S-P17S
170W
160W
150W
140W
130W
120W
110W
100W
10S
20S
30S
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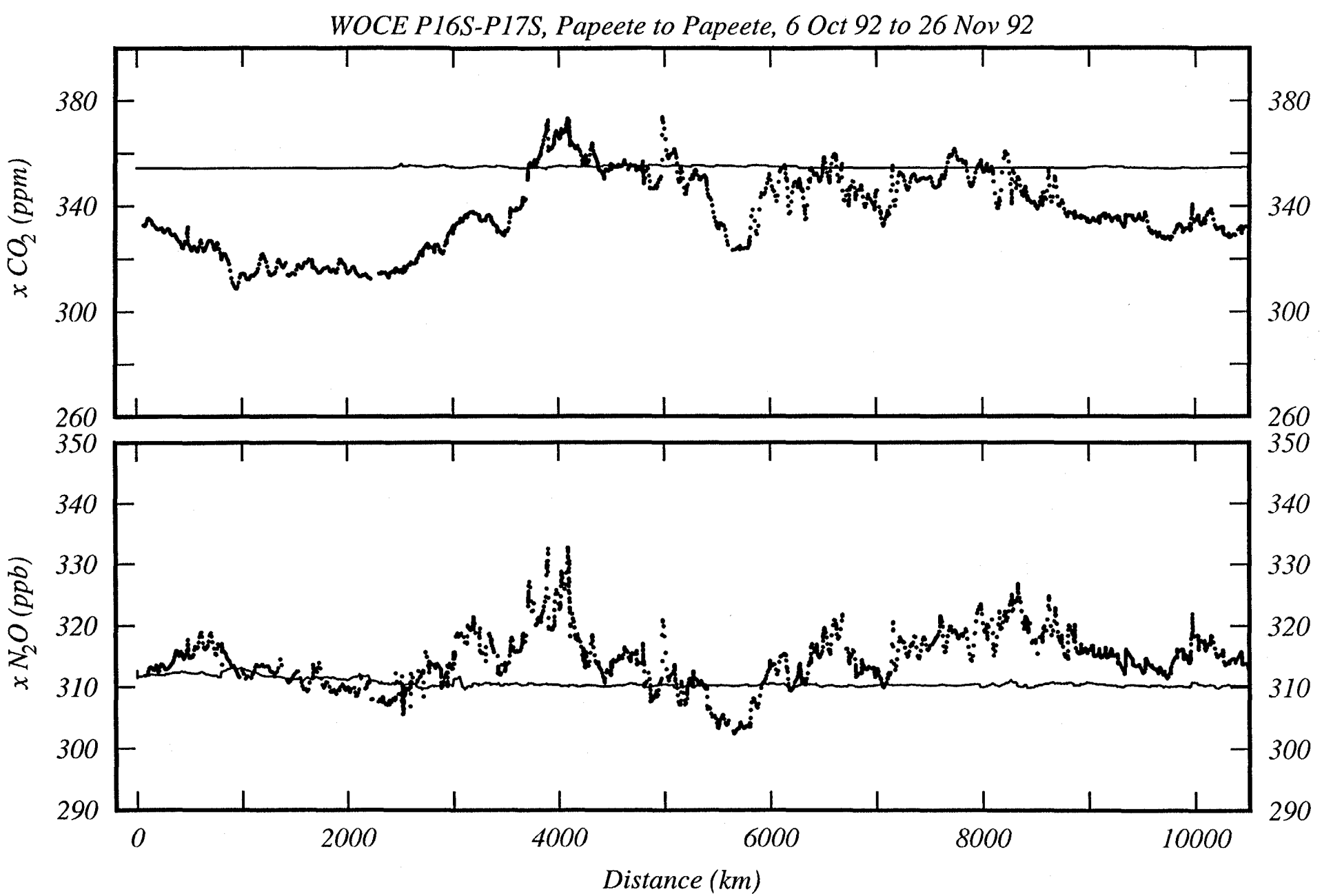
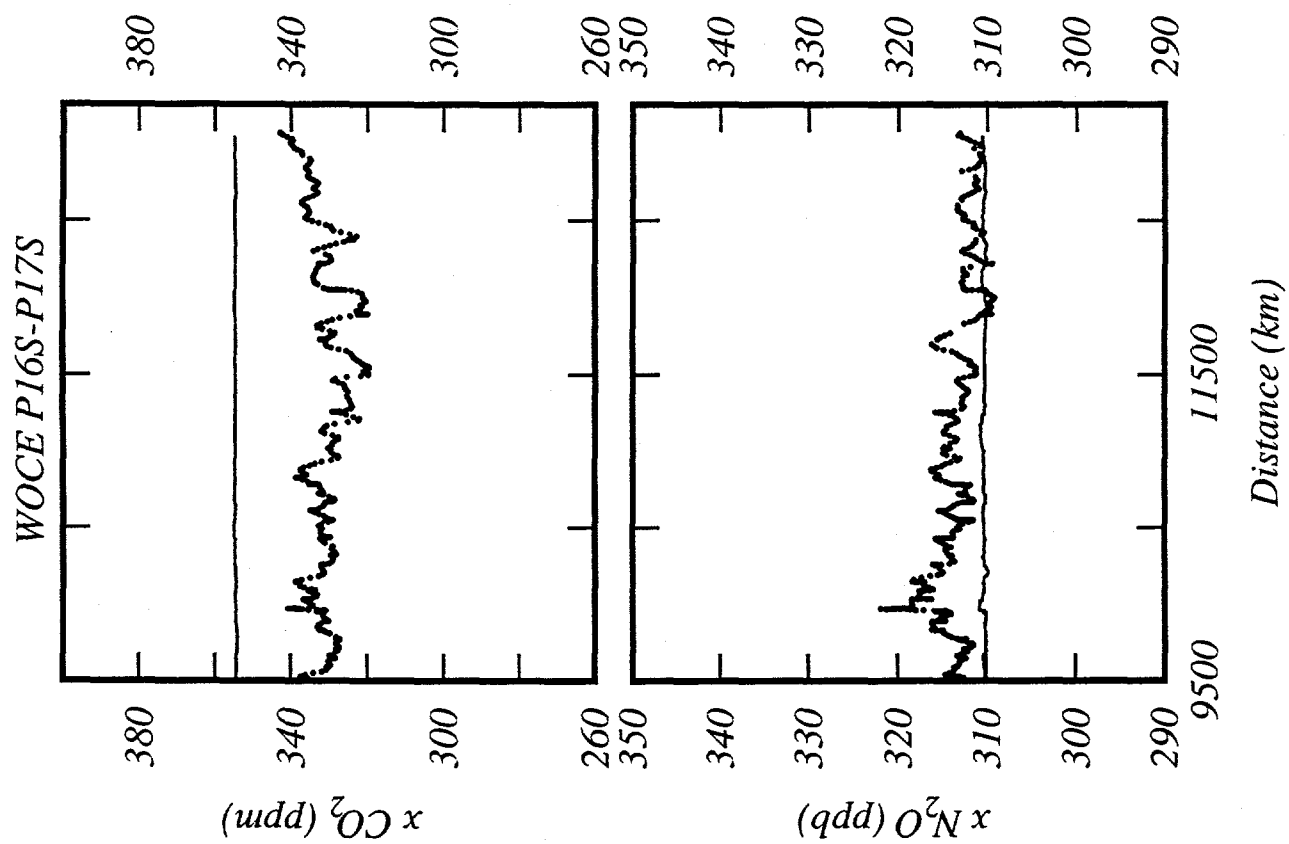
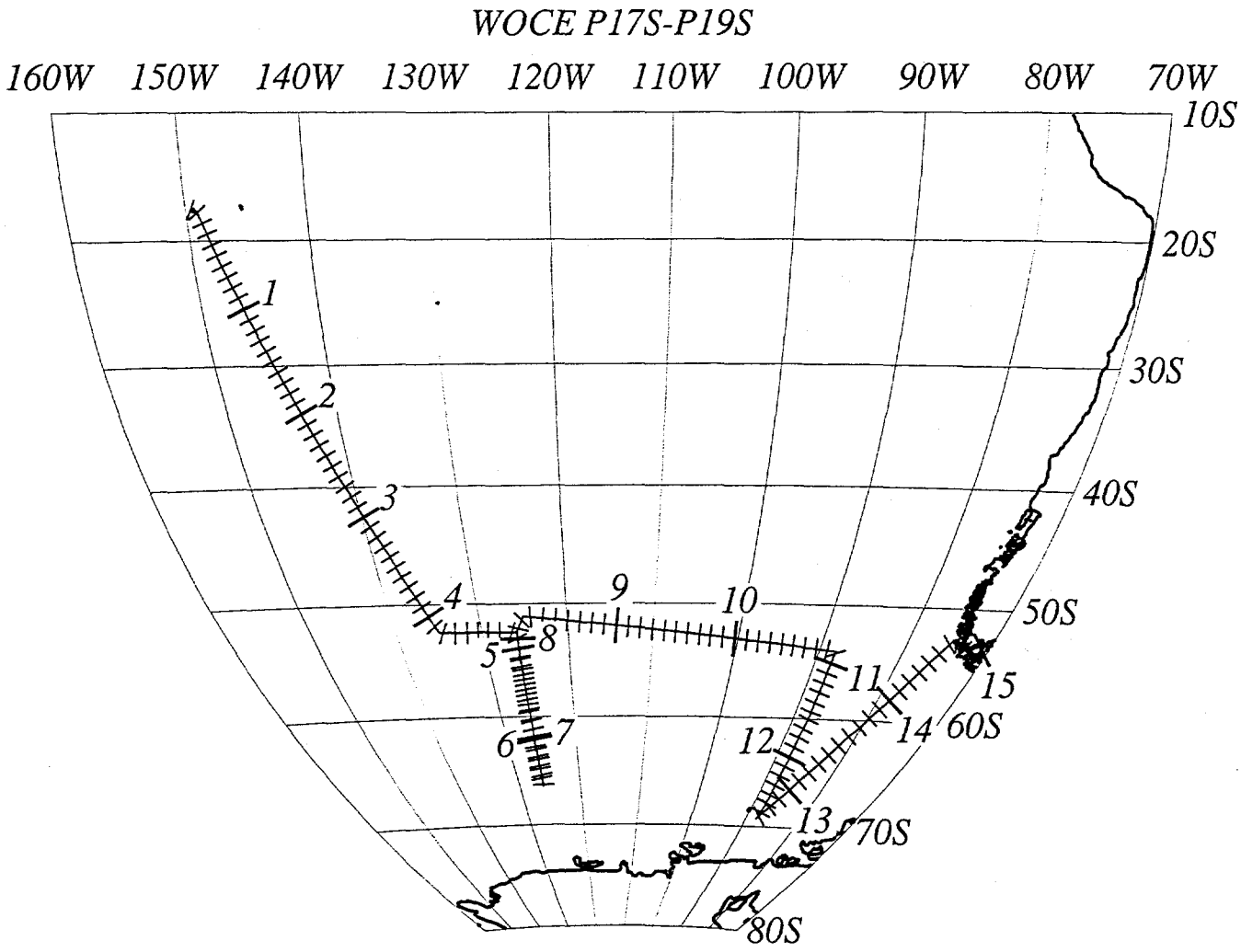
12
13


WOCE P16S-P17S, Papeete to Papeete, 6 Oct 92 to 26 Nov 92
x CO2 (ppm)
380
340
300
260
x N2O (ppb)
350
340
330
320
310
300
290
0
2000
4000
6000
8000
10000
Distance (km)


WOCE P16S-P17S
x CO2 (ppm)
380
340
300
260
x N2O (ppb)
350
340
330
320
310
300
290
9500
11500
Distance (km)


WOCE P17S-P19S
160W
150W
140W
130W
120W
110W
100W
90W
80W
70W
10S
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30S
40S
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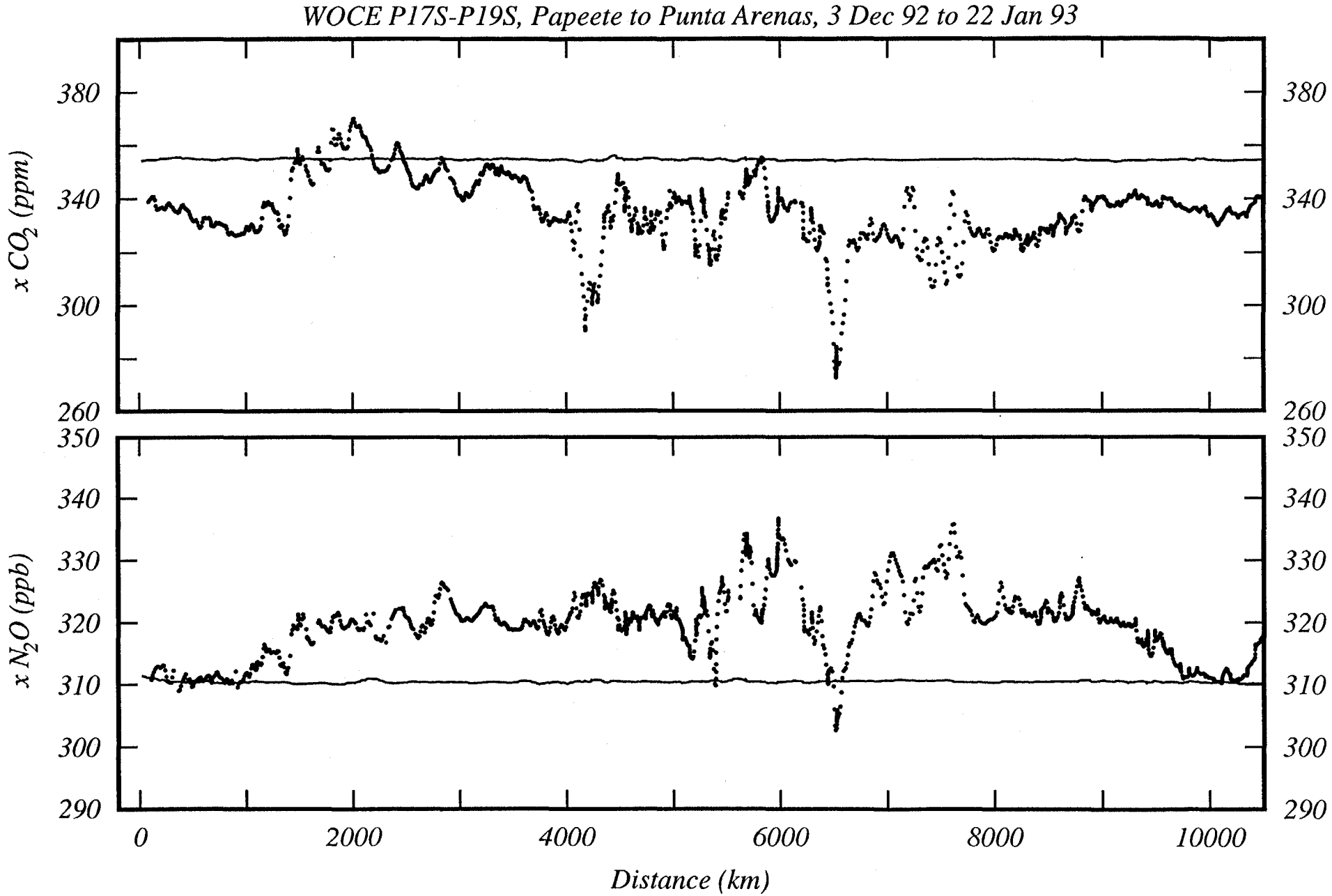
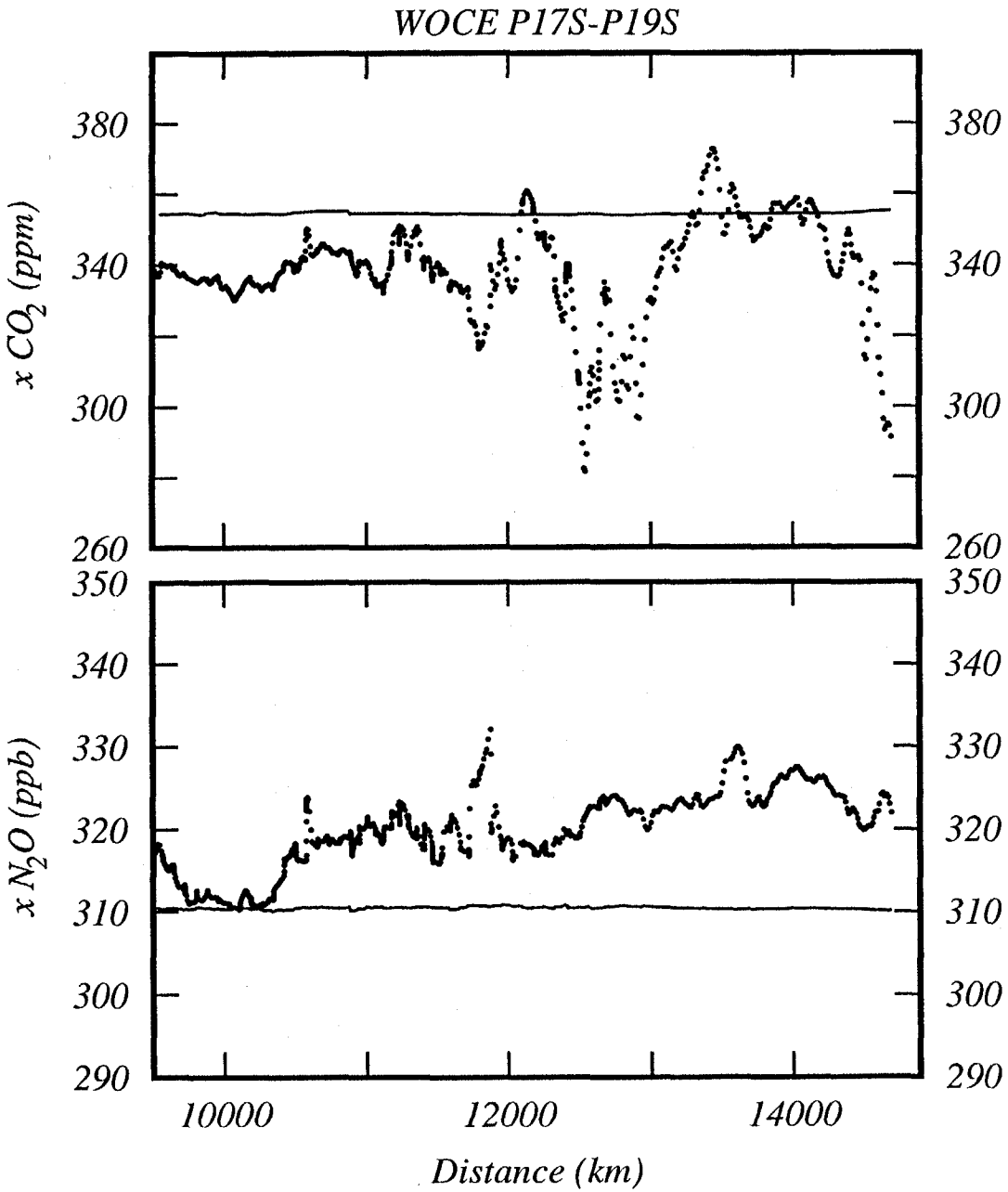
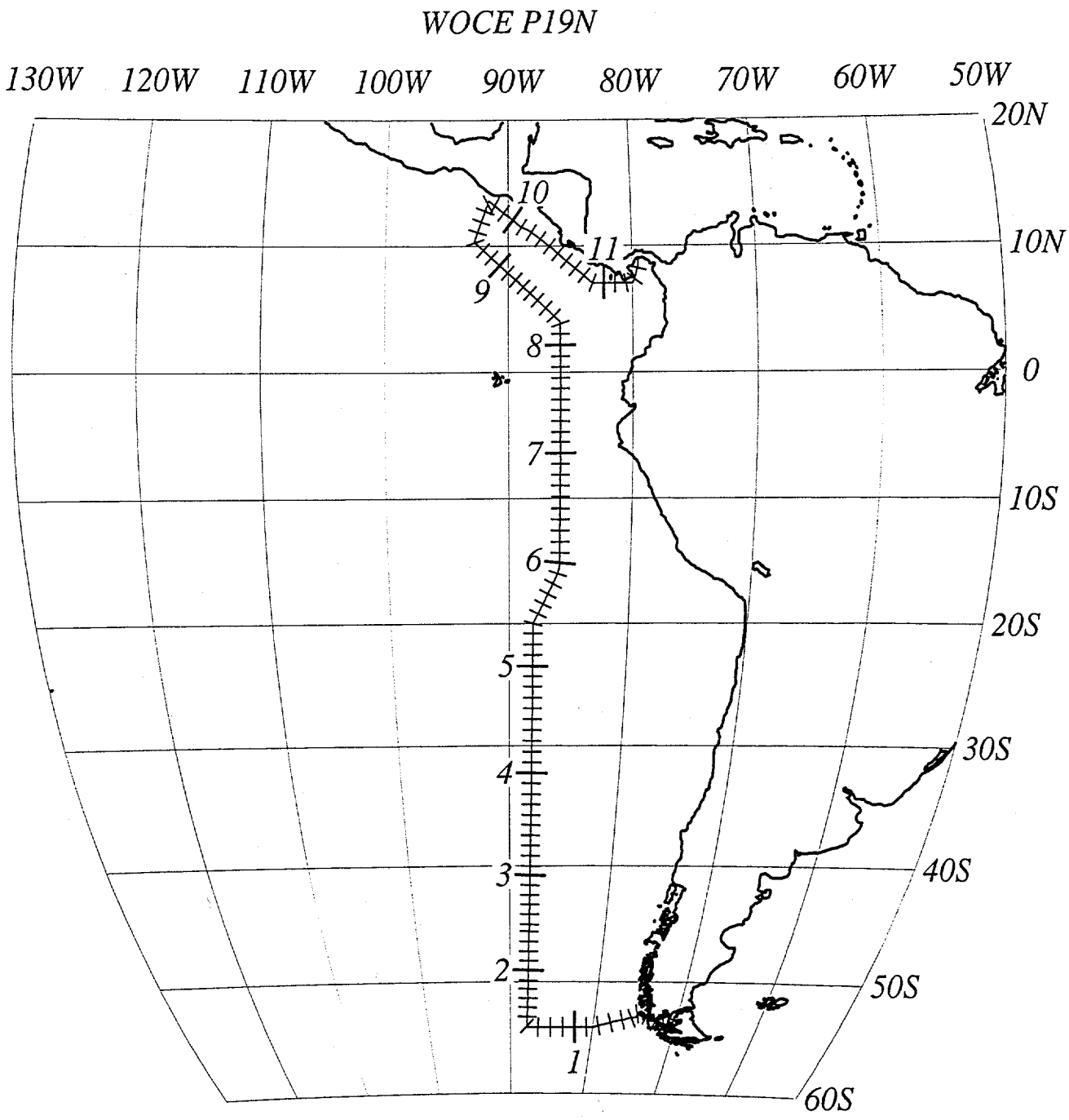
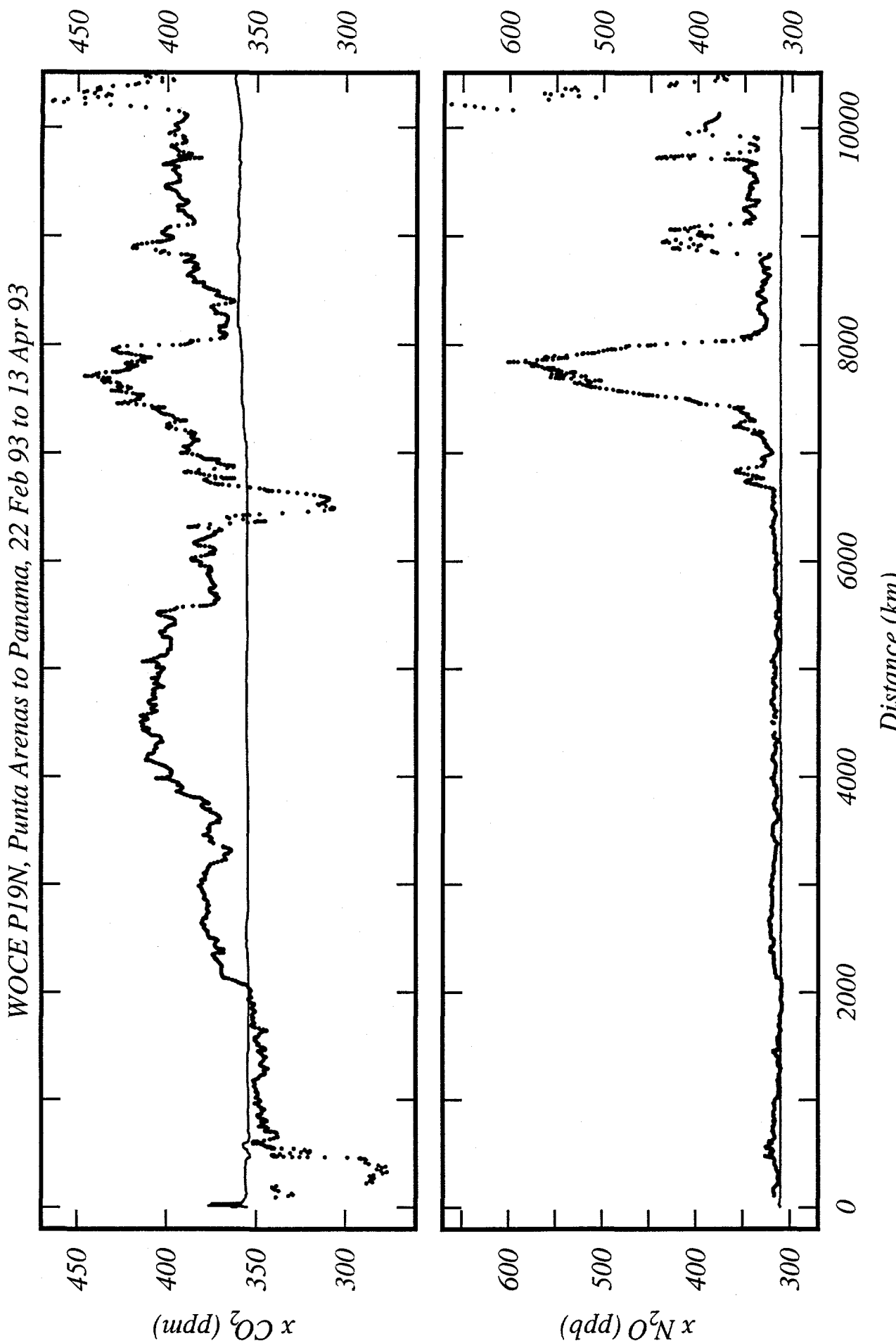

WOCE P17S-P19S, Papeete to Punta Arenas, 3 Dec 92 to 22 Jan 93
x CO2 (ppm)
380
340
300
260
x N2O (ppb)
350
340
330
320
310
300
290
0
2000
4000
6000
8000
10000
Distance (km)


WOCE P17S-P19S
x CO_2 (ppm)
380
340
300
260
x N_2O (ppb)
350
340
330
320
310
300
290
10000
12000
14000
Distance (km)


WOCE P19N
130W
120W
110W
100W
90W
80W
70W
60W
50W
20N
10N
0
10S
20S
30S
40S
50S
60S
10
11
9
8
7
6
5
4
3
2
1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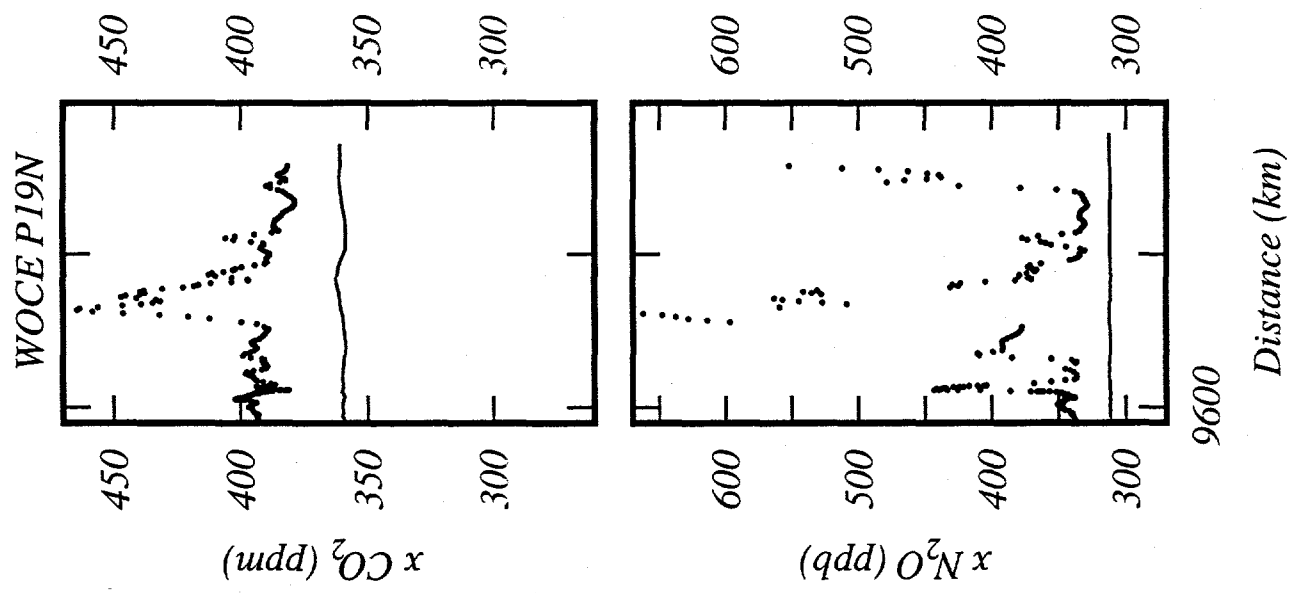
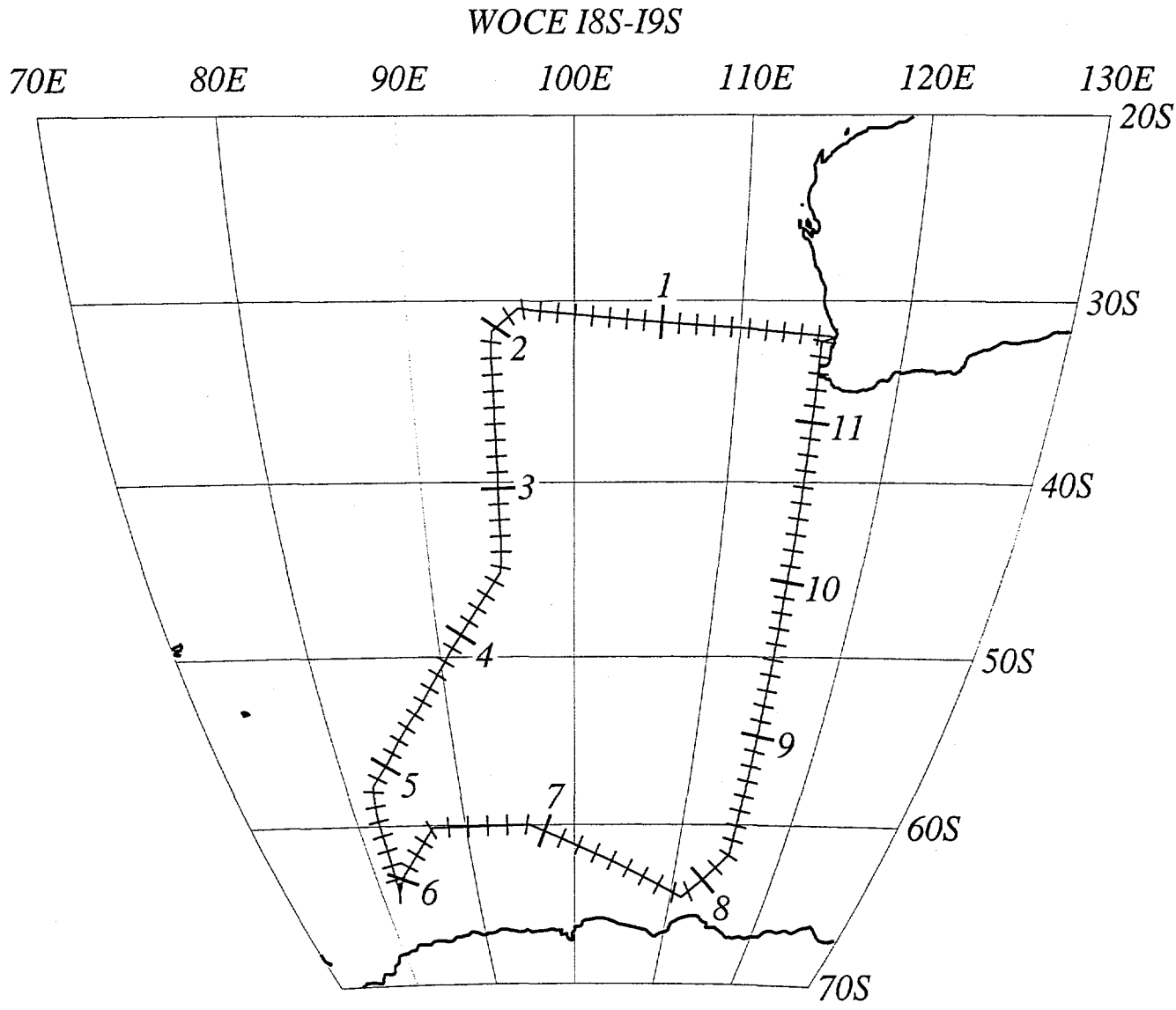
x CO2 (ppm)
x N2O (ppb)
Distance (km)
450
400
350
300
600
500
400
300
0
2000
4000
6000
8000
10000


WOCE P19N
450
400
350
300
$x\ CO_2$ (ppm)
600
500
400
300
$x\ N_2O$ (ppb)
9600
Distance (km)


WOCE I8S-I9S
70E
80E
90E
100E
110E
120E
130E
20S
30S
40S
50S
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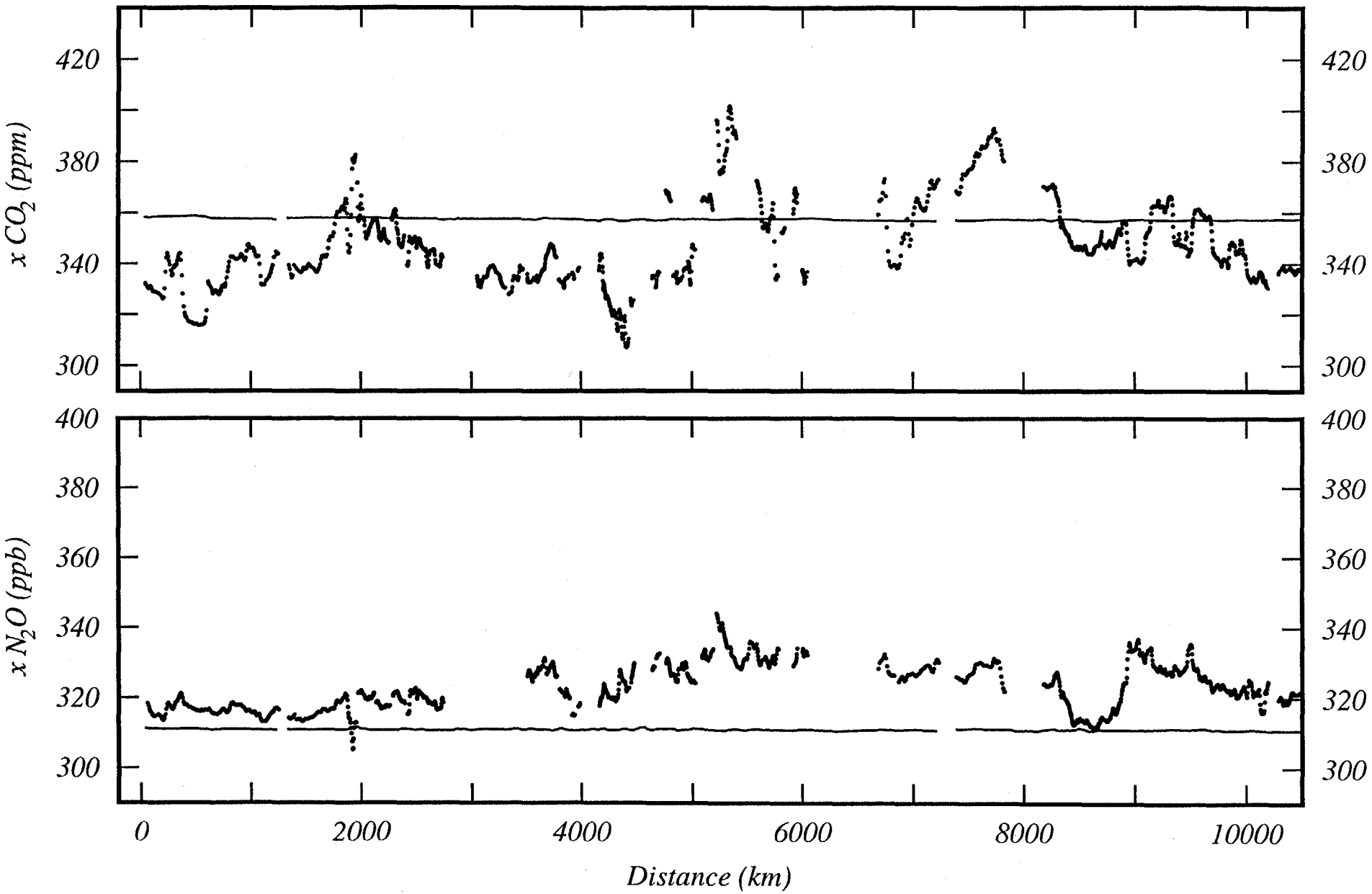
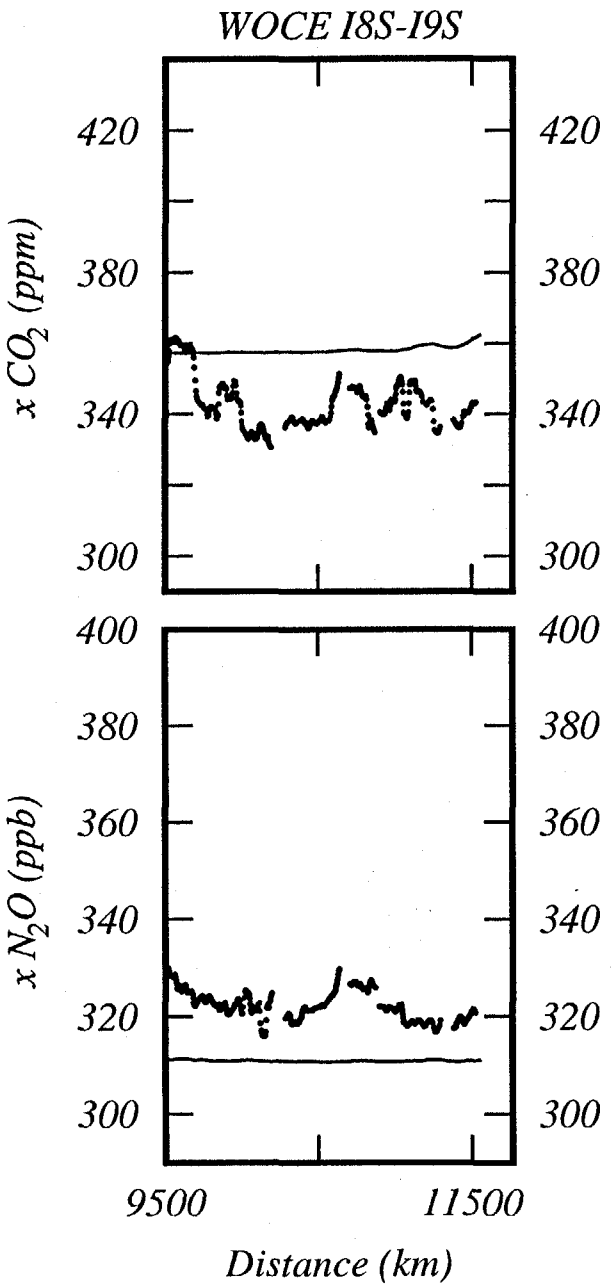
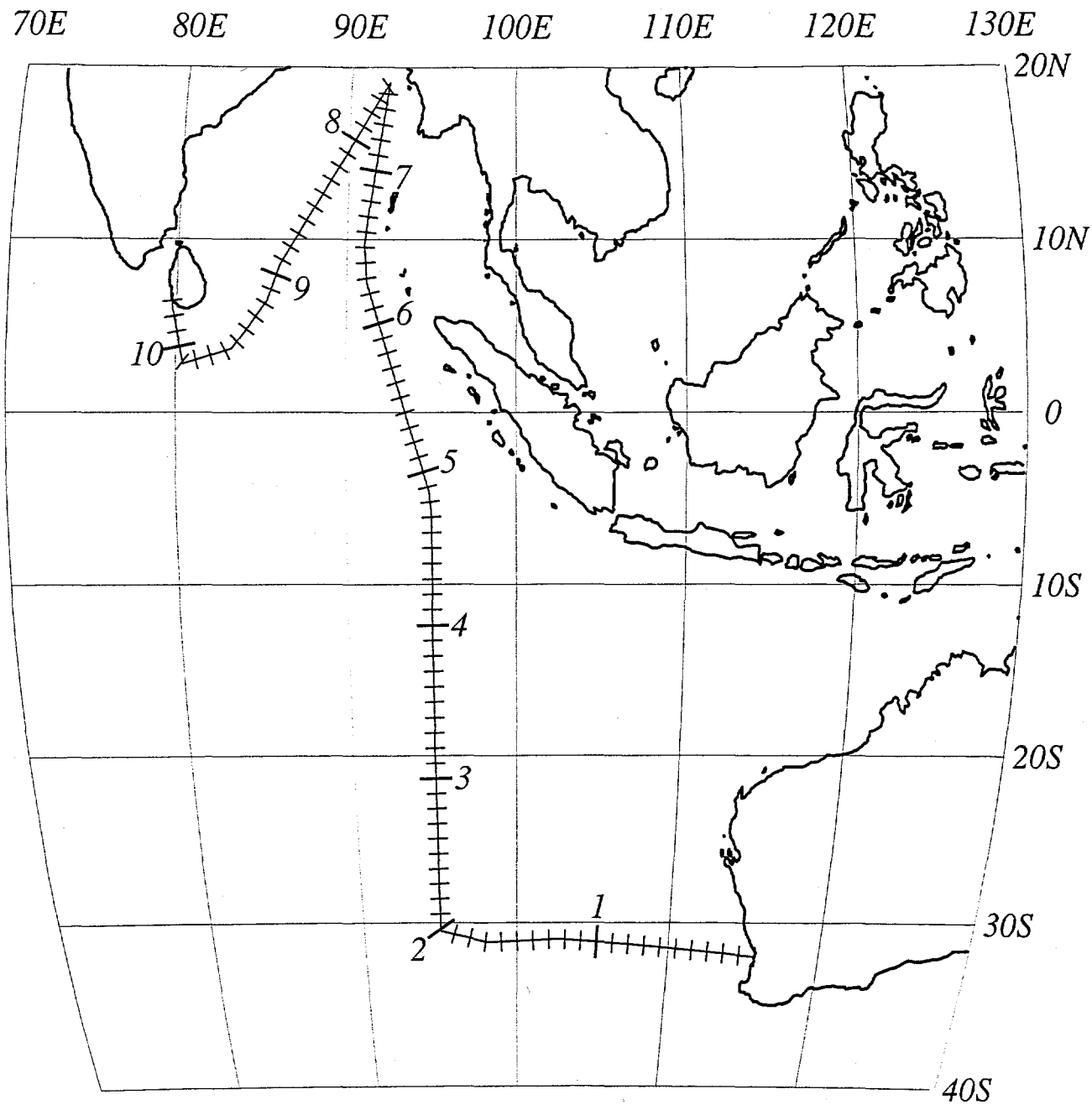
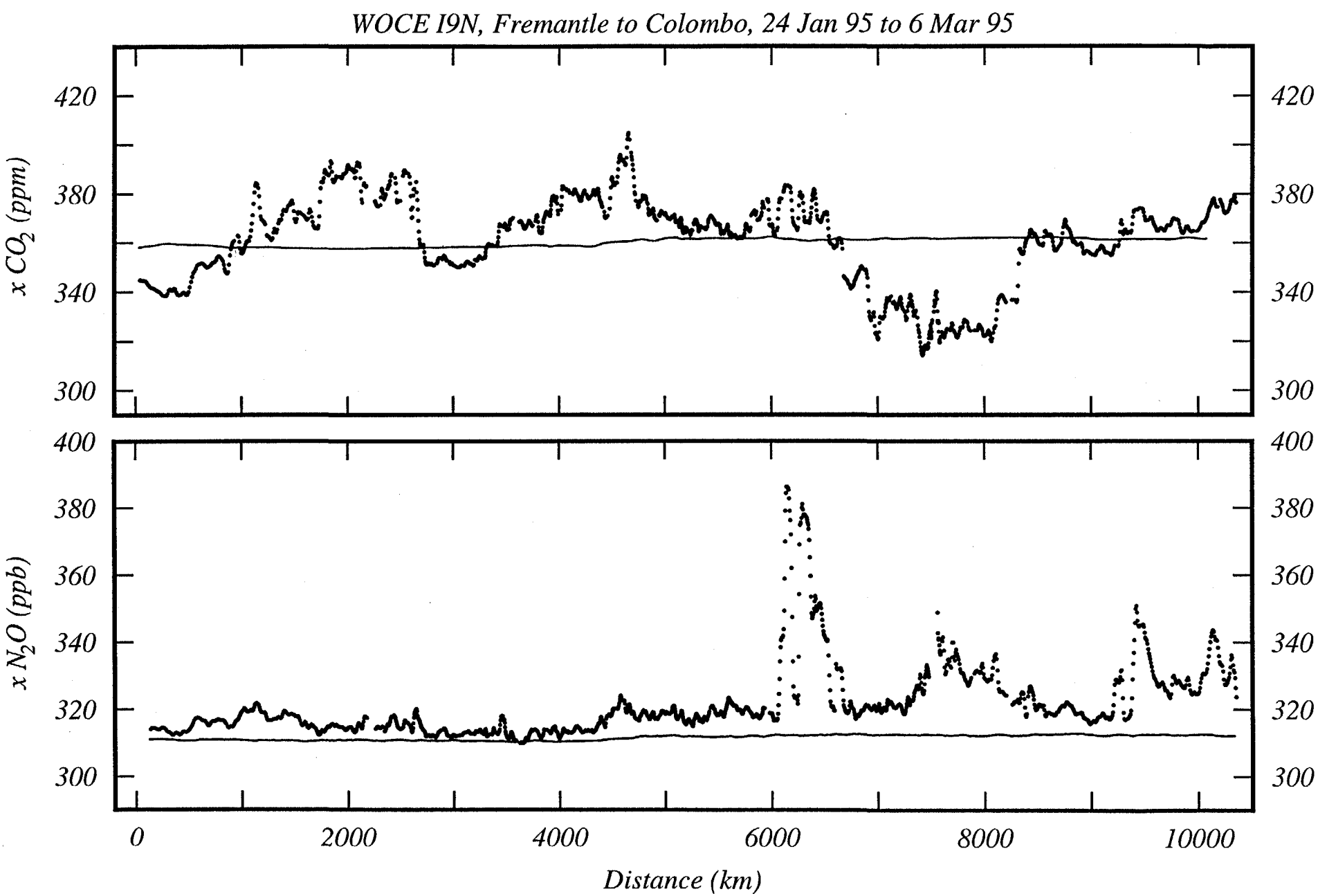

WOCE I8S-I9S, Fremantle to Fremantle, 1 Dec 94 to 19 Jan 95
x CO2 (ppm)
420
380
340
300
x N2O (ppb)
400
380
360
340
320
300
0
2000
4000
6000
8000
10000
Distance (km)

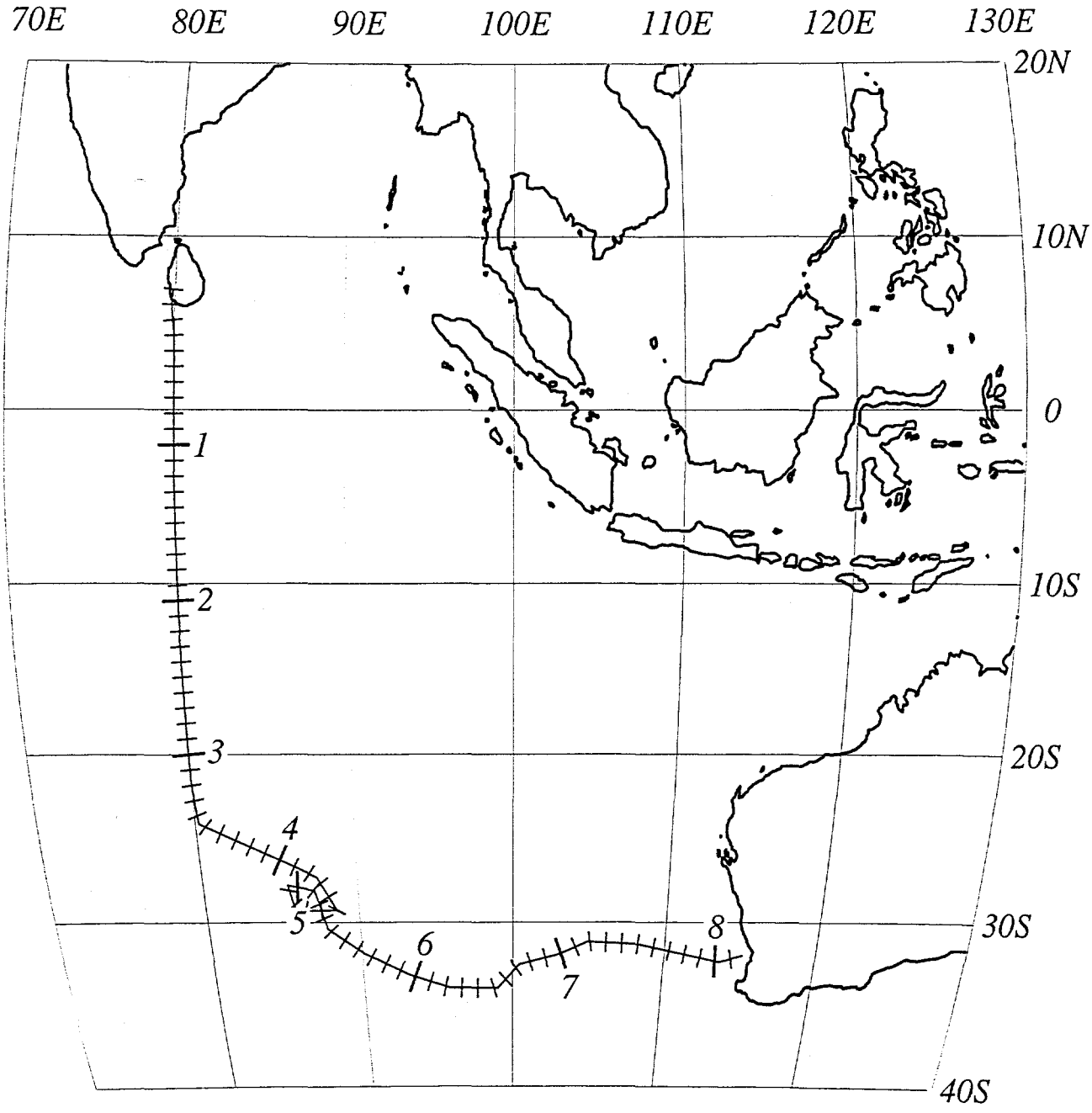

WOCE I8S-I9S
420
380
340
300
x CO_2 (ppm)
400
380
360
340
320
300
x N_2O (ppb)
9500
11500
Distance (km)

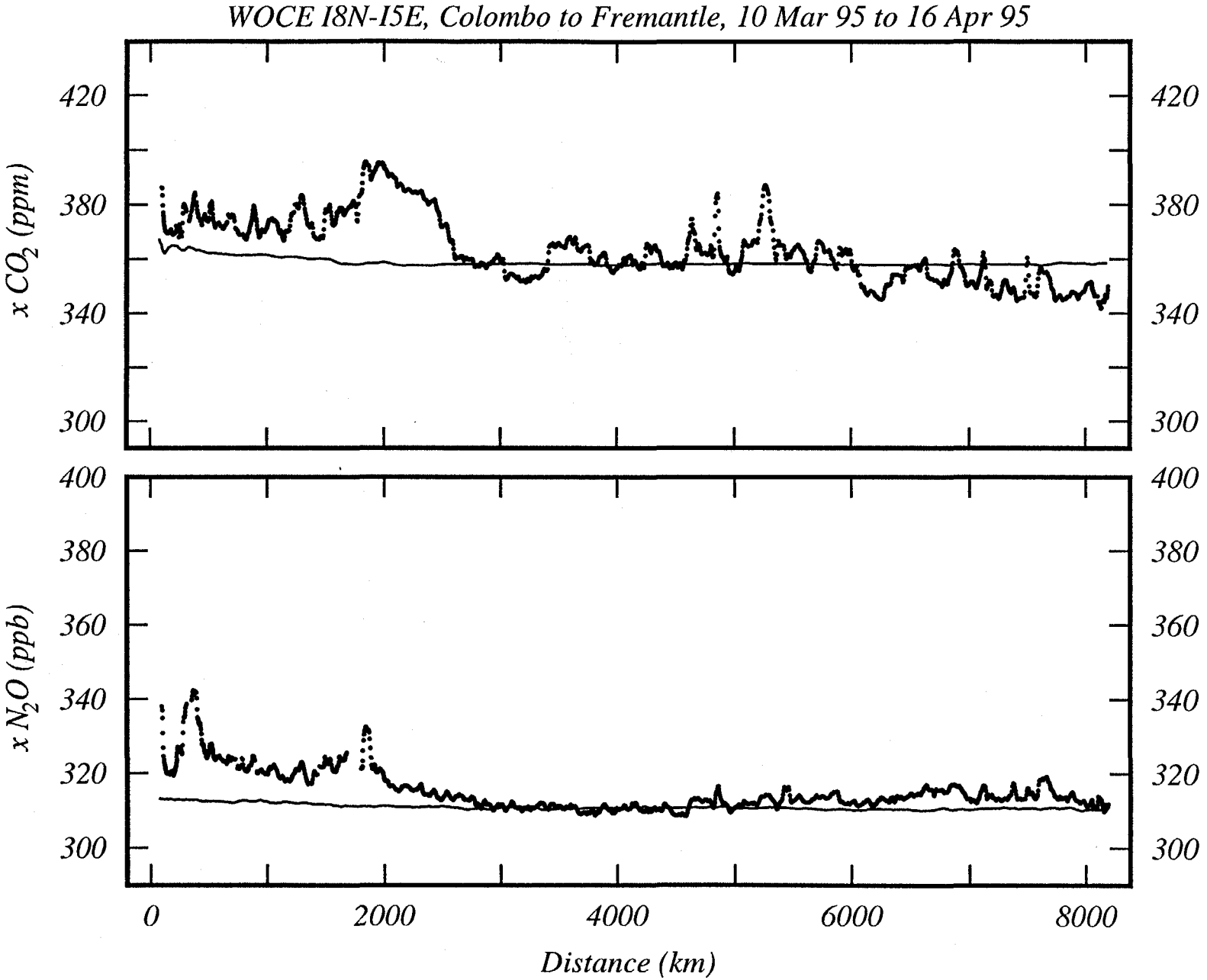
WOCE I9N

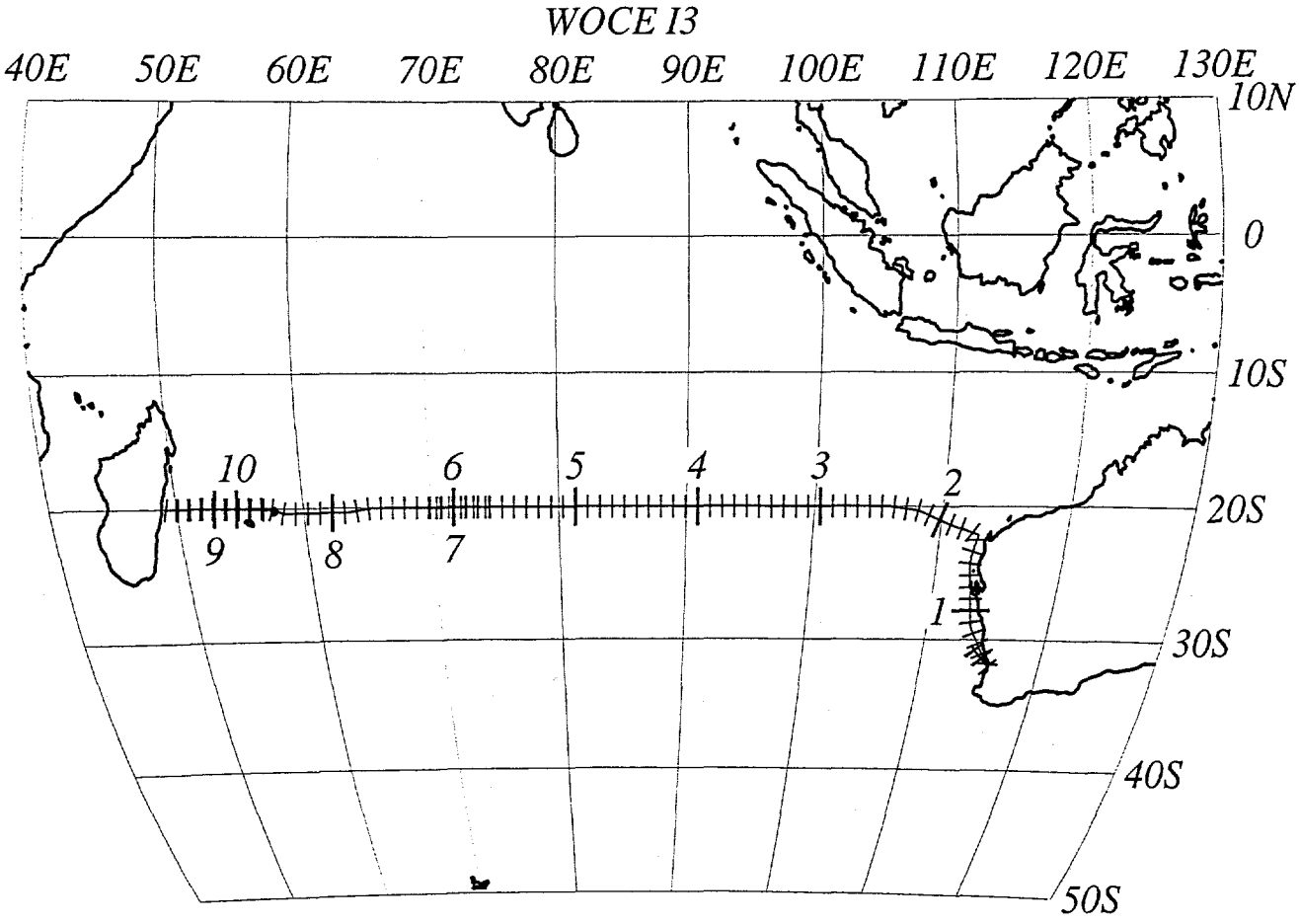

70E
80E
90E
100E
110E
120E
130E
20N
10N
0
10S
20S
30S
40S
1
2
3
4
5
6
7
8
9
10

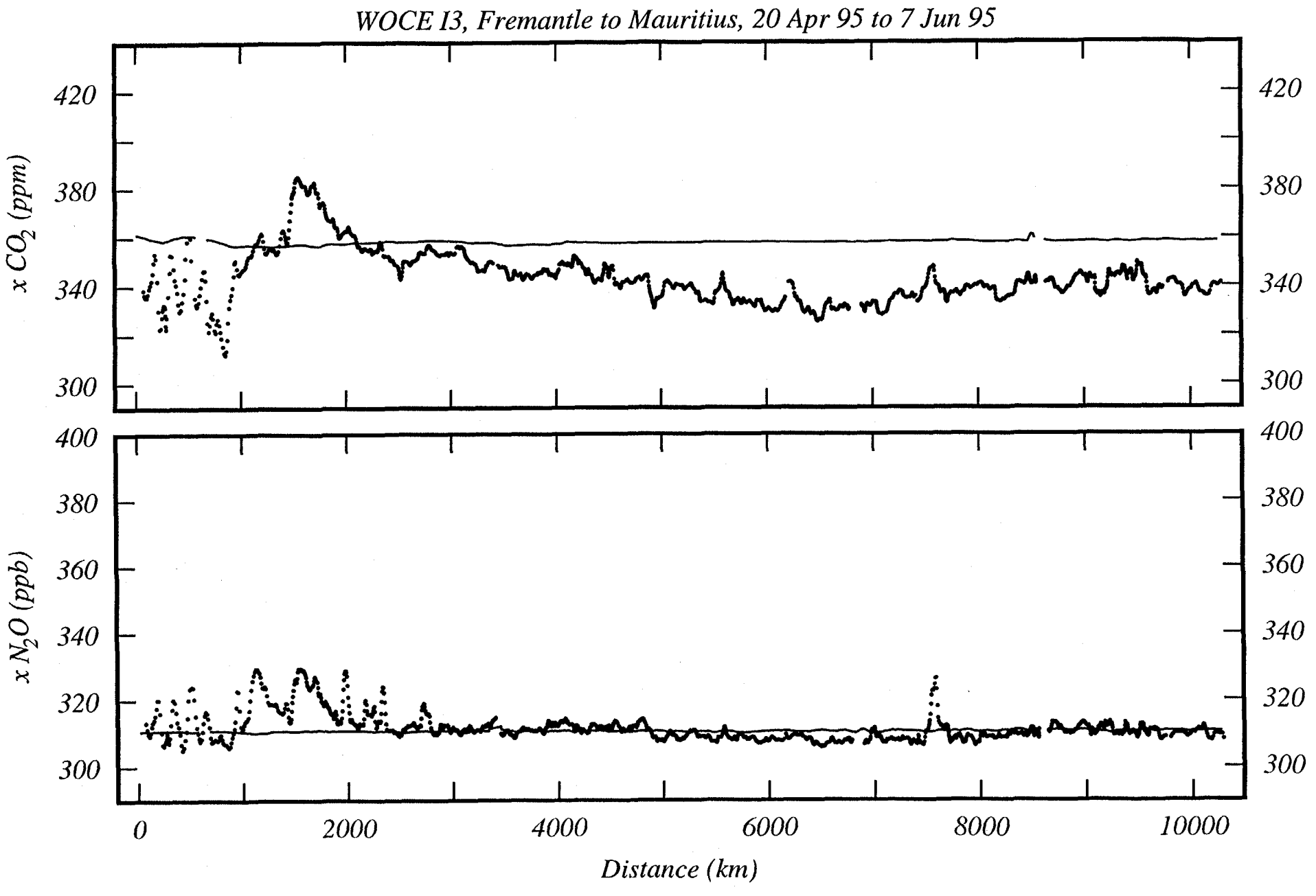

WOCE I9N, Fremantle to Colombo, 24 Jan 95 to 6 Mar 95
x CO_2 (ppm)
420
380
340
300
x N_2O (ppb)
400
380
360
340
320
300
0
2000
4000
6000
8000
10000
Distance (km)

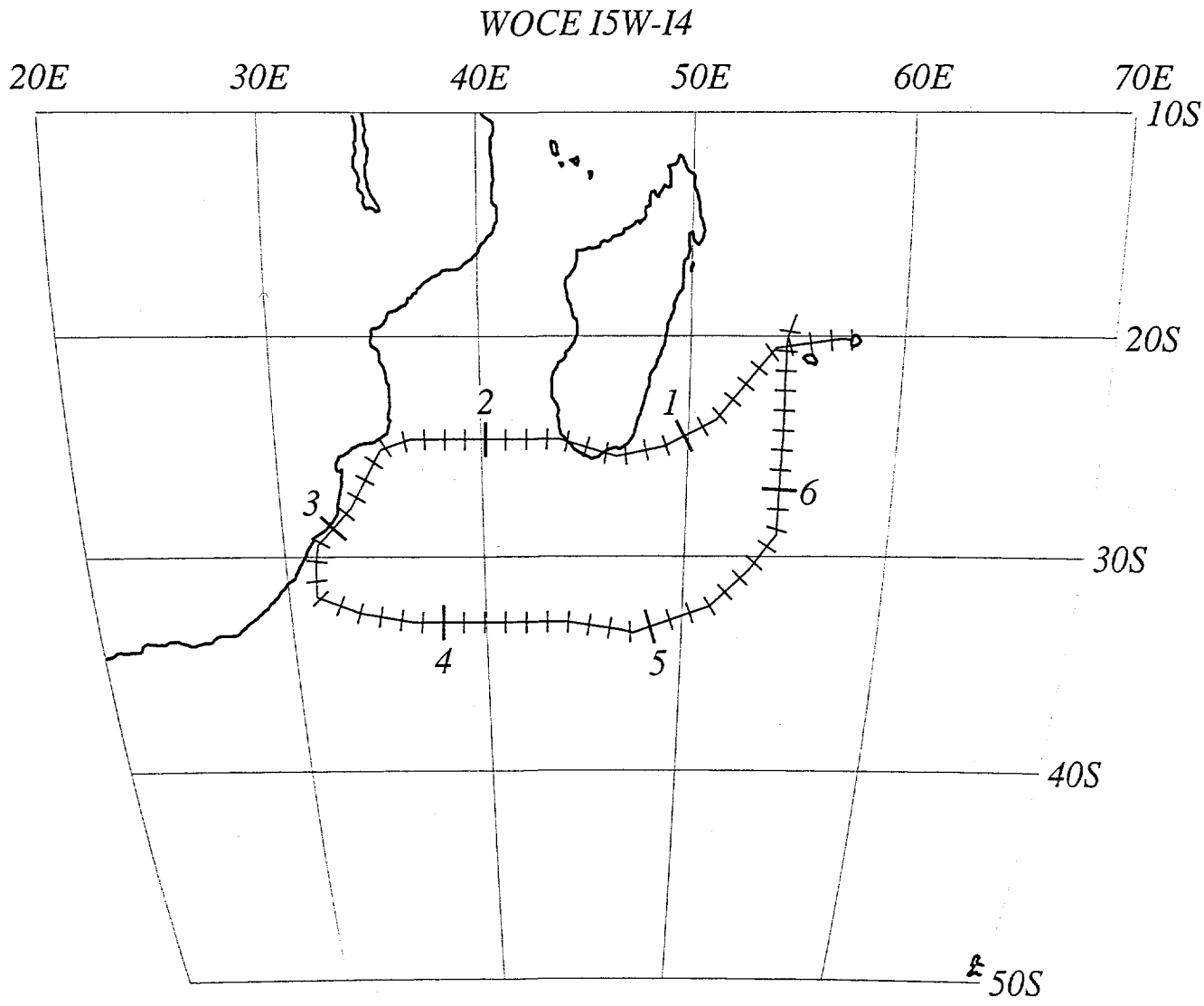
WOCE I8N-I5E

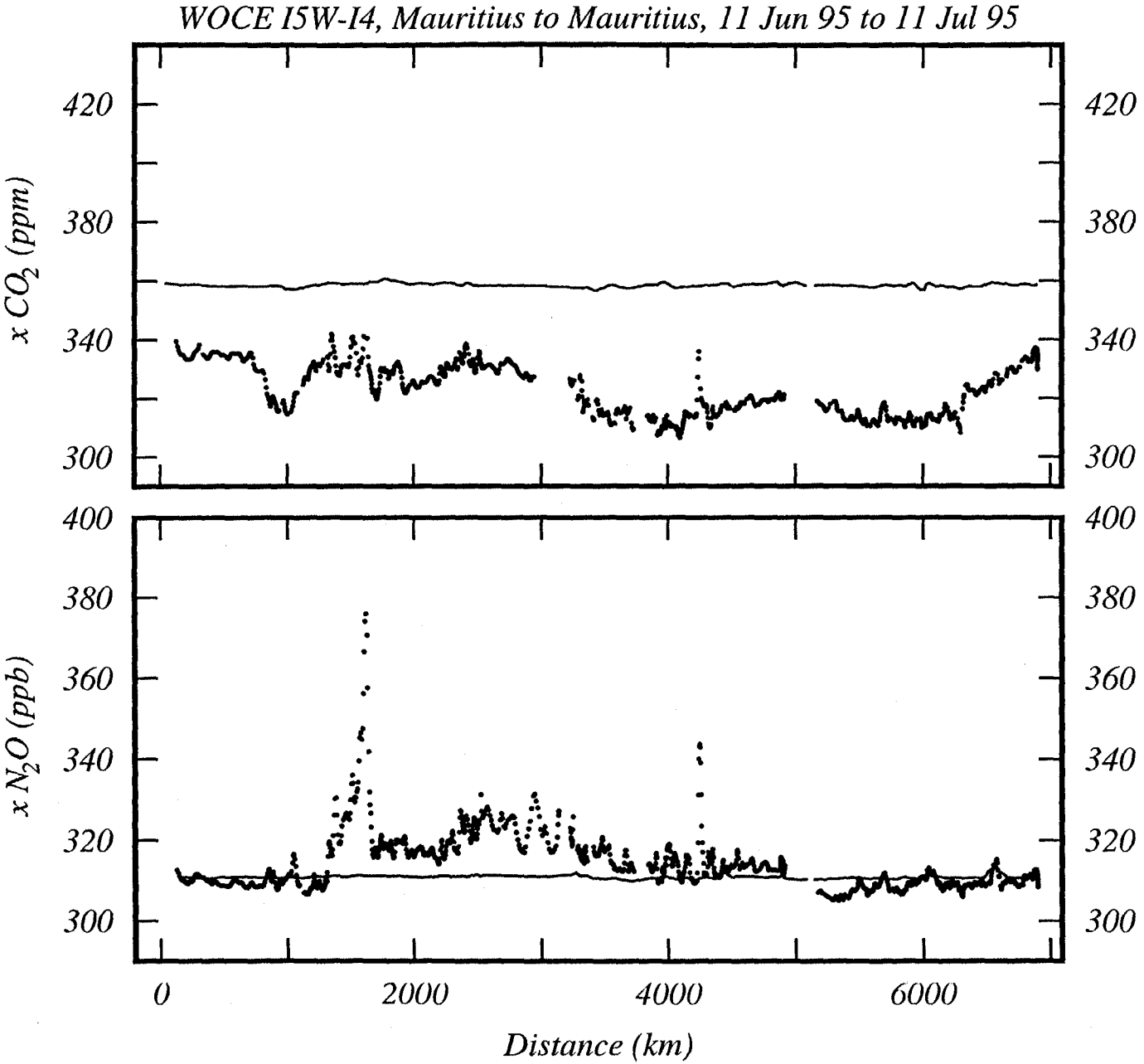

70E
80E
90E
100E
110E
120E
130E
20N
10N
0
10S
20S
30S
40S
1
2
3
4
5
6
7
8

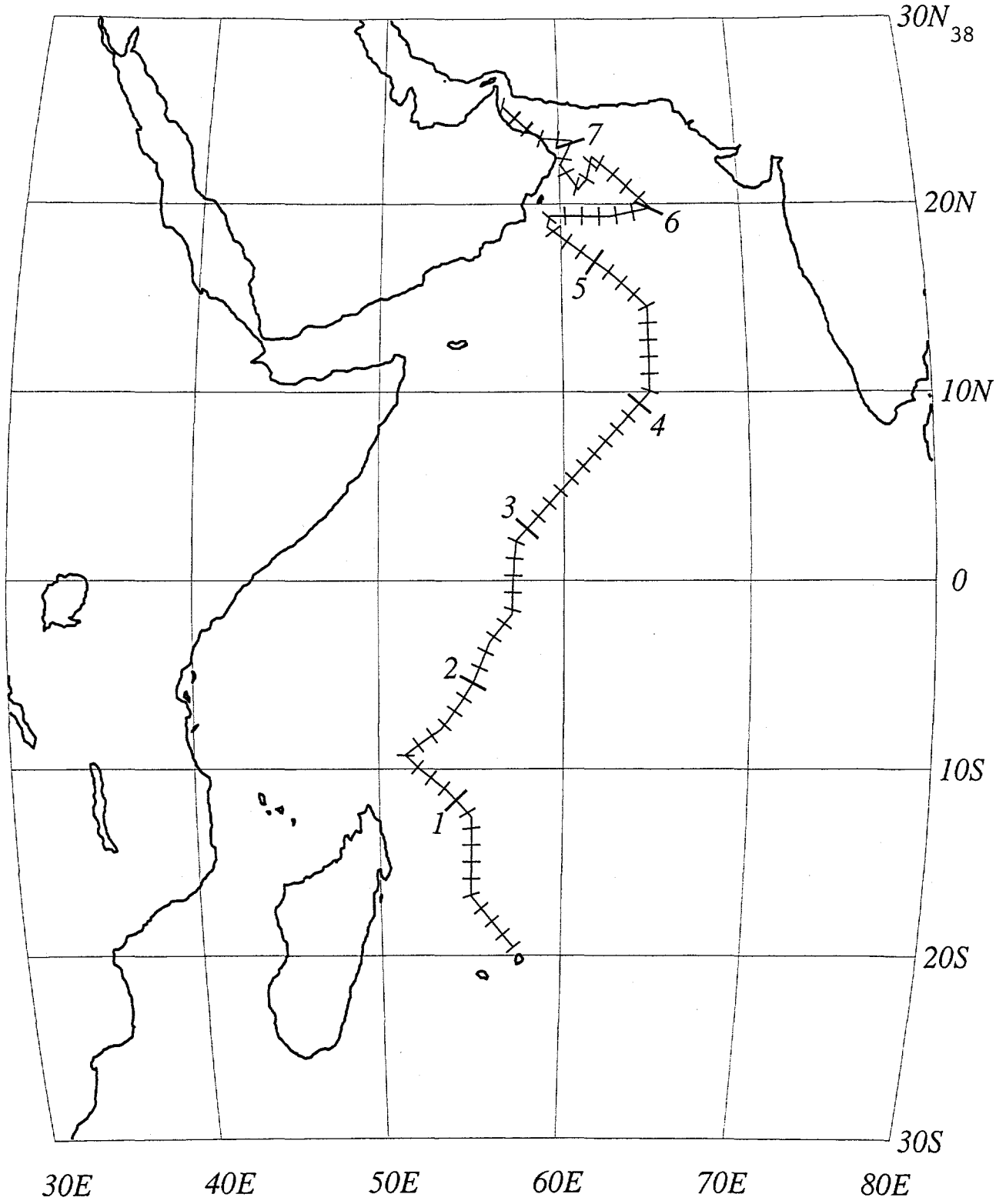

WOCE I8N-I5E, Colombo to Fremantle, 10 Mar 95 to 16 Apr 95
x CO2 (ppm)
420
380
340
300
x N2O (ppb)
400
380
360
340
320
300
0
2000
4000
6000
8000
Distance (km)


WOCE I3
40E
50E
60E
70E
80E
90E
100E
110E
120E
130E
10N
0
10S
20S
30S
40S
50S
10
9
8
7
6
5
4
3
2
1

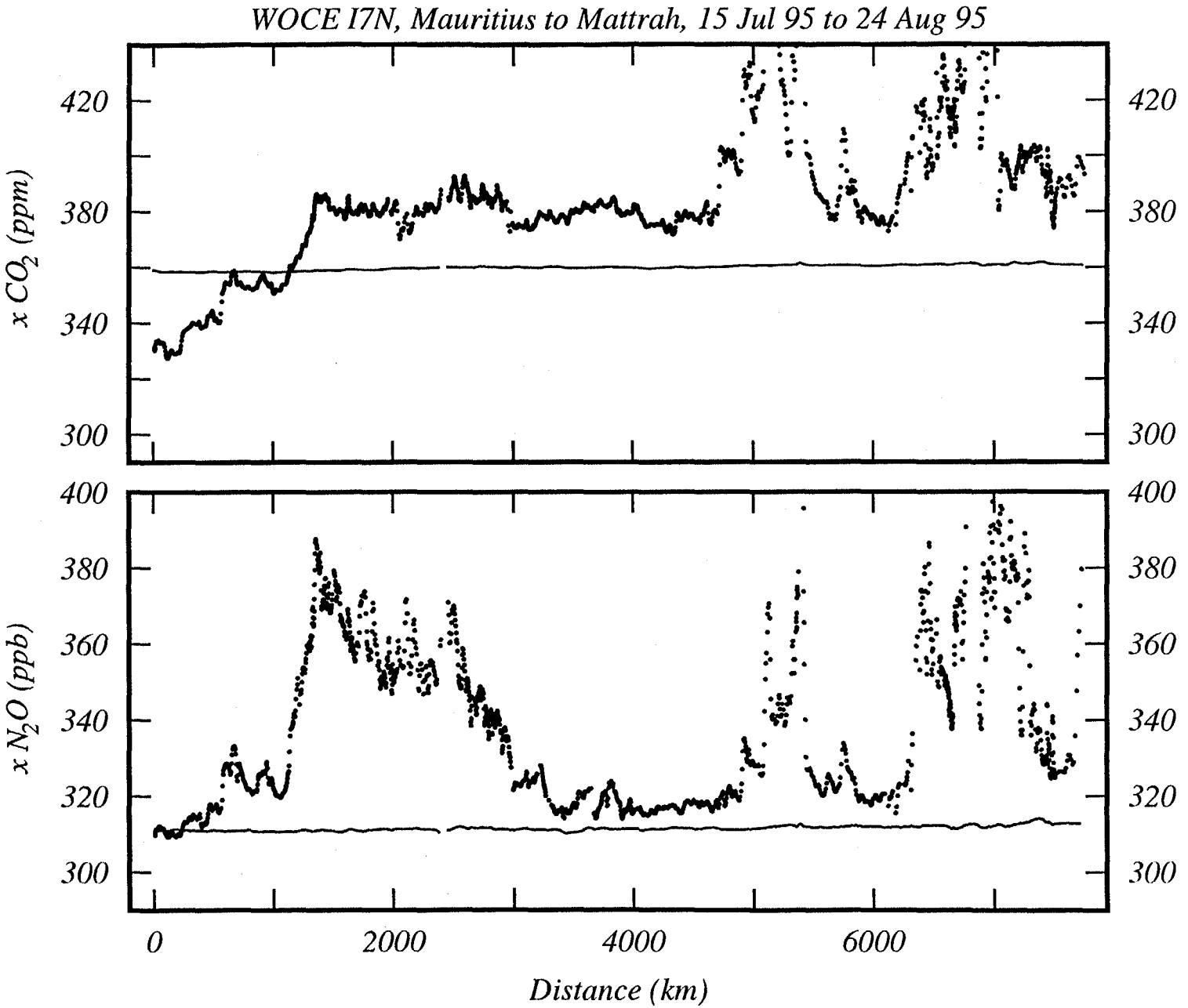

WOCE I3, Fremantle to Mauritius, 20 Apr 95 to 7 Jun 95
x CO2 (ppm)
420
380
340
300
x N2O (ppb)
400
380
360
340
320
300
0
2000
4000
6000
8000
10000
Distance (km)

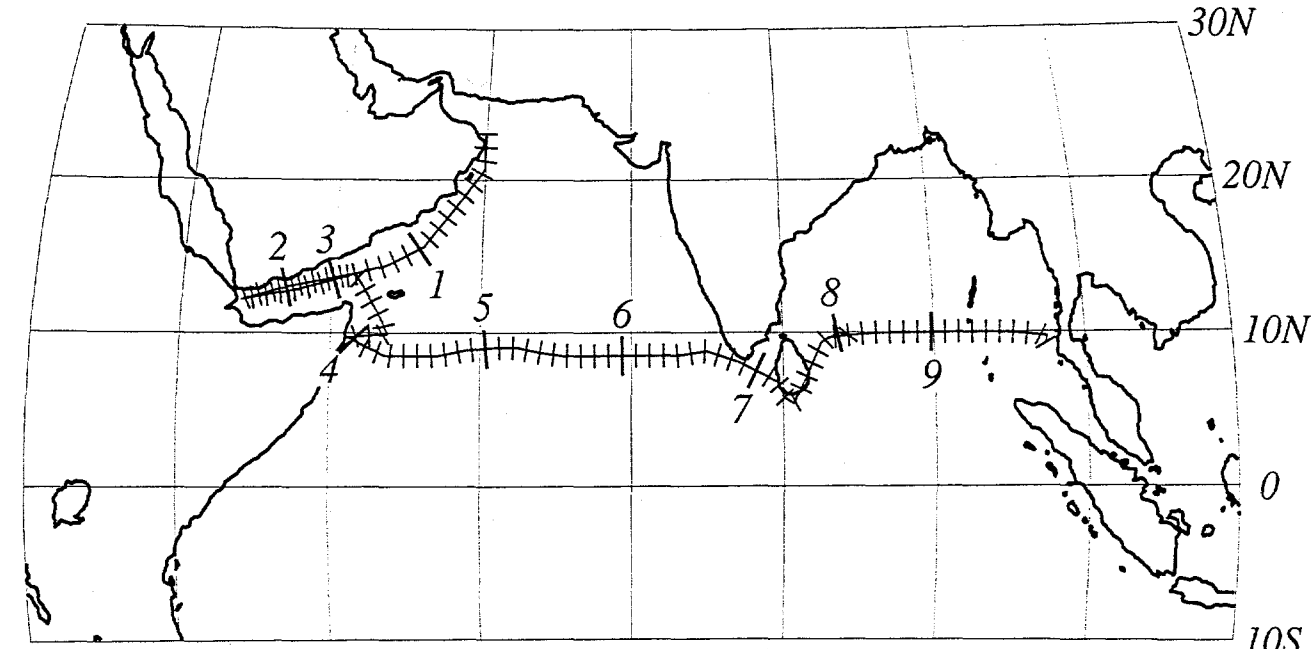

WOCE I5W-I4
20E
30E
40E
50E
60E
70E
10S
20S
30S
40S
50S
1
2
3
4
5
6


WOCE I5W-I4, Mauritius to Mauritius, 11 Jun 95 to 11 Jul 95
x CO2 (ppm)
420
380
340
300
x N2O (ppb)
400
380
360
340
320
300
0
2000
4000
6000
Distance (km)

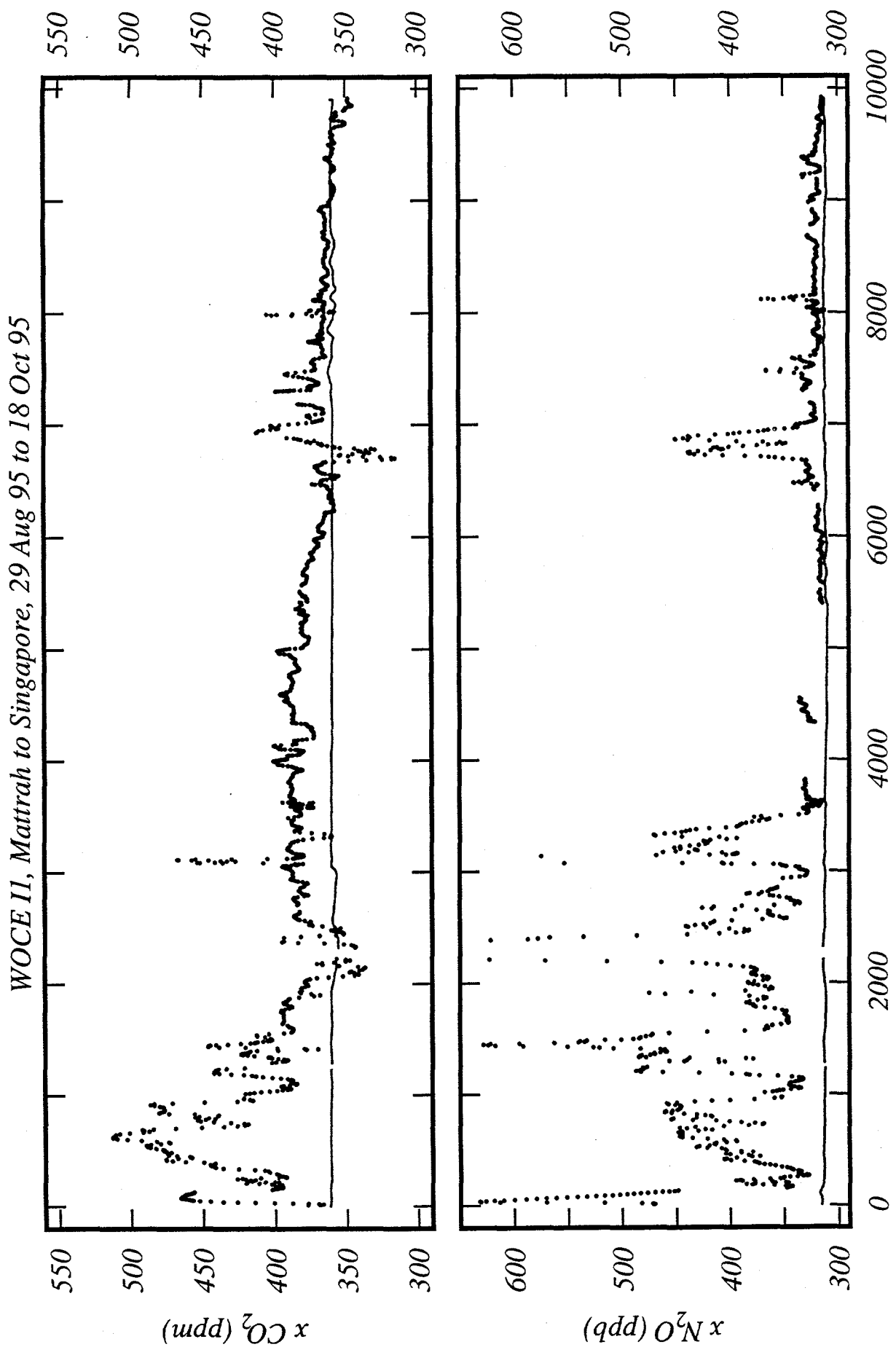


WOCE I7N

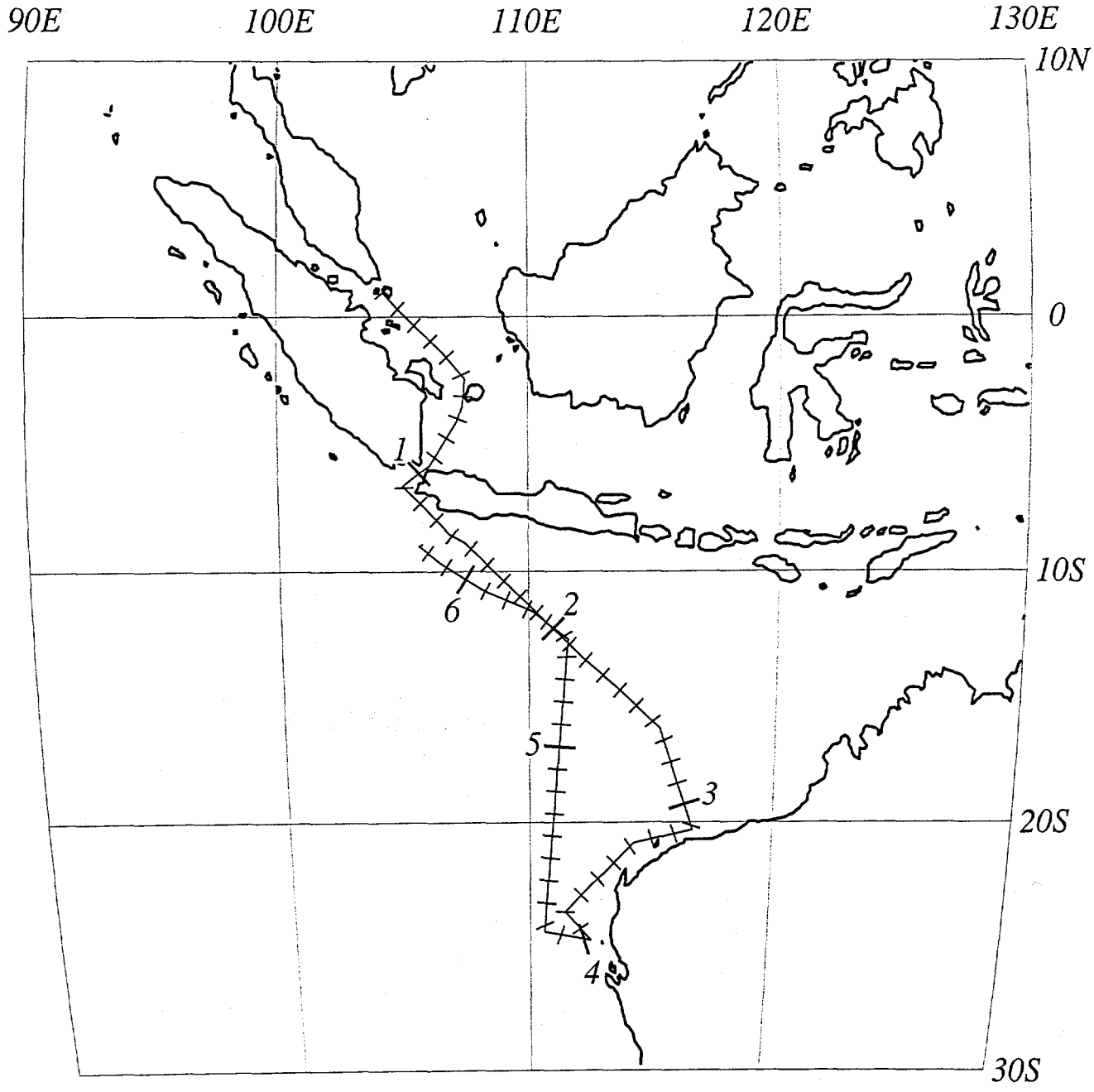

WOCE I7N, Mauritius to Mattrah, 15 Jul 95 to 24 Aug 95
x CO2 (ppm)
420
380
340
300
x N2O (ppb)
400
380
360
340
320
300
0
2000
4000
6000
Distance (km)

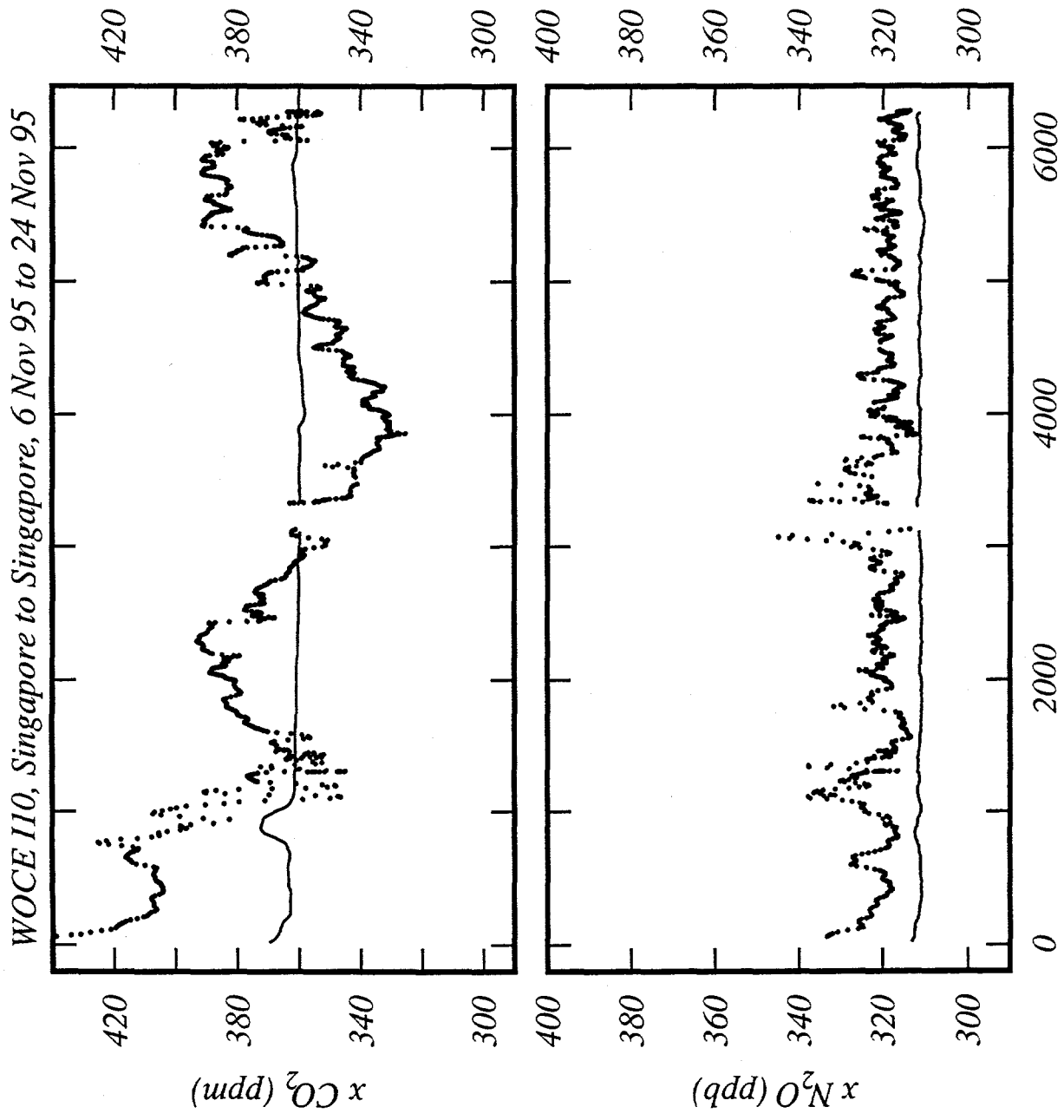

30N
20N
10N
0
10S
30E
40E
50E
60E
70E
80E
90E
100E
110E
1
2
3
4
5
6
7
8
9

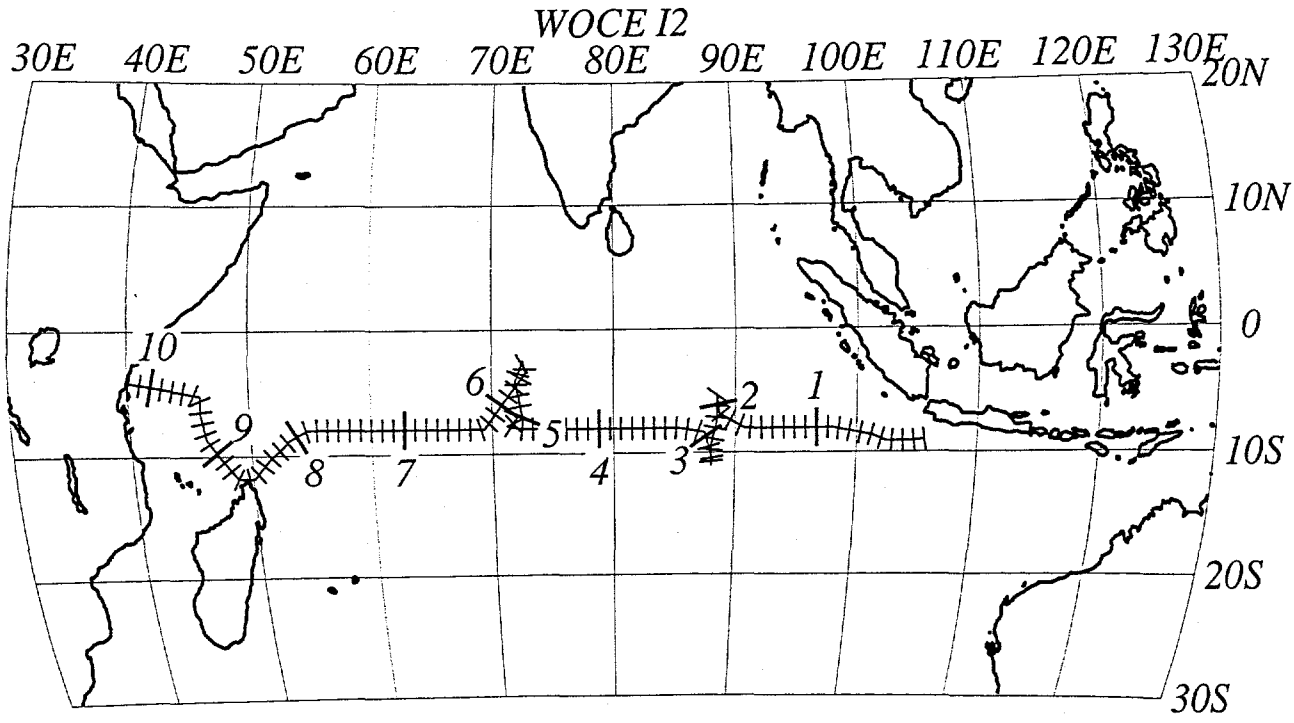
WOCE I1

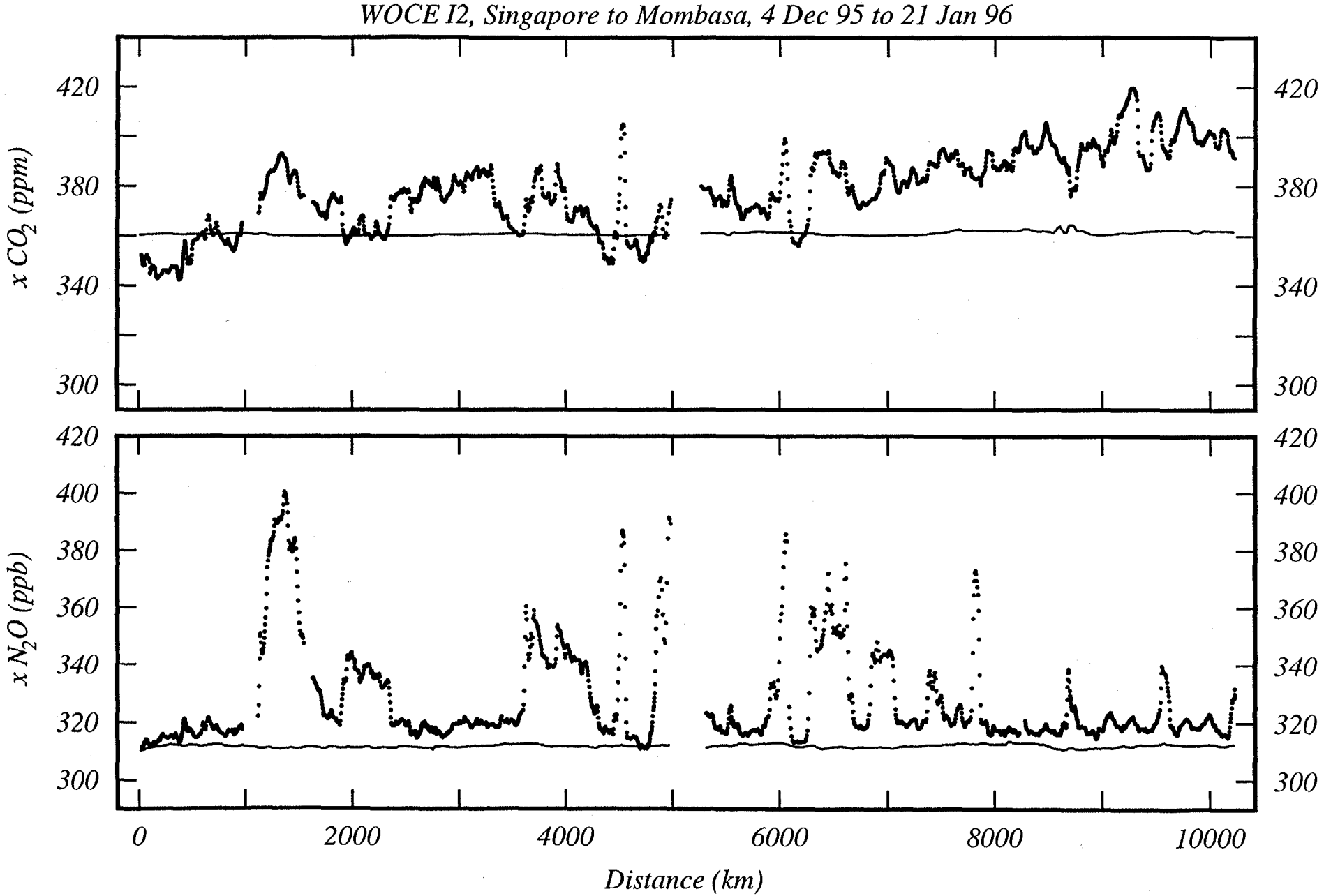

WOCE I1, Mattrah to Singapore, 29 Aug 95 to 18 Oct 95
x CO2 (ppm)
x N2O (ppb)
Distance (km)
550
500
450
400
350
300
600
0
2000
4000
6000
8000
10000

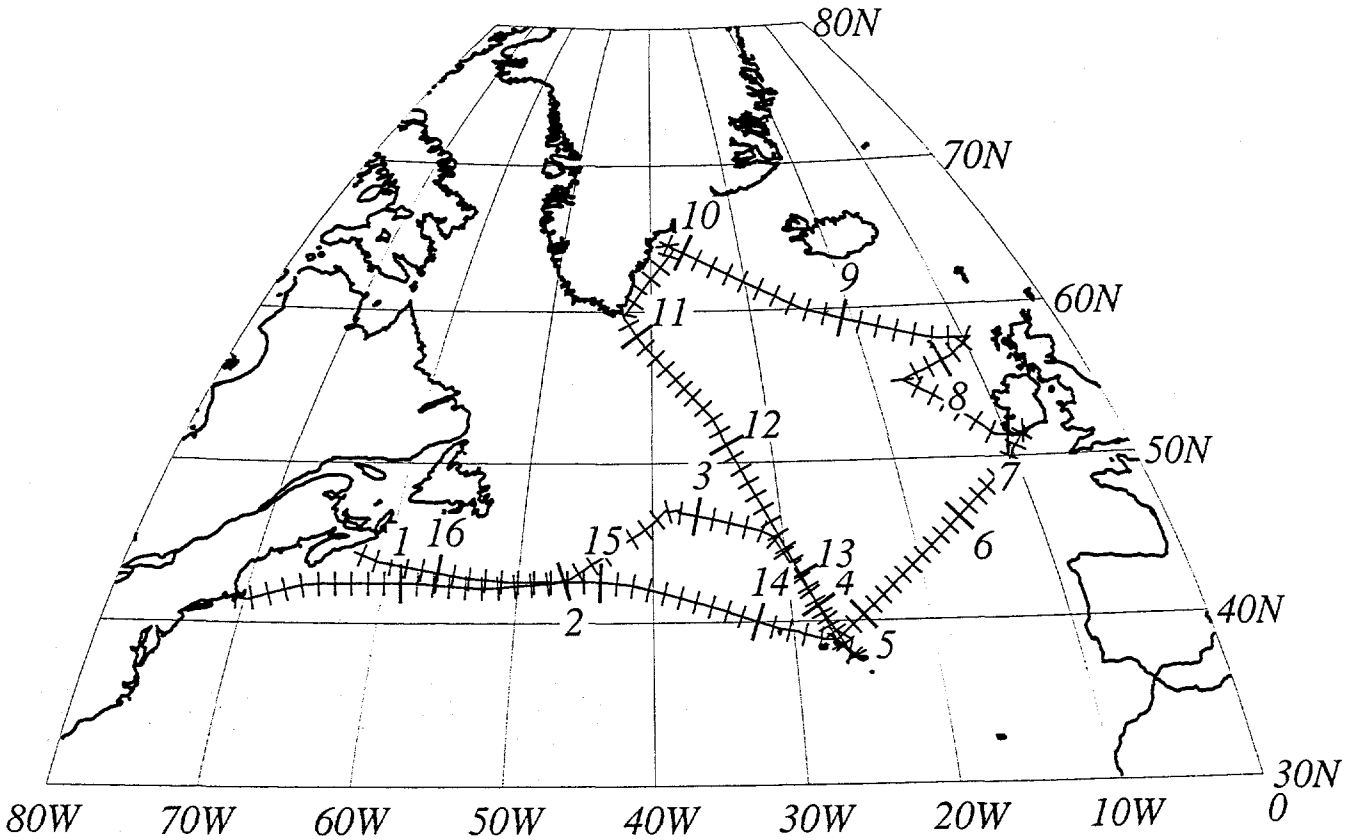
WOCE I10



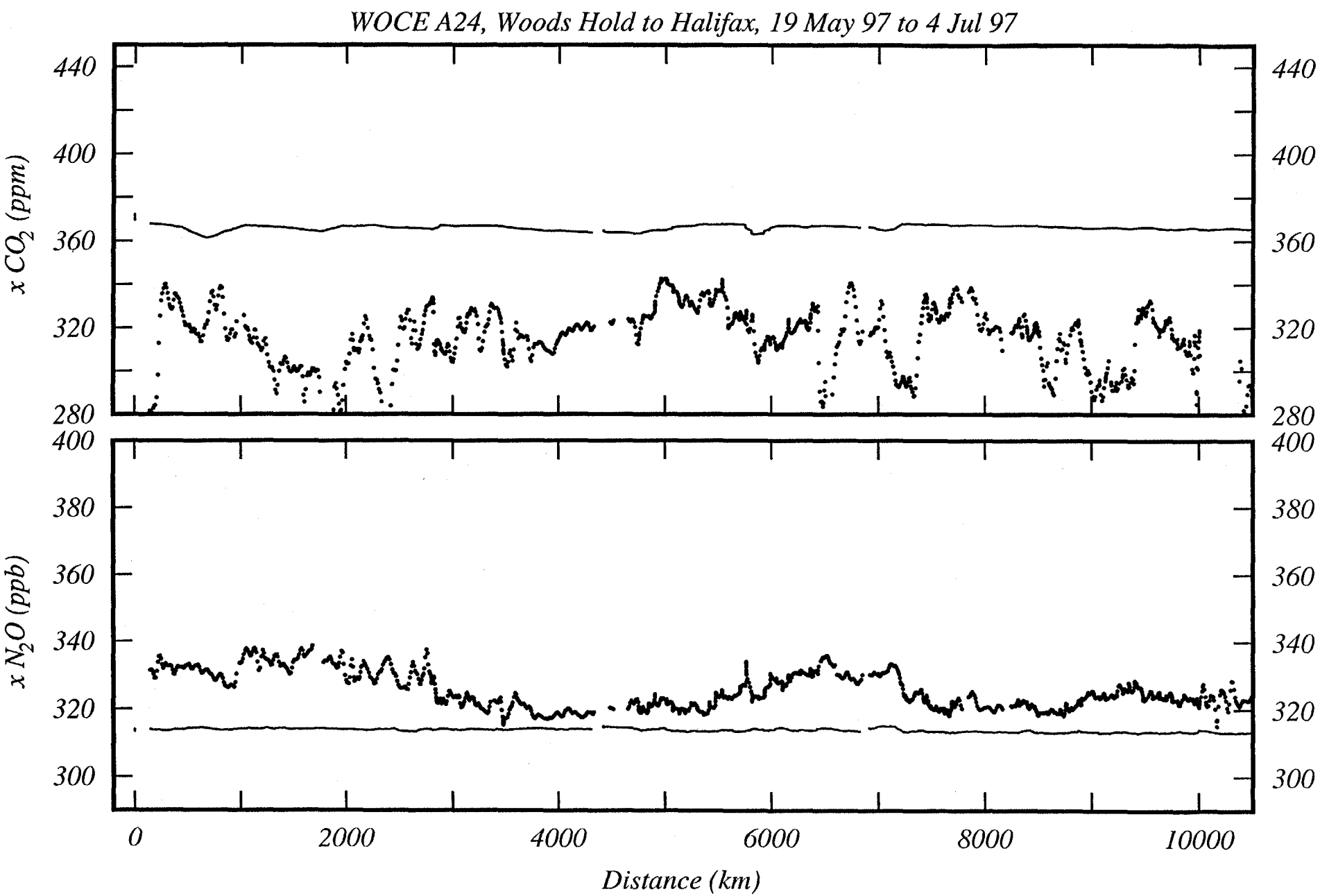

WOCE I10, Singapore to Singapore, 6 Nov 95 to 24 Nov 95
x CO2 (ppm)
x N2O (ppb)
Distance (km)
420
380
340
300
400
360
320
0
2000
4000
6000

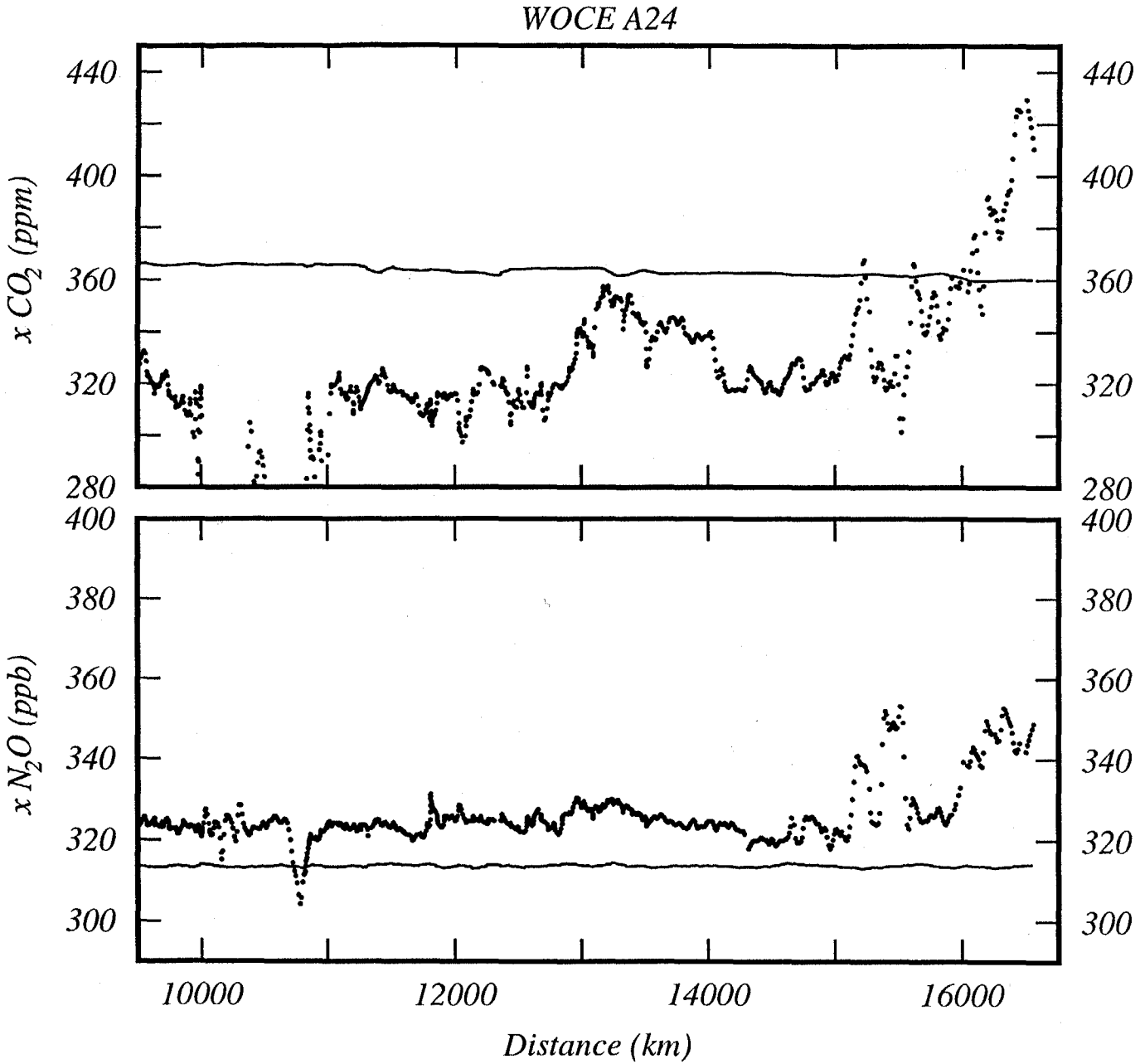

WOCE I2
30E
40E
50E
60E
70E
80E
90E
100E
110E
120E
130E
20N
10N
0
10S
20S
30S
1
2
3
4
5
6
7
8
9
10

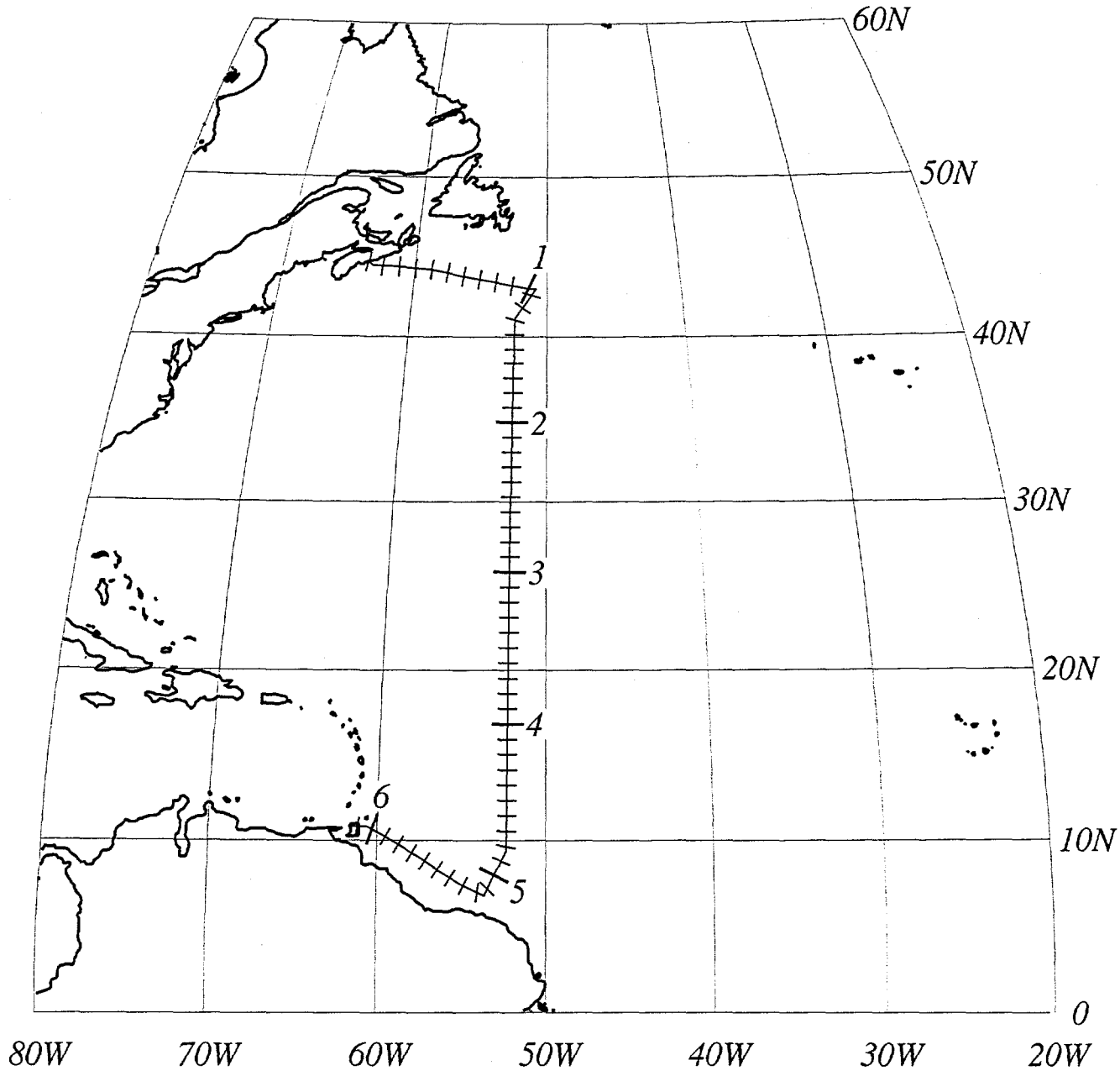

WOCE I2, Singapore to Mombasa, 4 Dec 95 to 21 Jan 96
x CO2 (ppm)
420
380
340
300
x N2O (ppb)
420
400
380
360
340
320
300
0
2000
4000
6000
8000
10000
Distance (km)


80N
70N
60N
50N
40N
30N
80W
70W
60W
50W
40W
30W
20W
10W
0
1
16
15
2
3
12
11
10
9
8
7
6
13
14
4
5

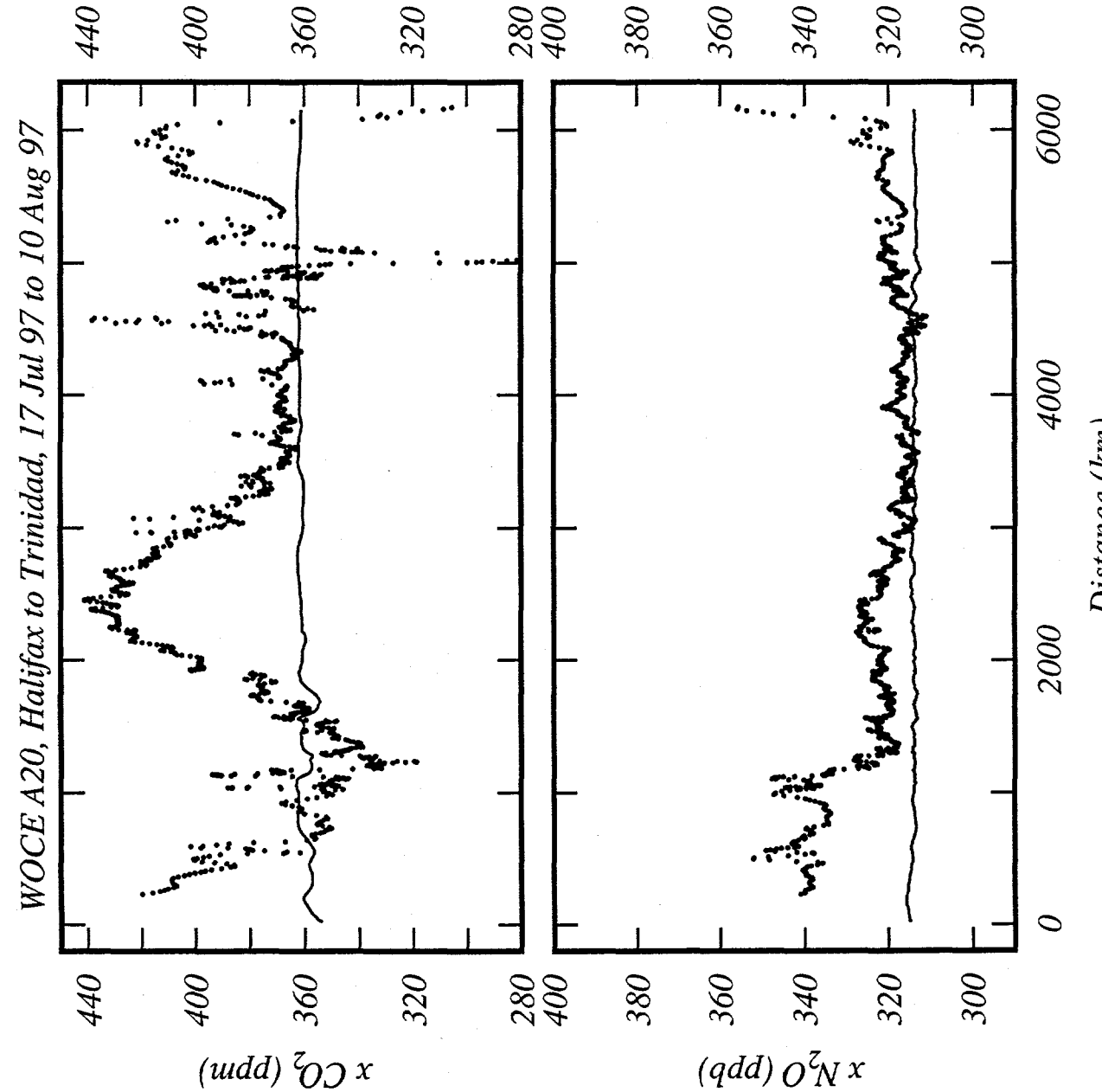
WOCE A24

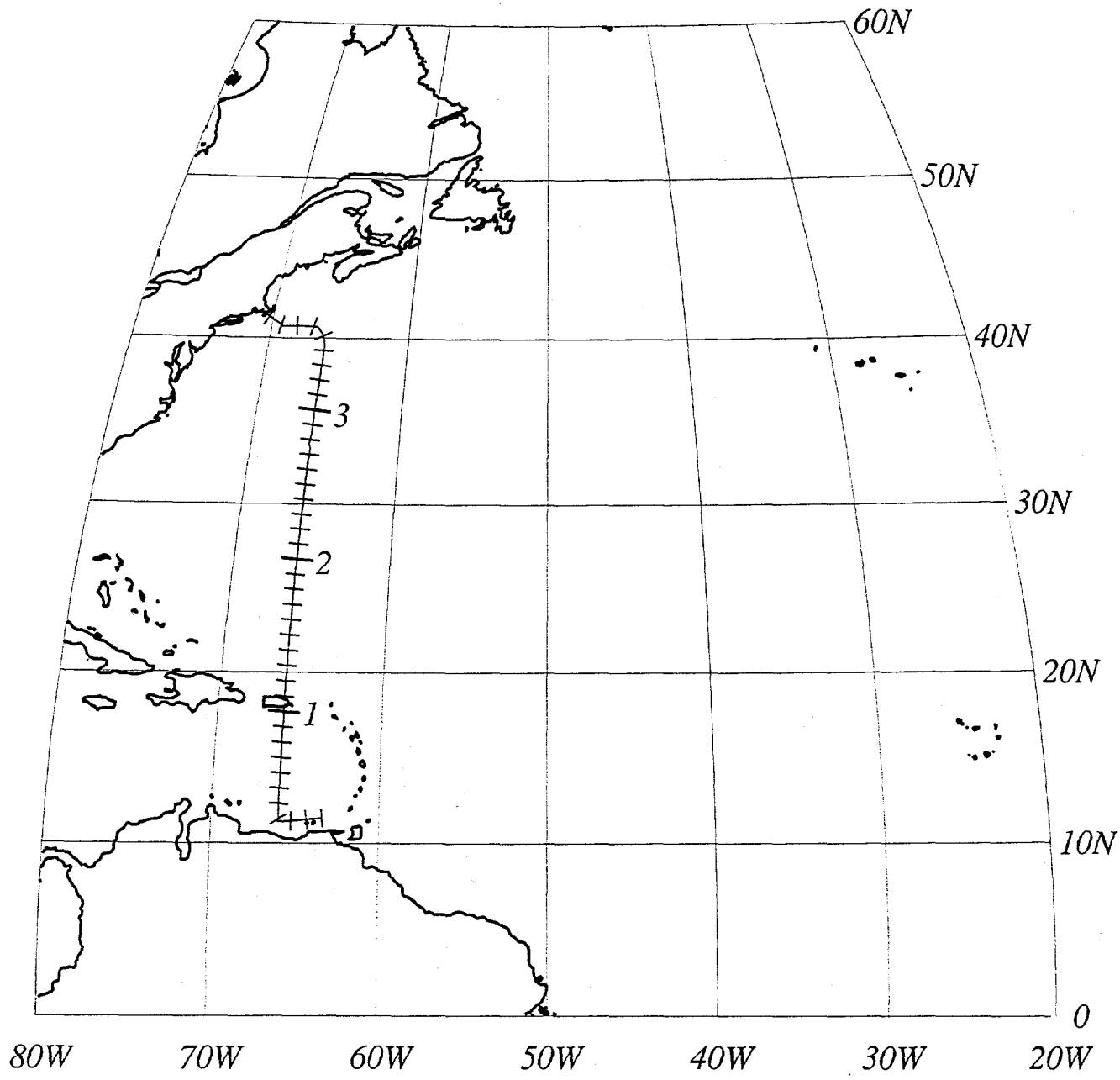

WOCE A24, Woods Hold to Halifax, 19 May 97 to 4 Jul 97
x CO2 (ppm)
440
400
360
320
280
x N2O (ppb)
400
380
360
340
320
300
0
2000
4000
6000
8000
10000
Distance (km)


WOCE A24
x CO_2 (ppm)
440
400
360
320
280
x N_2O (ppb)
400
380
360
340
320
300
10000
12000
14000
16000
Distance (km)



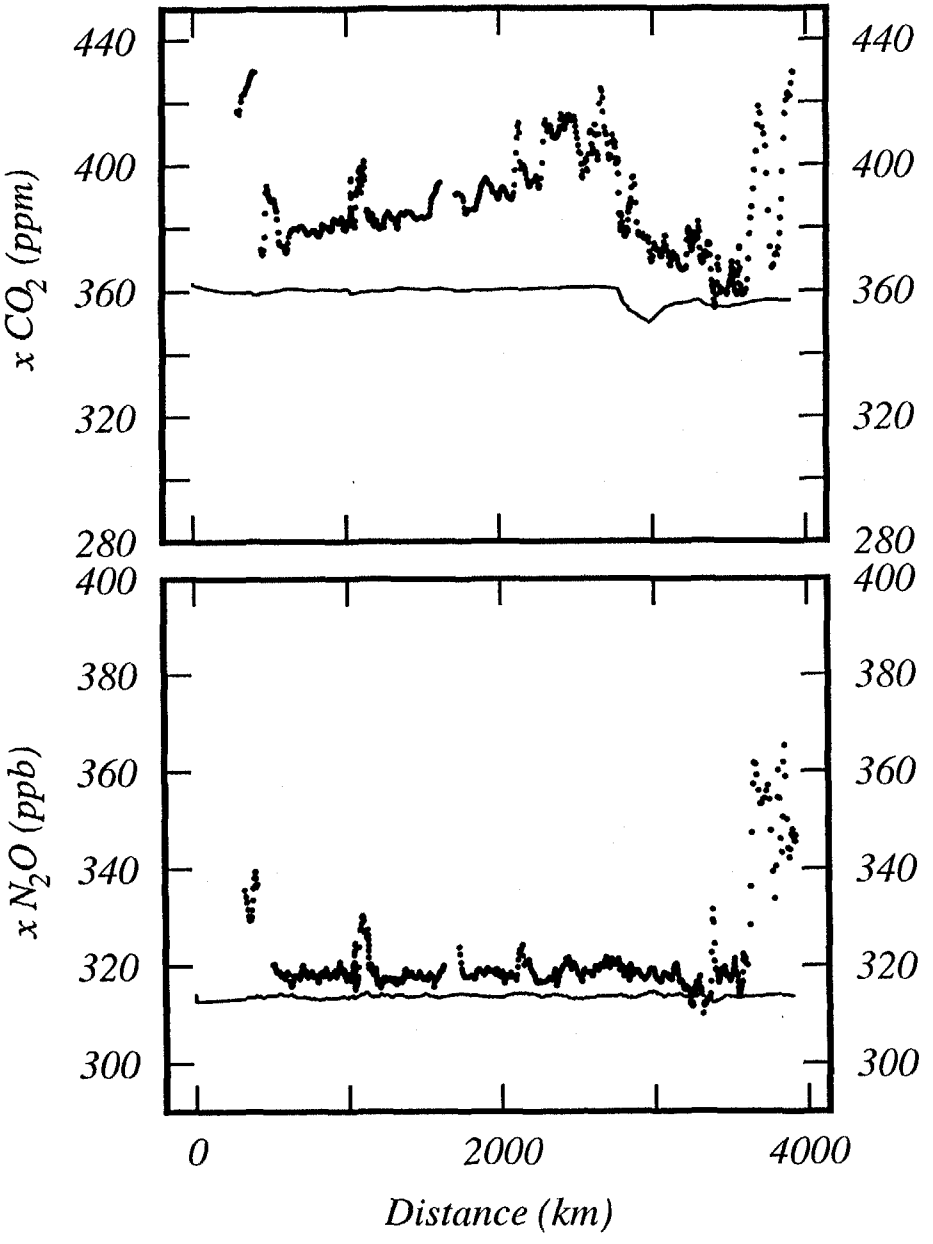
WOCE A20

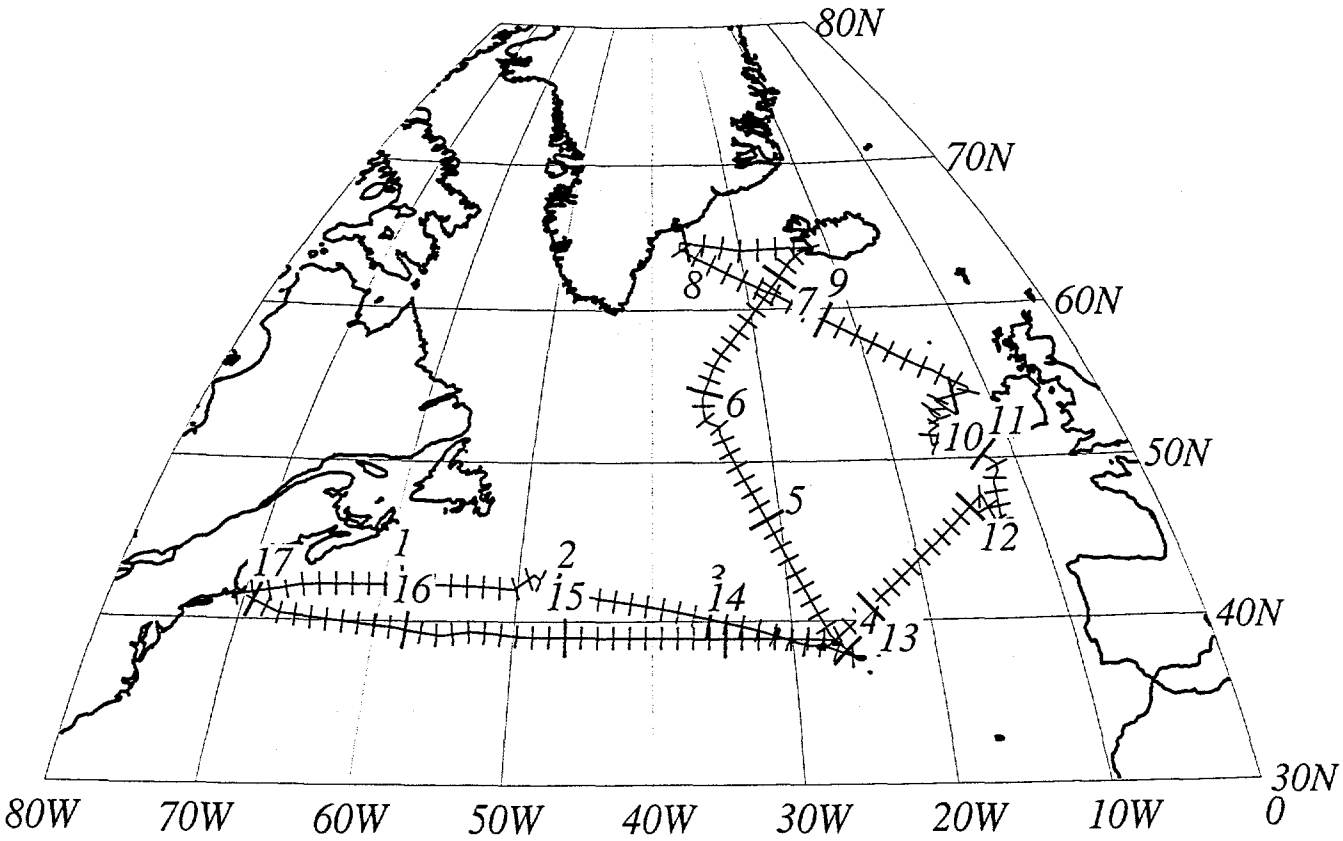

WOCE A20, Halifax to Trinidad, 17 Jul 97 to 10 Aug 97
x CO2 (ppm)
x N2O (ppb)
Distance (km)
0
2000
4000
6000
440
400
360
320
280
380
340
300



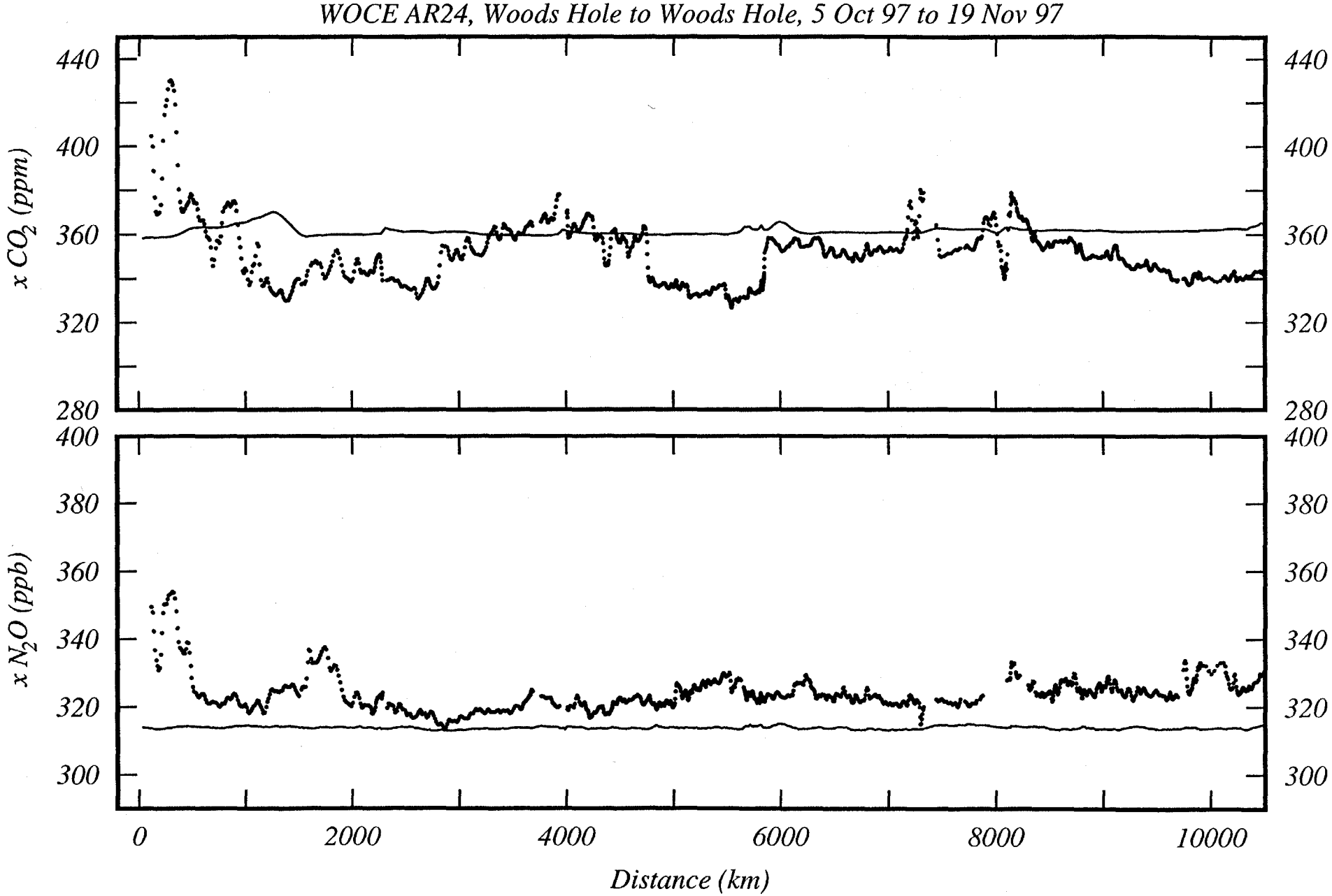
WOCE A22

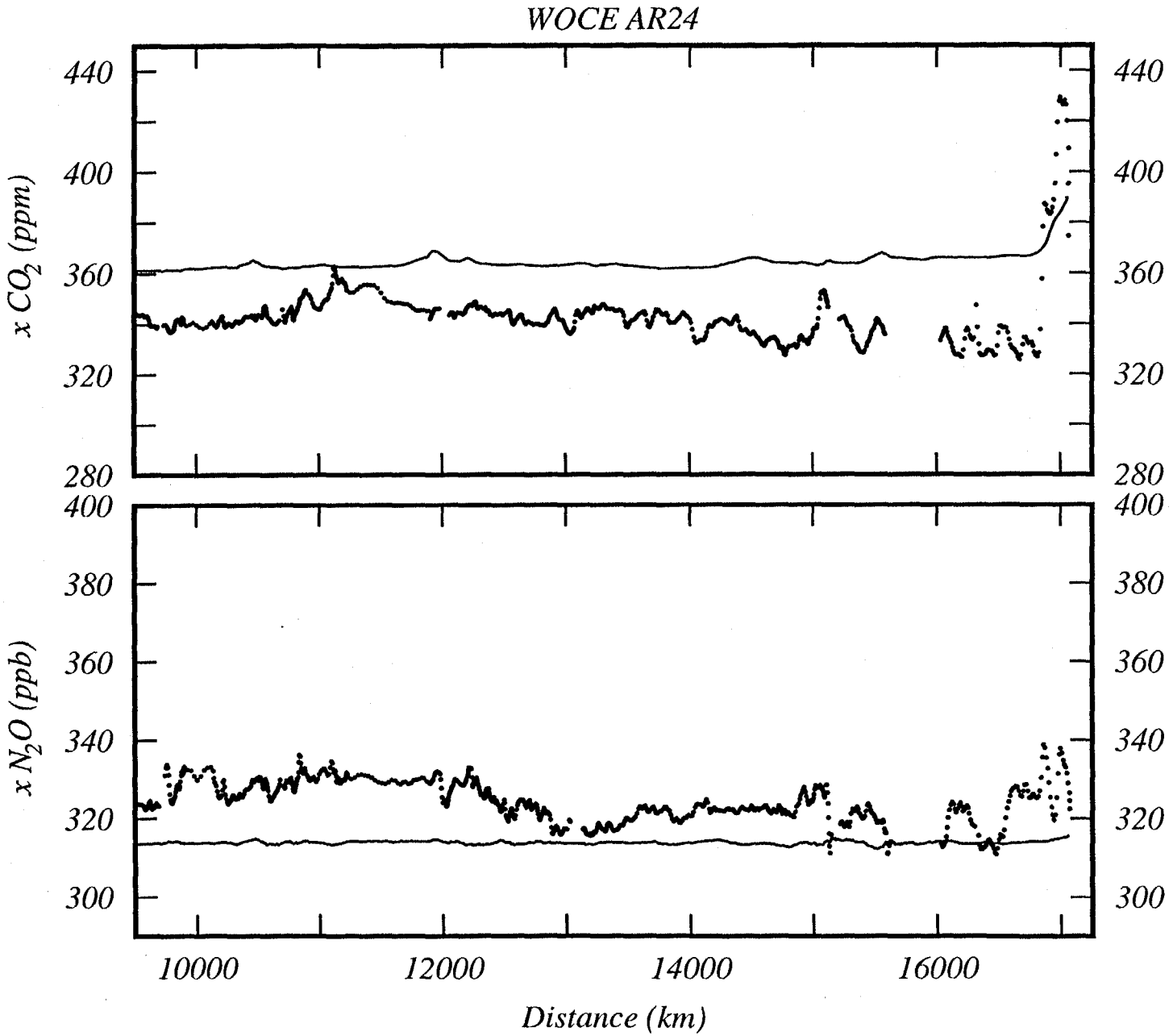
WOCE A22, Trinidad to Woods Hole, 15 Aug 97 to 3 Sep 97




80N
70N
60N
50N
40N
30N
80W
70W
60W
50W
40W
30W
20W
10W
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17

WOCE AR24


WOCE AR24, Woods Hole to Woods Hole, 5 Oct 97 to 19 Nov 97
x CO2 (ppm)
440
400
360
320
280
x N2O (ppb)
400
380
360
340
320
300
0
2000
4000
6000
8000
10000
Distance (km)


WOCE AR24
x CO_2 (ppm)
440
400
360
320
280
x N_2O (ppb)
400
380
360
340
320
300
10000
12000
14000
16000
Distance (km)