



## CDIC NUMERIC DATA COLLECTION

### Transient Tracers in the Oceans (TTO)—Hydrographic Data and Carbon Dioxide Systems with Revised Carbon Chemistry Data

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*Information Resources Organization at Oak Ridge National Laboratory  
MARTIN MARIETTA ENERGY SYSTEMS, INC.  
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Oak Ridge Gaseous Diffusion Plant*

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<sup>\*</sup>Sponsored by the Carbon Dioxide Research Division (CDRD), Office of Basic Energy Sciences (BES), Office of Energy Research, U.S. Department of Energy.

TRANSIENT TRACERS IN THE OCEANS (TTO) - HYDROGRAPHIC  
DATA AND CARBON DIOXIDE SYSTEMS WITH REVISED CARBON CHEMISTRY DATA

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September 1986

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U. S. DEPARTMENT OF ENERGY  
under contract No. DE-AC05-84OR21400



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# TABLE OF CONTENTS

	<u>PAGE</u>
List of Tables .....	v
Abstract .....	1
Magnetic Tape Contents .....	9
Magnetic Tape Descriptive File .....	10
FORTTRAN IV Data Retrieval Program Listing .....	12
Pertinent Literature .....	15
<p>Brewer, P.G., A.L. Bradshaw, and R.T. Williams. 1986.  Measurements of total carbon dioxide and alkalinity in the  North Atlantic Ocean in 1981. pgs 348-370 In <u>The Changing  Carbon Cycle: A Global Analysis</u>, J.R. Trabalka and D.E.  Reichle editors, Springer-Verlag, New York.</p>	
<p>Takahashi, T., and P.G. Brewer. 1986. Hydrographic and chemistry  data for the TTO/NAS expedition, April - October, 1981:  Revised carbon chemistry data. (letter to CDIC).</p>	



## LIST OF TABLES

<u>Table</u>	<u>Page</u>
1. Listing of the variables, format, definitions, and units contained in the original TTO data .....	6
2. Sample listing of the original TTO data and the output for selected parameters from the first station .....	8
3. Sample listing of the revised TTO data as printed by the FORTRAN data retrieval program .....	13



**CDIC NUMERIC DATA PACKAGE  
ABSTRACT**

**1. NUMERIC DATA PACKAGE NAME**

Transient Tracers in the Oceans (TTO)-Hydrographic Data and Carbon Dioxide Systems with Revised Carbon Chemistry Data

**2. CONTRIBUTORS (arranged alphabetically)**

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Participating Institutions in the TTO North Atlantic Experiment: Lamont-Doherty Geological Observatory, Columbia University; Princeton University; Scripps Institution of Oceanography, University of California; Rosenstiel School of Marine and Atmospheric Science, University of Miami; Woods Hole Oceanographic Institution.

The TTO North Atlantic Experiment was sponsored by the National Science Foundation and the U.S. Department of Energy.

**3. CITATION OF THE PACKAGE**

The Carbon Dioxide Information Center (CDIC) recommends the following citation for those citing or referencing this package:

Brewer, P.G., T. Takahashi, and R.T. Williams. 1986. Transient Tracers in the Oceans (TTO) - Hydrographic data and carbon dioxide systems with revised carbon chemistry data. NDP-004/R1, Carbon Dioxide Information Center, Oak Ridge National Laboratory, Oak Ridge, Tennessee. doi: 10.3334/CDIAC/otg.ndp004

**4. HISTORICAL BACKGROUND INFORMATION**

The Transient Tracers in the Ocean (TTO) study was an experiment to investigate ocean mixing as deduced from the distribution of radiochemical tracers introduced into the atmosphere and subsequently into the oceans during the 1958-1962 nuclear bomb tests. The results of this study together with

knowledge about the chemistry of oceanic CO<sub>2</sub> can be used to help understand oceanic uptake of fossil fuel CO<sub>2</sub>. The experiment lasted 4 years and consisted of the following parts: (1) preparation, calibration, and test cruise (1980); (2) field work (1981); (3) laboratory analysis (1982); and (4) completion, data analysis, and reporting (1983). Shipboard measurements were published by the Scripps Physical and Chemical Oceanographic Data Facility as the T.T.O. Preliminary Hydrographic Data Reports Vols. I-IV. Recently, revisions to some of the previously reported measurements have been made and estimates of total CO<sub>2</sub> have been calculated.

## 5. SOURCE AND SCOPE OF THE DATA

Oceans take up about 40% of the fossil fuel CO<sub>2</sub> introduced into the atmosphere by man. Presently, more information is needed on the physical and chemical processes involved in this uptake, such as gas exchange, winter water mass formation, and water mass circulation, before predictions can be made about the sensitivity of these processes to future climate change caused by increased atmospheric CO<sub>2</sub> concentrations. The TTO study provides the type of information needed to better understand the physical and chemical processes involved in the uptake of CO<sub>2</sub> by oceans.

The TTO North Atlantic experiment cruise consisted of seven legs during which a total of 250 hydrographic stations were occupied in 200 days. About 9,000 water samples were taken with most of the samples being analyzed for salinity, oxygen, and nutrients. Over 3,000 samples for tritium analysis were collected and over 1,000 samples for radiocarbon were taken.

Leg 1 of the cruise (stations 1-14) was designed to allow two crossings of the western boundary undercurrent (WBUC) and the Gulf Stream and to allow remeasurement of the tracer field in the current off the Blake-Bahamas outer ridge at 30°N where tritium penetration had been previously observed. Leg 2 (stations 15-41) studied the southern extremity of the WBUC and reoccupied several 1972 GEOSECS stations (TTO stations 32-38). Leg 3 (stations 42-109) of the cruise track crossed the mid-Atlantic ridge and studied eddy and mean-flow fields south of the Azores. Leg 4 (stations 110-140) made observations in the eastern basin of the Atlantic where the Mediterranean outflow occurs and in the Gibbs Fracture Zone. Leg 5 (stations 110-167) explored the Norwegian and Greenland Seas. Leg 6 (stations 168-210) examined the Denmark Strait outflow and Labrador Sea stations, connecting with work done on Leg 4. Leg 7 (stations 211-250) crossed the Grand Banks and followed the 1972 line of GEOSECS stations to 28°N, then to Nova Scotia for completion of the field work.

The total CO<sub>2</sub> concentration data obtained during the program should be revised based on the results of a review of the data by Brewer et al. (1986) (included in this package) and from the results of other studies. This revised data package includes measured quantities of pCO<sub>2</sub> for seawater at 20° C and the total CO<sub>2</sub> concentration values, which were computed using the measured alkalinity and pCO<sub>2</sub> values. These new CO<sub>2</sub> concentration values are smaller by about 20 uM/kg and the discrepancy is greatest for

seawater samples collected at depths less than several hundred meters. These computed CO<sub>2</sub> values are more reliable and should be used for interpretive studies instead of the previously reported ones (Takahashi and Brewer 1986) (included in this package).

## **6. APPLICATIONS OF THE DATA**

The data can be used to calibrate and test models of ocean CO<sub>2</sub> uptake. Almost all of the successful ocean CO<sub>2</sub> models rely on the tracer approach and particularly carbon 14 and tritium. This approach is necessary because unlike atmospheric CO<sub>2</sub> there are no direct accurate methods of measuring ocean CO<sub>2</sub> for extended periods of time. Also, the early ocean CO<sub>2</sub> measurements are not accurate enough to be useful. Comparison of data from the GEOSECS program and the TTO data can also be made. The chemical tracer data provide information about deep ocean circulation and mixing processes. The correlation of carbon dioxide with many tracers will make it possible to study the flux of fossil fuel CO<sub>2</sub> into the ocean. The C14 data will provide estimates of the exchange of carbon dioxide between the atmosphere and the ocean, and C14 and tritium profile distributions are the basis for calibrating models of ocean mixing.

## **7. LIMITATIONS AND RESTRICTIONS**

Shipboard measurements data published as the TTO Preliminary Hydrographic Data Reports Vols. I-IV are to be used with caution because salinities were calculated using the Practical Salinity Scale of 1978, and densities were determined from the new International Equation of State. The densities differ significantly from those given in GEOSECS reports and these differences should be considered when comparing the two data sets. Shorebased measurements of total CO<sub>2</sub> by a gas extraction and manometric procedure were made on a limited number of samples. The revised estimates of total CO<sub>2</sub> provided in this package have been determined from alkalinity and pCO<sub>2</sub> measurements. Any combination of two of the four variables pH, pCO<sub>2</sub>, alkalinity, and total CO<sub>2</sub> permits a complete description of the CO<sub>2</sub> system, within the limits of accuracy of the thermodynamic constants required for the calculation, and thus provide excellent checks on the accuracy of individual measurement.

## **8. KEYWORDS**

GEOCHEMICAL SURVEYS, CARBON CYCLE, WATER CHEMISTRY.

## **9. CONTENTS OF THE PACKAGE**

This numeric data package provides the revised TTO data on a microfiche (inside of back cover), the format, description, and units for the original TTO data (Table 1), a sample listing of

the original TTO data, and pertinent literature to describe both data sets (a).

a. Included in the package:

Brewer, P.G., A.L. Bradshaw, and R.T. Williams. 1986. Measurements of total carbon dioxide and alkalinity in the North Atlantic Ocean in 1981. pgs. 348-370 In The Changing Carbon Cycle: A Global Analysis, J.R. Trabalka and D.E. Reichle editors, Springer-Verlag, New York.

Takahashi, T., and P.G. Brewer. 1986. Hydrographic and chemistry data for the TTO/NAS expedition, April - October, 1981: Revised carbon chemistry data. (letter to CDIC).

b. Background information:

Bradshaw, A.L., Brewer, P.G., Schaefer, D.K., and R.T. Williams. 1981. Measurements of total carbon dioxide and alkalinity by potentiometric acid titration in the GEOSECS Program. Earth and Planetary Science Newsletter 55:99-115.

Brewer, P.G. 1983. The TTO North Atlantic Study - A progress report, in Proceedings: Carbon Dioxide Research Conference: Carbon Dioxide, Science, and Consensus. CONF-820970, September 19-23, 1983, Berkeley Springs, West Virginia, U.S. Department of Energy, Washington, D.C.

Takahashi, T., D. Chipman, N. Schechtman, J. Goddard, and R. Wanninkhof. 1982. Measurements of the partial pressure of CO<sub>2</sub> in discrete water samples during the North Atlantic Expedition, the Transient Tracers of Oceans Program. Technical Report submitted to the National Science Foundation, Lamont-Doherty Geological Observatory of Columbia University, Palisades, N.Y. 10964, 268 pp.

Takahashi, T., R.T. Williams, and D.L. Bos. 1982. Carbonate Chemistry. Chapter 3, in GEOSECS Pacific Expedition, Hydrographic Data 1973-1974, Vol. 3., by W.S. Broecker, D.W. Spencer, and H. Craig, 77-82, U.S. Government Printing Office, Washington, D.C.

Takahashi, T., W.S. Broecker, and S. Langer. 1985. Redfield ratio based on chemical data from isopycnal surfaces. Journal of Geophysical Research 90:6907-6924.

## 10. HOW TO OBTAIN THE PACKAGE

The document contains a microfiche with the revised TTO data for the use of requesters who may not need the automated data. The revised and original digitized data are also available on magnetic tape upon request from CDIC. The magnetic tape will contain a descriptive file (pg. 10), a FORTRAN data retrieval

code to read and list the revised TTO data (pg. 12), the revised TTO data, and the original TTO data. Requests for magnetic tapes should include any specific instructions for transmitting the data required by the user to access the data. Requests should be addressed to:

Carbon Dioxide Information Center  
Oak Ridge National Laboratory  
Post Office Box X  
Oak Ridge, Tennessee 37831-6050  
Telephone: (615) 574-0390  
            FTS 624-0390

#### 11. DATE OF ABSTRACT

September 1986

Each numeric data package (NDP) assembled by CDIC goes through a process of assuring the quality of the data. This process includes review(s) by the contributors of the data to ensure that, in compiling the data, CDIC does not misrepresent or inaccurately describe the data. NDPs are not distributed without the written consent of the contributors.

**TABLE 1.** Listing of the variables, format, definitions, and units contained in the original TTO data file.

HEADER RECORD 1

Variable	Column	Format	Definition
IO	1	I1	Continuation Indicator
ICNTRY	2-4	A3	Originators Nationality
IRECID	14-15	I2	19 for Nansen Cast Rec. ID
ITENSQ	18-21	I4	Canadian 10-deg. Square
IONESQ	22-23	I2	One-degree Square
ITWOSQ	24-25	I2	Two-degree Square
IFIVESQ	26	I1	Five-degree Square
LATHEM	27	A1	N or S hemisphere
LATDEG	28-29	I2	Latitude Degrees
LATMIN	30-31	I2	Minutes Latitude
LIMN TH	32	I1	Minutes Latitude, Tenths
LONHEM	33	A1	E or W Hemisphere
LONDEG	34-36	I3	Degrees Longitude
LONMIN	37-38	I2	Minutes Longitude
LMN TH	39	I1	Minutes Longitude, Tenths
IQUARTR	40	I1	Quarter-degree Square
IYEAR	41-42	I2	Year
MONTH	43-44	I2	Month of Year
IDAY	45-46	I2	Day of Month
STIME	47-49	I3	Station Time
ISHIP	50-55	A6	Alphanumeric Ship Name
IDBOT	56-60	I5	Depth to Bottom, meters
MNDPTYH	71-74	I4	First Obs. Depth
MXDPTH	75-78	I4	Maximum Depth, meters
NXTRC1	79	I1	Always 2, Next Record Ind.
IREC1	80	I1	Always 1, Record Ind.

HEADER RECORD 2

Variable	Column	Format	Definition
IDFDPTH	1-4	I4	Difference Depth, meters
IDALPCT	7	I1	Percent Salinity Present
IOXPCT	8	I1	Percent Oxygen Present
IPO4PCT	9	I1	Percent PO4 Present
ITOTPCT	10	I1	Percent Total P Present
ISTOPCT	11	I1	Percent Silicates Present
NO2PCT	12	I1	Percent Nitrites Present
NO3PCT	13	I1	Percent Nitrates Present
IPHPCT	14	I1	Percent pH Present
IORGRS	15-17	A3	Alpha Originators Cruise
IORGSTA	18-26	A9	Alpha Orig. Station
NUMOBS	62-64	I3	Number of Observed Depths
NUMDET	67-69	I3	Number of Detail Depths
NXTRC2	79	I1	Next Record Indicator
IREC2	80	I1	Always 2, Record Indicator

TABLE 1 (continued)

## DATA RECORDS

Variable	Column	Format	Definition
IDEPOBS	1-5	I5	Depth, meters
IPQUAL	6	A1	Pressure Quality Ind.
ICO2Q	7	A1	CO2T Quality Ind.
TMPOBS	9-12	F5.3	Temperature, Celsius
ITEMPRC	13	I1	Temperature, Precision
ITQUAL	14	A1	Temp. Quality Ind.
SALOBS	15-19	F5.3	Salinity, parts/thousand
ISALAPR	20	I1	Salinity precision
ISQUAL	21	A1	Salinity Quality Ind.
IOQUAL	22	A1	Oxygen Quality Ind.
IPHOSQ	23	A1	Phosphate Quality Ind.
INO2Q	24	A1	NO2 Quality Ind.
INO3Q	25	A1	NO3 Quality Ind.
IALKQ	26	A1	Alkalinity Quality Ind.
IPRESS	27-31	I5	Pressure, decibars
ISILQ	32	A1	Silicate Quality Ind.
OXYOBS	33-36	I4	Oxygen, uM/kg
ALK	37-40	I4	Alkalinity, ueq/kg
CO2T	41-44	I4	CO2 Titration, uM/kg
ICAST	45-46	I2	Cast Number
IBOTL	47-48	I2	Bottle Number
PHOSP	49-52	F4.2	Inorganic Phosphate, uM/kg
PHOSPR	53	I1	Phosphate Precision
CO2GC	54-57	F4.0	CO2 GC, uM/kg
ICO2GC	58	A1	CO2 GC Quality Ind.
SIO3	59-62	F4.1	Silicates, uM/kg
ISIO3PR	63	I1	Silicates Precision
NO2	64-66	F3.2	Nitrites, uM/kg
NO2PR	67	I1	Nitrites Precision
NO3	68-70	F3.1	Nitrates, uM/kg
NO3PR	71	I1	Nitrates Precision
PH	72-74	F3.2	pH
IPHPR	75	I1	pH Precision
NXTPBS	79	I1	Next Record Type
IOBSTYP	80	I1	Always 3, Record Type

Missing data are noted by blanks.

**TABLE 2.** Sample listing of the original TTO data and the output for selected parameters from the first station. The variables, format, and units are described in Table 1.

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---

```

10116021 0 31      19 120990803N39482W 70 50381 4 2
32      999-999- 771
043      10 112773 351993      10 26323332089 227 612      9 9
043      55 112223 351853      55 26023352091 228 632      531 232 861 9
      541 232 871 9
900043      155 126523 356573      156 23423602109 229 702      541 2421011
900043      308 85443 351323      310 15623312181 230 1492      1461 222341
900043      704 47383 349693      710 246      232 1232      1261 021891
900043      803 45863 349633      811 25023122152 233 1222      1251 021861
900043      951 44023 349583      960 25123212154 234 1202      1241 021831
900043      1048 43183 349613      1058 25923182151 235 1192      1251 021831
900043      1160 41773 349653      1172 26323212152 236 1182      1251 021811

```

YEAR	MONTH	DAY	STAID	DEPTH	TEMP	SAL	PRES	OXY	ALK	CO2T	PO4	SI02	NO3
81	4	2	1	10	11.277	35.199	10	263	2333	2089	0.61	5.3	8.6
81	4	2	1	55	11.222	35.185	55	260	2335	2091	0.63	5.4	8.7
81	4	2	1	155	12.652	35.657	156	234	2360	2109	0.70	5.4	10.1
81	4	2	1	308	8.544	35.132	310	156	2331	2181	1.49	14.6	23.4
81	4	2	1	704	4.738	34.969	710	246			1.23	12.6	18.9
81	4	2	1	803	4.586	34.963	811	250	2312	2152	1.22	12.5	18.6
81	4	2	1	951	4.402	34.958	960	251	2321	2154	1.20	12.4	18.3
81	4	2	1	1048	4.318	34.961	1058	259	2318	2151	1.19	12.5	18.3
81	4	2	1	1160	4.177	34.965	1172	263	2321	2152	1.18	12.5	18.1

---



# MAGNETIC TAPE CONTENTS

File # and Description	Mode	DCB Parameters		
		Record Format	Block Size	Logical Record Length
1. General Descriptive Information File	EBCDIC	FB	4240	80
2. FORTRAN Data Retrieval Code to Read and Print Revised TTO Data	EBCDIC	FB	4240	80
3. Revised TTO Data	EBCDIC	FB	6000	120
4. Original TTO Data	EBCDIC	FB	3200	80

## **MAGNETIC TAPE DESCRIPTIVE FILE**

**DATASET TITLE:** Transient Tracers in the Oceans (TTO) -  
Hydrographic Data and Carbon Dioxide Systems  
with Revised Carbon Chemistry Data

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Lamont-Doherty Geological Observatory, Columbia University  
Princeton University  
Scripps Institution of Oceanography, University of California  
Rosenstiel School of Marine and Atmospheric Science, Univ. of  
Miami  
Woods Hole Oceanographic Institution.

The TTO study was sponsored by the National Science  
Foundation and the U.S. Department of Energy.

**SCOPE OF THE DATA:** The transient tracers in the ocean (TTO) study was an experiment to investigate the manner and time scale of ocean mixing, as deduced from the distribution of radiochemical tracers injected into the oceans from nuclear bomb tests during the period 1958-1962. The data provide a crucial test for models of oceanic CO<sub>2</sub> uptake. Virtually all successful models of oceanic CO<sub>2</sub> uptake rely on the tracer approach since there is no comparable direct time series of ocean CO<sub>2</sub> measurements as is the case for atmospheric CO<sub>2</sub>.

A total of 250 hydrographic stations were occupied during the TTO study. Approximately 9000 individual water samples were taken, with most being analyzed for salinity, oxygen, and nutrients. Over 3000 samples for tritium analysis were collected and over 1000 samples for radiocarbon were taken.

Any combination of two of the four variables: pH, pCO<sub>2</sub>, alkalinity, and total CO<sub>2</sub> permits a complete description of the carbon dioxide system, within the limits of the accuracy of the thermodynamic constants required for the calculation.

**DATA FORMAT:** Two data files are provided with the package. One file is the original TTO data which is formatted as described in Table 1. The second data file is a revision of the original data which contains revised estimates of total CO<sub>2</sub> and also contains pCO<sub>2</sub> values.

#### REFERENCES

- Brewer, P.G., A.L. Bradshaw, and R.T. Williams. 1986. Measurements of total carbon dioxide and alkalinity in the North Atlantic Ocean in 1981. pgs 348-370 In The Changing Carbon Cycle: A Global Analysis, J.R. Trabalka and D.E. Reichle editors, Springer-Verlag, New York.
- Takahashi, T., and P.G. Brewer. 1986. Hydrographic and chemistry data for the TTO/NAS expedition, April - October, 1981: Revised carbon chemistry data. (letter to CDIC).

# FORTRAN IV DATA RETRIEVAL PROGRAM LISTING

```

C
C FORTRAN RETRIEVAL CODE TO READ AND PRINT TTO DATA
C
14      CONTINUE
        WRITE(6,20)
20      FORMAT(/)
C READ THE HEADER RECORD FOR EACH STATION
        READ(5,15) ILEG,ISTN,LATDEG,LATMIN,LATDIR,LONDEG,LONMIN,LONDIR,
1      IYEAR,IMTH,IDAY,IGMT,IDEPTH
15      FORMAT(1X,I1,1X,I3,1X,I2,F5.1,1X,A1,I3,F5.1,1X,A1,1X,I2,
1      1X,I2,1X,I2,1X,I4,1X,I4)
C WRITE THE HEADER RECORD INFORMATION
        WRITE(6,16) ILEG,ISTN,LATDEG,LATMIN,LATDIR,LONDEG,LONMIN,LONDIR,
1      IYEAR,IMTH,IDAY,IGMT,IDEPTH
16      FORMAT(1X,'LEG=' ,I1,1X,'STATION # ' ,I3,1X,'LATITUDE ' ,I2,1X,F5.1,
1      1X,A1,1X,'LONGITUDE ' ,I3,F5.1,1X,A1,1X,'YEAR ' ,I2,1X,'MONTH ' ,I2,
2      1X,'DAY=' ,I2,1X,'GMT=' ,I4,1X,'BOTTOM DEPTH=' ,I4)
        WRITE(6,18)
18      FORMAT(1X,'BOTTLE',1X,'PRESS.',1X,'DEPTH',1X,'TEMP',2X,'POT.',2X,
1      1X,'SALINITY',1X,'THETA',1X,'SIGMA',2X,'SIGMA',2X,'O2',1X,
2      1X,'SILICATE',1X,'PO4',1X,'NO3',1X,'NO2',1X,'ALKALINITY',1X,'TOTAL',
3      1X,'PCO2',3X,'TOTAL',/ 3X,'#',23X,'TEMP',17X,'2000',3X,'4000',
4      39X,'CO2',10X,'CO2')
1      CONTINUE
C READ THE TTO DATA FOR EACH STATION
        READ(5,100,END=99) IBOT,IPRESS,IDEPTH,TEMP,TEMPPT,SALIN,THETA,
1      SIGMA,FOUR,IOXYG,SIL,PH,NIT,NITR,ALK,TOTCO,PCO,TOTCOR
100     FORMAT(2X,I3,1X,I4,1X,I4,1X,F6.3,1X,F6.3,1X,F6.3,1X,F6.3,1X,
1      1X,F6.3,1X,F6.3,1X,I3,1X,F5.1,1X,F4.2,1X,F4.1,1X,F4.2,1X,I4,1X,I4,
2      1X,F6.1,1X,F6.1)
C IF THE PROGRAM HAS REACHED THE BLANK LINE DELIMITER BETWEEN
C STATIONS, GO AND READ THE NEXT STATION HEADER RECORD
        IF(IBOT .EQ. 0) GO TO 14
C WRITE THE TTO DATA FOR EACH STATION
        WRITE(6,200) IBOT,IPRESS,IDEPTH,TEMP,TEMPPT,SALIN,THETA,
1      SIGMA,FOUR,IOXYG,SIL,PH,NIT,NITR,ALK,TOTCO,PCO,TOTCOR
200     FORMAT(2X,I3,3X,I4,2X,I4,2X,F6.3,1X,F6.3,1X,F6.3,1X,F6.3,1X,
1      1X,F6.3,1X,F6.3,1X,I3,1X,F5.1,1X,F4.2,1X,F4.1,1X,F4.2,4X,I4,3X,I4,
2      1X,F6.1,1X,F6.1)
        GO TO 1
99      CONTINUE
        STOP
        END

```

**TABLE 3.** Sample listing of the revised TTO data as printed by the FORTRAN data retrieval program. The header record contains the leg #, station number, latitude degrees, latitude minutes, longitude hemisphere, longitude degrees, longitude minutes, longitude hemisphere, date (YY MM DD), GMT time of the station, and the bottom depth respectively. Each bottle record that follows contains the bottle number, pressure, depth, temperature, potential temperature, salinity, sigma theta, sigma 2000, sigma 4000, oxygen, silicate, phosphate, nitrate, nitrite, alkalinity, total CO<sub>2</sub> (by titrator), pCO<sub>2</sub> (at 20°C), and calculated total CO<sub>2</sub> (from pCO<sub>2</sub> & alkalinity). Missing data are represented by -9, -9.9, -999, or -999.9 and the units for the revised data are identical to the original data.

LEG=1 STATION #		1	LATITUDE	39	48.2	N	LONGITUDE	70	5.0	W	YEAR	81	MONTH	4	DAY=	2	GMT=	0	BOTTOM	DEPTH=	0
BOTTLE	PRESS.	DEPTH	POT.	SALINITY	TEMP	THETA	SIGMA	SIGMA	O2	SILICATE	PO4	NO3	NO2	ALKALINITY	TOTAL	PCO2	TOTAL	CO2	TOTAL	CO2	
227	10	10	11.277	35.199	26.881	35.636	44.008	263	5.3	0.60	8.4	0.23	2352	2105	471.2	2111.7					
228	55	55	11.222	35.185	26.881	35.639	44.013	260	5.4	0.63	8.5	0.23	2354	2107	475.1	2115.0					
229	156	155	12.652	35.657	26.977	35.672	43.988	234	5.4	0.71	9.9	0.24	2378	2125	457.1	2125.3					
230	310	308	8.544	35.132	27.300	36.173	44.655	156	14.6	1.49	23.4	0.02	2350	2198	822.4	2205.6					
232	710	704	4.738	34.969	27.688	36.744	45.398	246	12.6	1.23	18.8	0.0	-999	-999	769.3	-999.9					
233	811	803	4.586	34.963	27.701	36.765	45.427	250	12.5	1.22	18.6	0.0	2331	2169	758.1	2177.0					
234	960	951	4.402	34.958	27.718	36.793	45.464	251	12.4	1.20	18.3	0.0	2339	2171	792.1	2191.0					
235	1058	1048	4.318	34.961	27.730	36.810	45.485	259	12.5	1.19	18.2	0.0	2336	2168	758.8	2181.6					
236	1172	1160	4.177	34.965	27.750	36.836	45.519	263	12.5	1.19	18.0	0.0	2339	2169	733.8	2178.7					

  

LEG=1 STATION #		2	LATITUDE	38	50.0	N	LONGITUDE	69	30.0	W	YEAR	81	MONTH	4	DAY=	3	GMT=	0	BOTTOM	DEPTH=	3200
BOTTLE	PRESS.	DEPTH	POT.	SALINITY	TEMP	THETA	SIGMA	SIGMA	O2	SILICATE	PO4	NO3	NO2	ALKALINITY	TOTAL	PCO2	TOTAL	CO2	TOTAL	CO2	
101	11	11	8.819	34.117	26.456	35.330	43.814	310	2.3	0.38	2.7	0.13	-999	-999.9	-999.9	-999.9					
102	154	153	11.751	35.479	27.013	35.746	44.097	240	5.7	0.71	10.6	0.39	-999	-999.9	-999.9	-999.9					
103	305	303	9.311	35.219	27.245	36.083	44.533	150	14.5	1.47	23.5	0.03	-999	-999.9	-999.9	-999.9					
104	404	401	7.171	35.066	27.453	36.389	44.931	176	15.2	1.48	23.1	0.02	-999	-999.9	-999.9	-999.9					
105	504	500	5.874	35.002	27.576	36.575	45.176	209	14.2	1.38	21.1	0.01	-999	-999.9	-999.9	-999.9					
106	605	600	5.132	34.987	27.656	36.692	45.327	-9	13.3	1.29	19.6	0.02	-999	-999.9	-999.9	-999.9					
107	706	700	4.691	34.969	27.693	36.751	45.408	246	12.8	1.43	18.8	0.13	-999	-999.9	-999.9	-999.9					
108	807	800	4.522	34.974	27.716	36.784	45.449	252	12.5	1.22	18.4	0.01	-999	-999.9	-999.9	-999.9					
109	908	899	4.346	34.971	27.734	36.811	45.485	258	12.4	1.20	18.2	0.01	-999	-999.9	-999.9	-999.9					
110	1008	998	4.168	34.962	27.747	36.833	45.516	262	12.4	1.19	18.0	0.01	-999	-999.9	-999.9	-999.9					
111	1105	1094	4.070	34.958	27.755	36.847	45.534	265	12.4	1.18	17.9	0.01	-999	-999.9	-999.9	-999.9					
112	1305	1291	3.934	34.961	27.773	36.873	45.568	269	12.8	1.18	17.8	0.01	-999	-999.9	-999.9	-999.9					
113	1510	1493	3.865	34.965	27.785	36.889	45.588	268	13.1	1.18	17.8	0.01	-999	-999.9	-999.9	-999.9					
114	1767	1746	3.687	34.969	27.808	36.923	45.632	269	14.4	1.18	17.9	0.01	-999	-999.9	-999.9	-999.9					
115	2023	1998	3.456	34.966	27.830	36.958	45.679	269	16.1	1.19	18.0	0.01	-999	-999.9	-999.9	-999.9					
116	2222	2194	3.284	34.959	27.842	36.981	45.711	269	17.8	1.20	18.1	0.01	-999	-999.9	-999.9	-999.9					
117	2426	2394	3.073	34.948	27.855	37.005	45.747	270	18.6	1.19	17.9	0.01	-999	-999.9	-999.9	-999.9					
118	2619	2583	2.901	34.943	27.868	37.028	45.780	272	19.2	1.19	17.8	0.01	-999	-999.9	-999.9	-999.9					
119	2822	2782	2.650	34.928	27.879	37.054	45.819	276	19.3	1.16	17.3	0.01	-999	-999.9	-999.9	-999.9					
120	2915	2873	2.530	34.921	27.884	37.066	45.838	277	20.2	1.16	17.2	0.01	-999	-999.9	-999.9	-999.9					
121	3015	2971	2.407	34.915	27.890	37.079	45.858	276	21.6	1.17	17.3	0.01	-999	-999.9	-999.9	-999.9					
122	3115	3069	2.294	34.908	27.894	37.090	45.875	276	22.8	1.17	17.4	0.01	-999	-999.9	-999.9	-999.9					
123	3166	3119	2.268	34.905	27.894	37.092	45.879	275	23.9	1.19	17.6	0.01	-999	-999.9	-999.9	-999.9					
124	3209	3161	2.234	34.904	27.897	37.096	45.885	275	25.5	1.21	17.8	0.01	-999	-999.9	-999.9	-999.9					



PERTINENT LITERATURE

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**HYDRGRAPHIC AND CHEMISTRY DATA  
FOR THE TTO/NAS EXPEDITION,  
APRIL - OCTOBER, 1981 :  
REVISED CARBON CHEMISTRY DATA**

by

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March, 1986

**INTRODUCTION**

The original hydrographic and ocean chemistry data set collected during the 1981 Transient Tracers in the Oceans Program in the North Atlantic Ocean (TTO/NAS) was submitted to the Carbon Dioxide Information Center on October 22, 1984. This is one of the most extensive chemical oceanographic data sets obtained in the North Atlantic Ocean, and includes temperature, salinity, dissolved oxygen and nutrient concentrations as well as the total concentration of CO<sub>2</sub> dissolved in seawater and the alkalinity in seawater. The quality of the data has been reviewed recently by Brewer et al. (1986). This and other recent studies have shown that the total CO<sub>2</sub> concentration data listed in the original tape require some revision. We have therefore prepared this tape to amend and supplement the earlier data set. Added are the observed pCO<sub>2</sub> values exerted by sea water samples at 20.0°C, and the total CO<sub>2</sub> concentration values, which have been computed using the measured alkalinity and pCO<sub>2</sub> values. These computed total CO<sub>2</sub> concentration values are systematically smaller than the previously reported values by up to about 20 uM/kg, and the discrepancy is especially pronounced for the seawater samples collected at depths shallower than several hundred meters. We believe that these computed total CO<sub>2</sub> values are more reliable, and thus recommend this revised set of the total CO<sub>2</sub> concentration data for interpretive studies.



## TECHNICAL EXPLANATION

### 1) Scientific Basis for Revision:

During the TTO/NAS Program, three quantities relevant to carbon chemistry were measured by the following means:

Alkalinity by the potentiometric acid titration method aboard the ship (Bradshaw et al., 1981). The alkalinity values thus obtained are listed in the original tape, and are not subject to the present revision.

Total CO<sub>2</sub> concentration a) by the potentiometric acid titration method aboard the ship (Bradshaw et al., 1981), and b) by the manometric method for a limited number of poisoned and stored water samples (C.D. Keeling of Scripps Institution of Oceanography). The total CO<sub>2</sub> concentration values obtained by means of the first method are listed in the original tape, and are revised in this up-dated tape.

Partial pressure of CO<sub>2</sub> (pCO<sub>2</sub>) exerted by water samples at 20.00C by means of the equilibrator-gas chromatograph method aboard the ship (Takahashi et al., 1982-a). These measured pCO<sub>2</sub> values are listed in this revised tape, and are used with the alkalinity values to compute the total CO<sub>2</sub> concentration values listed in this revised tape.

When any two of the three carbon chemistry parameters (i.e. alkalinity, total CO<sub>2</sub> concentration and pCO<sub>2</sub>) are known, the third can be computed using the thermodynamic relationships of the carbon dioxide system in seawater. Since all of these three have been determined during the TTO program, the internal consistency of the carbon chemistry measurements can be critically tested. An internal consistency analysis for the carbon data has shown:

a) The total CO<sub>2</sub> concentration measured by the titration method is greater than that computed using the alkalinity and pCO<sub>2</sub> values by as much as 20 uM/kg in the water samples collected at depths shallower than about 800 meters, and by about 5 uM/kg on the average in water samples collected below about 800 meters (Takahashi et al, 1985).

b) The total CO<sub>2</sub> concentration measured by the titration method is also greater by a similar amount than that obtained by C.D. Keeling of Scripps Institution of Oceanography using the manometric method for a limited number of the poisoned and stored seawater samples (Brewer et al, 1986).

c) The total CO<sub>2</sub> concentration values computed using the pCO<sub>2</sub> and alkalinity data are consistent with those obtained by C.D. Keeling using the manometric method (Takahashi et al, 1985).

d) The cause for the systematic error in the titrimetric total CO<sub>2</sub> measurement has not been understood. It should be pointed out that a detailed knowledge on the electrochemical behavior of seawater is required for computation of the total CO<sub>2</sub> concentration values using the acid titration data as described by Bradshaw et al. (1981). However, since our knowledge on seawater electrochemistry is not complete, some assumptions have been made. For example, the effect of a small quantity of various organic acids dissolved in seawater is neglected. Thus, it is possible that the assumptions made in the titration data reduction scheme might sensitively affect the computed total CO<sub>2</sub> values. On the other hand, the data reduction scheme for the manometric measurement is straight forward, and thus is immune to the problems, which would affect the titrimetric total CO<sub>2</sub> measurement.

## 2) pCO<sub>2</sub> Data:

Since the scientific nature of this pCO<sub>2</sub> data set is somewhat unique and its applications are not widely known in the scientific community, it will be explained below in some details:

a) The pCO<sub>2</sub> values are given in micro-atmosphere (or 10<sup>-6</sup> atm), and represent the values at 20.00°C under one atmosphere total pressure. If an user wishes to compute the pCO<sub>2</sub> values at in situ water temperature ( and under 1 atmosphere total pressure), the values must be corrected for the difference between the reference temperature (20.00°C) and the in situ temperature using the following equation;

$$(dp/dT)/p = 0.043 \text{ } ^\circ\text{C}^{-1}$$

$$p \text{ (at } T) = p_0 \cdot \exp (0.043 (T - 20.00)),$$

where p is pCO<sub>2</sub>, p<sub>0</sub> is pCO<sub>2</sub> at 20.00°C, and T is the in situ temperature in degrees C. The temperature coefficient has been determined in our laboratory, and represents a mean surface water value. This value is, however, a weak function of temperature and the concentrations of phosphoric and silicic acids dissolved in seawater in various quantities, and varies by about 1%. Exact functionality is currently being investigated.

b) The measurements were made aboard the research ship using the equilibrator-gas chromatograph method described by Takahashi et al. (1982-a).

c) The calibration of the gas chromatograph for pCO<sub>2</sub> measurements is based on the WMO CO<sub>2</sub> standard gas mixtures supplied by C.D. Keeling of the Scripps Institution of Oceanography, La Jolla, California. The measurements were made in a temperature range of 20.0 ± 0.1°C, and the final values have been corrected to 20.00°C. The reproducibility of the measurements have been estimated to be ± 0.1% of the reported values.

### 3) Computation of the Total CO<sub>2</sub> Concentration:

The revised total CO<sub>2</sub> values which are listed in the tape are computed using the alkalinity and pCO<sub>2</sub> values and the following dissociation constants;

Mehrbach et al (1973) for carbonic acid,  
Lyman (1956) for boric acid,  
Sillen and Martell (1964) for silicic acid,  
Kester and Pytkowicz (1967) for phosphoric acid,  
Millero (1979) for water,  
Culberson and Pytkowicz (1973) for the activity of water,  
and  
Weiss (1974) for CO<sub>2</sub> solubility in seawater.

More detailed discussion and numerical examples are presented in Takahashi et al. (1982-b). A FORTRAN program for this computation is attached to this tape, and is also listed in Takahashi et al. (1982-a).

# REFERENCES CITED

- Bradshaw, A.L., Brewer, P.G., Schaefer, D.K. and Williams, R.T., (1981), Measurements of total carbon dioxide and alkalinity by potentiometric acid titration in the GEOSECS Program, Earth and Planet. Sci. Lett., 55, 99-115.
- Brewer, P.G., Bradshaw, A.L. and Williams, R.T., (1986), Measurements of total carbon dioxide and alkalinity in the North Atlantic Ocean in 1981. In "The Changing Carbon Cycle: A Global Analysis", J.R. Trabalka and D.E. Reichele editors, Springer-Verlag, New York.
- Culberson, C. and Pytkowicz, R.M., (1973), Ionization of water in seawater, Marine Chemistry, 1, 403-417.
- Kester, D. and Pytkowicz, (1967), Determination of the apparent dissociation constants of phosphoric acid in seawater, Limnology and Oceanography, 12, 243-252.
- Lyman, J., (1956), Buffer mechanisms in sea water, Ph.D. Thesis, Univ. of California, Los Angeles, CA, 196 pp.
- Mehrbach, C., Culberson, C.H., Hawley, J.E. and Pytkowicz, R.M., (1973), Measurement of apparent dissociation constants of carbonic acid in seawater at atmospheric pressure, Limnology and Oceanography, 18, 533-541.
- Millero, F.J., (1979), The thermodynamics of the carbonate system in seawater, Geochimica et Cosmochimica Acta, 43, 1651-1661.
- Sillen, L.G. and Martell, A.E., (1964), Stability constants of metal-ion complexes, The Chemical Society (London), Special Publication 17, 751 pp.
- Takahashi, T., Chipman, D., Schechtman, N., Goddard, J. and Wanninkhof, R., (1982-a), "Measurements of the partial pressure of CO<sub>2</sub> in discrete water samples during the North Atlantic Expedition, the Transient Tracers of Oceans Program", Technical Report submitted to the National Science Foundation, Lamont-Doherty Geological Observatory of Columbia University, Palisades, N.Y. 10964, 268 pp.
- Takahashi, T., Williams, R. T. and Bos, D.L., (1982-b), Carbonate Chemistry, Chapt. 3, in "GEOSECS Pacific Expedition, Hydrographic Data 1973-1974", Vol.3, by W.S. Broecker, D.W. Spencer and H. Craig, 77-82, U.S. Government Printing Office, Washington, D.C.
- Takahashi, T., Broecker, W.S. and Langer, S., (1985), Redfield ratio based on chemical data from isopycnal surfaces, Jour. Geophys. Res., 90, 6907-6924.
- Weiss, R.F., (1974), Carbon dioxide in water and seawater: the solubility of a non-ideal gas, Marine Chemistry, 2, 203-215.