

Explorer of the Seas METADATA - 2004

Class of Data: Surface ocean carbon dioxide concentrations

Dataset Identifier: Explorer of the Seas

Two Files: Explorer_2004_East
Explorer_2004_West

Statement of how to cite dataset:

Explorer website: http://www.aoml.noaa.gov/ocd/gcc/explorer_cruisetracks.php

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Measurement platform identifier: Explorer of the Seas

Cruise Information:

Weekly cruises through the Caribbean departing from Miami, Florida.

Project Information:

This project represents a collaboration between Royal Caribbean International, the University of Miami's Rosenstiel School of Marine and Atmospheric Science, the National Oceanic and Atmospheric Administration, the National Science Foundation, the Office of Naval Research, and the National Aeronautics and Space Administration.

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Timestamp for initial submission of dataset: 7/11/07

Timestamp for the most recent update of dataset: 7/11/07

Timestamp period the dataset refers to: 1/02/2005 - 12/18/2005

Geographic area the dataset refers to:

16 N to 28 N
62 W to 90 W

Eastern Cruise Track:

Day 1 - Miami, Florida (25.8 N/80.7 W)
Day 3 - San Juan, Puerto Rico (18.5 N/66.1 W)
Day 4 - Philipsburg, St. Maarten (18.0 N/63.0 W)
Day 5 - Charlotte Amalie, St. Thomas (18.3 N/64.9 W)
Day 7 - Nassau, Bahamas (25.1 N/77.3 W)
Day 8 - Miami, Florida (25.8 N/80.7 W)

Western Cruise Track for EX0401W and EX0403W:

Day 1 - Miami, Florida (25.8 N/80.7 W)
Day 3 - Labadee, Hispaniola (19.8 N/72.3 W)
Day 4 - Ocho Rios, Jamaica (18.4 N/77.1 W)
Day 6 - Cozumel, Mexico (20.5 N/87.0 W)
Day 8 - Miami, Florida (25.8 N/80.7 W)

Western Cruise Track for EX0405W, EX0409W, EX0411W,
EX0413W, EX0415W, and EX0417W:

Day 1 - Miami, Florida (25.8 N/80.7 W)
Day 3 - Labadee Hispaniola (19.8 N/72.3 W)
Day 4 - Ocho Rios, Jamaica (18.4 N/77.1 W)
Day 5 - George Town, Grand Cayman (19.3 N/81.4 W)
Day 6 - Cozumel, Mexico (20.5 N/87.0 W)
Day 8 - Miami, Florida (25.8 N/80.7 W)

Western Cruise Track for the remaining Western cruises:

Day 1 - Miami, Florida (25.8 N/80.7 W)
Day 3 - Belize City, Belize (17.8 N/88.3 W)
Day 4 - Costa Maya, Mexico (18.7 N/87.7 W)
Day 5 - Cozumel, Mexico (20.5 N/87.0 W)
Day 6 - George Town, Grand Cayman (19.3 N/81.4 W)
Day 8 - Miami, Florida (25.8 N/80.7 W)

List of variables included in this dataset:

COLUMN	HEADER	EXPLANATION
1.	Group_Ship:	AOML_Explorer for all Explorer of the Seas data.
2.	Cruise:	Cruise Name (For example, EX0546W: EX = Explorer of the Seas, 05 = 2005, 46 = 46th weekly cruise, and W = western track).
3.	JD_GMT:	Decimal year day.

4. Date_DDMMYYYY: The date format has been changed to comply with the IOCCP recommendations.
5. TIME_HH:MM:SS: GMT time.
NOTE: local time = GMT - 4 hr or GMT - 5 hr.
6. Lat_dec_degree: Latitude in decimal degrees (negative values are in the southern hemisphere).
7. Long_dec_degree: Longitude in decimal degrees (negative values are in the western latitudes).
8. xCO2eq_ppm: Mole fraction of CO2 (dry) in the headspace equilibrator at equilibrator temperature (Teq) in parts per million.
9. xCO2a_ppm: Mole fraction of CO2 in air in parts per million.
This field is not measured on the Explorer of the Seas - all data initialized to -9.
10. Pres_Equil_hPa: Barometric pressure in the lab in hectopascals (1 hectopascal = 1 millibar).
11. Pres_sealevel_hPa: Barometric pressure from ship's barometer, corrected to sea level in hectopascals (1 hectopascal = 1 millibar).
12. EqTemp_C: Temperature in equilibrator water in degrees centigade. Temperature in equilibrator measured with a calibrated thermistor.
13. SST(TSG)_C: Temperature from the ship's thermosalinograph in degrees centigrade.
14. Sal(TSG)_Permil: Salinity from the ship's thermosalinograph on the Practical Salinity Scale.
15. Water_flow_l/min: Water flow through equilibrator in liters per minute.
16. Gasflow_IR_ml/min: Gas flow through the Licor infrared analyzer before the flow is stopped in milliliters per minute.
17. Temp_IR_C: Temperature of the Licor infrared analyzer sample cell in degrees centigrade.
18. Pres_IR_hPa: Pressure in the Licor infrared analyzer in hectopascals.
NOTE: There is no pressure sensor in the Licor but since it is vented to atmosphere prior to measurement, this value is the same as the pressure in the lab (number 10 above). (1 hectopascal = 1 millibar).
19. Ship_heading_true_degree: Ship's heading from ship's navigation system in degrees with 0 = North and 90 = East.
20. Ship_speed_knot: Ship's speed from ship's navigation system in knots.
21. Wind_dir_rel_degree: Wind direction relative to the ship from ship's navigation system in degrees with 0 = from the bow and 90 = from starboard.

22. Wind_speed_rel_m/s: Wind speed relative to the ship from ship's navigation system in meters per second.
23. fCO2W@SST_uatm: Fugacity of CO2 in sea water in microatmospheres calculated as outlined below.
24. Qcflag_water: Quality control flag for sea water xCO2 and fCO2 values with 2 = good value, 3 = questionable value, 4 = bad value, and 9 = no measurement taken.
25. fCO2a_uatm: Fugacity of CO2 in air in microatmospheres. This field is not measured on the Explorer of the Seas - all data initialized to -9.
26. Qcflag_air: Quality control flag for air xCO2 and fCO2. Since no air values were taken, all values are initialized to 9.
27. dfCO2_uatm: Sea water fCO2 - air fCO2 in microatmospheres. This uses the average air value for the current hour. This field is not measured on the Explorer of the Seas - all data initialized to -9.
28. Fluoro_ug/l: Reading from the fluorometer in micrograms per liter.
29. Wind_speed_true_m/s: True wind speed in meters per second.
30. Wind_dir_true_degree: True wind direction in degrees were 0 = North and 90 = East.
31. Air_Temp_C: Outside air temperature from ship's computer system in degrees centigrade.
32. Oxygen: Units not known at this time.

The following fields have been QC'ed by the CO2 group:

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Group_Ship
Cruise
JD_GMT
DATE_DDMMYYYY
TIME_HH:MM:SS
Lat_dec_degree
Long_dec_degree
xCO2eq_ppm
Pres_Equil_hPa
EqTemp_C
Water_flow_l/min
Gasflow_IR_ml/min
Temp_IR_C
Pres_IR_hPa
fCO2W@SST_uatm
Qcflag_water

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The following fields are from ship's onboard systems and the quality of this data cannot be verified:

Pres_sealevel_hPa
SST(TSG)_C
Sal(TSG)_Permil
Ship_heading_true_degree
Ship_speed_knot
Wind_dir_rel_degree
Wind_speed_rel_m/s
Fluoro_ug/l
Wind_speed_true_m/s
Wind_dir_true_degree
Air_Temp_C
Oxygen

Narrative description of system design:

CO2 ANALYTICAL SYSTEM:

The concentration of carbon dioxide (CO₂) in surface ocean water is determined by measuring the concentration of CO₂ in gas that is in contact with the water. Surface water is pumped over 200 m through 7/8" Teflon tubing from an inlet in the ship's bow to the equilibration chamber. Water comes from the bow intake 2 m below the water line and the TSG is located close to the inlet. Since the sea surface temperature is high and the ship is well air-conditioned, the T_{eq} is on average about 0.4 °C lower than SST. The equilibration chamber has an enclosed volume of gas, or headspace, and a pool of seawater that continuously overflows to a drain. As the water flows through the chamber, the dissolved gases (like CO₂) partition between the water and the headspace. At equilibrium, the ratio of CO₂ in the water and in the headspace is influenced most by temperature, and that relationship is known. By measuring the concentration of CO₂ in the headspace and the temperature in the chamber, the partial pressure (or fugacity) of CO₂ in the surface water can be calculated.

INSTRUMENT DESCRIPTION

The general principle of instrumental design can be found in Wanninkhof and Thoning (1993), Ho et al. (1995), and Feely et al. (1998). The concentration of CO₂ in the headspace gas is measured using the adsorption of infrared (IR) radiation, which results from changes in the rotational and vibrational energy state of the CO₂ molecule. The LI-COR detector passes IR radiation through two 6" cells. The reference cell is flushed with a gas of known CO₂ concentration. The sample cell is flushed with the headspace gas. A vacuum-sealed, heated filament is the broadband IR source. The IR radiation alternates between the two cells via a chopping shutter disc. An optical filter selects an adsorption band specific for CO₂ (4.26 micron) to reach the detector. The solid state (lead selenide) detector is kept at -12 degrees °C for excellent stability and low signal noise (less than 0.2 ppm).

Several steps are taken to reduce interferences and to increase the accuracy of the measurements. After the equilibration chamber, the headspace travels through a drying trap to remove water vapor. During each analysis, the headspace gas is compared to a reference gas of known concentration. To improve the accuracy of the measurements, three different gaseous standards for CO₂ are analyzed once an hour instead of the headspace gas.

Analyzer: LI-COR 6252 (analog output) infrared (IR) analyzer.

Method of Analysis: Differential analyses relative to a reference gas which is close to the CO₂ concentration of the middle standard. Measures dried equilibrator headspace gas. Gas flow is stopped prior to IR readings.

Drying Method: The equilibrator headspace sample gas first goes through an air filter and a thermoelectric refrigerator (~6-10 °C). The sample and standard gases pass through a Perma Pure (Nafion) dryer and a short column of magnesium perchlorate before reaching the analyzer. The counter flow in the Perma Pure tube is the reference gas.

Equilibrator (setup, size, flows): The equilibrator was fabricated using a filter housing (ColeParmer, U-010509-00) with ~0.5 L water reservoir and ~0.8 L gaseous headspace. Water flow rate is ~1.5 L/min. Headspace recirculation rate is ~80 ml/min.

Narrative statement identifying measurement method for each required parameter:

CALCULATIONS:

The mixing ratios of ambient air and equilibrated headspace air are calculated by fitting a second-order polynomial through the hourly averaged millivolt response of the detector versus mixing ratios of the standards. Mixing ratios of dried equilibrated headspace and air are converted to fugacity of CO₂ in surface seawater and water saturated air in order to determine the fCO₂. For ambient air and equilibrator headspace, the fCO_{2a} (or fCO_{2eq}) is calculated assuming 100% water vapor content:

$$fCO_{2eq} = xCO_{2eq}(P - p_{H_2O}) \exp(B_{11} + 2d_{12})P/RT$$

where fCO_{2eq} is the fugacity in the equilibrator, p_{H₂O} is the water vapor pressure at the sea surface temperature, P is the atmospheric pressure (in atm), T is the SST or equilibrator temperature (in K) and R is the ideal gas constant (82.057 cm³·atm·deg⁻¹·mol⁻¹). The exponential term is the fugacity correction where B₁₁ is the second virial coefficient of pure CO₂

$$B_{11} = -1636.75 + 12.0408T - 0.032795T^2 + 3.16528E-5 T^3$$

and d₁₂ = 57.7 - 0.118 T is the correction for an air-CO₂ mixture in units of cm³·mol⁻¹ (Weiss, 1974).

The calculation for the fugacity at SST involves a temperature correction term for the increase of fCO₂ due to heating of the water from passing through the pump and through 5 cm ID PVC tubing within the ship. The water in the equilibrator is typically 0.4 °C cooler than sea surface temperature. The empirical temperature correction from equilibrator temperature to SST is outlined in Weiss et al. (1982).

$$d\ln(fCO_2) = (T_{eq} - SST) (0.0317 - 2.7851E-4 T_{eq} - 1.839E-3 \ln(fCO_{2eq}))$$

where dln(fCO₂) is the difference between the natural logarithm of the fugacity at T_{eq} and SST, and T_{eq} is the equilibrator temperature in degrees C.

Sampling Cycle:

The system runs on an hourly cycle during which 3 standard gases, a reference gas and 20 surface water samples (from the equilibrator head space) are analyzed on the following schedule:

Mins. after hour =====	Sample =====
0:00	Low Standard
2:10	Mid Standard
4:25	High Standard
6:40	Reference
8:55	Water
11:28	Water
14:01	Water
16:34	Water
19:07	Water
21:40	Water
24:13	Water
26:46	Water
29:19	Water
31:52	Water
34:25	Water
36:58	Water
39:31	Water
42:04	Water
44:37	Water
47:10	Water
49:43	Water
52:16	Water
54:49	Water
57:22	Water

NOTES ON DATA:

Columns have a default value of -9 in case of instrument malfunction, erroneous readings or missing data. Furthermore, if a suspicious xCO₂ value, pressure or temperature value is encountered, the fCO₂ is not calculated.

Analytical Instrument Manufacturer/Model:

The Explorer of the Seas system was built by Dave Chipman in 2000. The analyzer is a LI-COR 6252 (analog output) infrared analyzer.

Standard Gases and Reference Gas: The three standard gases come from CMDL in Boulder and are directly traceable to the WMO scale. The reference gas is a non-calibrated gas from a commercial company. Any value outside the range of the standards (192 ppm, 426 ppm, and 514 ppm) should be considered approximate (5 ppm). While individual data points above 514 ppm or below 192 ppm may not be accurate, the general trends should be indicative of the seawater chemistry.

Description of any additional environmental control:

The system is located in the ocean laboratory of the Explorer of the Seas. The room is air-conditioned with little temperature fluctuation.

Resolution of measurement:

The resolution of the instrument is better than 0.1 ppm.

Estimated overall uncertainty of measurement:

The xCO₂eq measurements are believed accurate to 1 ppm. The fCO₂@SST measurements are believed to be precise to 2 ppm.

List of calibration gases used:

The standards used on the cruise are:

STANDARD	TANK #	CONCENTRATION	VENDOR
STD1	CA4563	192.34	CMDL
STD2	CA3253	426.92	CMDL
STD3	CA3758	514.24	CMDL

Traceability to an internationally recognized scale (including date/place of last calibration made):

All standards are obtained from NOAA/CMDL, now called the Global Monitoring Division of the Earth Research Laboratory and are directly traceable to WHO scale.

Uncertainty of assigned value of each calibration gas:

The uncertainty based on pre and post cruise calibrations is less than 0.05 ppm.

Pressure/Temperature/Salinity:

Thermosalinograph information can be found at <http://www.rsmas.miami.edu/rccl/facilities.html>.

Units:

All xCO₂ values are reported in parts per million (ppm) and fCO₂ values are reported in microatmospheres (uatm) assuming 100% humidity at the equilibrator temperature.

Bibliography:

- DOE (1994). Handbook of methods for the analysis of the various parameters of the carbon dioxide system in sea water; version 2. DOE.
- Feely, R. A., R. Wanninkhof, H. B. Milburn, C. E. Cosca, M. Stapp and P. P. Murphy (1998). A new automated underway system for making high precision pCO₂ measurements onboard research ships. *Analytica Chim. Acta* 377: 185-191.
- Ho, D. T., R. Wanninkhof, J. Masters, R. A. Feely and C. E. Cosca (1997). Measurement of underway fCO₂ in the Eastern Equatorial Pacific on NOAA ships BALDRIGE and DISCOVERER, NOAA data report ERL AOML-30, 52 pp., NTIS Springfield.
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- Weiss, R. F. (1974). Carbon dioxide in water and seawater: the solubility of a non-ideal gas. *Mar. Chem.* 2: 203-215.
- Weiss, R. F., R. A. Jahnke and C. D. Keeling (1982). Seasonal effects of temperature and salinity on the partial pressure of CO₂ in seawater.

Nature 300: 511-513.

Comments related to the individual legs:

Explorer of the Seas Naming Convention: EX04NNT where EX is the ship abbreviation, 04 is the year, NN is the number of the cruise which will be a number between 1 and 52, and T is the cruise track which will be either W for the west track or E for the east track.

For all legs, due to the slow response time of the system, the first 10 minutes of data for each hour for the entire leg was removed. This slow response time is not fully understood. On certain legs the response time was worse and up to 40 minutes of data was removed.

For all cruises, the first hour of data after leaving port is removed.

EX0401W: The system was down on 1/03/04 to 1/04/04 from 23:00 to 1:02. Merged missing Salinity, SST, Latitude and Longitude into the datafile.

EX0405W: Merged missing salinity, SST, latitude and longitude into the Datafile.

EX0407W: The water flow stopped at 12:03 on 2/18/04 to the end of the cruise.

EX0408E: Water meter broken. Merged water flow data from the VIDS Lab Feed Flow subdirectory into the data file before reducing the data.

Ex0409W: LI-COR was off from 2/28/04 (19:02) to 3/2/04 (16:02) - data was removed.

EX0411W: Incorrect voltages during the water phase on 3/14/2004 from 14:11 to 20:59 - data was removed.

EX0413W: The TSG data was missing - merged data from MicroTSG into datafile. Replaced all zeros with -9 in the Pres_sealevel_hPa field. Checked the BowWeatherPak directory and there was not data for JD 91.

EX0414E: The TSG data was missing - merged data from MicroTSG into datafile. On 4/06/04 the MicroTSG SST was about 2 degrees higher than the equilibrator temperature.

EX0415W: Water flow meter problems. Merged water flow from the VIDS Lab Feed Flow subdirectory into the data file before reducing the data. Voltage in the water phase was zero from 4/11/04 (22:08) to 4/12/04 (11:59) - changed these voltages to -9.

EX0416E: Missing salinity values on 4/17/04 from 16:02 to 22:16.

EX0419W: Missing water flow data, merged water flow from the VIDS Lab Feed Flow subdirectory into the data file. Questionable data was removed on 5/10/04 from 19:39 to 23:24. Questionable data was removed from on 5/10/04 to 5/11/04 from 1:36 to 10:40.

EX0423W: Questionable data was removed on 6/6/04 to 6/7/04 from 18:02 to 13:59. The equilibrator thermistor went bad. EQ_TEMP was calculated using a linear fit of EQ_TEMP - SST ($\text{EqTemp} = 0.8951 * \text{SST} + 2.45$) using the following six cruises: EX0417W, EX0418E, EX0419W, EX0420E, EX0421W, and EX0422E.

EX0424E: Due to the broken equilibrator thermistor, EQ_TEMP was calculated using a linear fit of EQ_TEMP - SST ($\text{EqTemp} = 0.8951 * \text{SST} + 2.45$) using the following six cruises: EX0417W, EX0418E, EX0419W, EX0420E, EX0421W and EX0422E. Problems with the gas flow, removed data from 6/19/04 (11:11) to 6/20/04 (9:08).

EX0425W: Due to the broken equilibrator thermistor, EQ_TEMP was calculated Using a linear fit of EQ_TEMP - SST ($\text{EqTemp} = 0.8951 * \text{SST} + 2.45$) using the following six cruises: EX0417W, EX0418E, EX0419W, EX0420E, EX0421W and EX0422E.

EX0426E: Due to the broken equilibrator thermistor, EQ_TEMP was calculated using a linear fit of EQ_TEMP - SST ($\text{EqTemp} = 0.8951 * \text{SST} + 2.45$) using the following six cruises: EX0417W, EX0418E, EX0419W, EX0420E, EX0421W and EX0422E. The system was down on 7/03/04 from 23:02 to 23:59. Replaced the zeros with -9 in the Pres_sealevel_hPa field; checked the BowWeatherPak data in the VIDs directory and there was not barometric pressure data for this cruise.

EX0427W: Due to the broken equilibrator thermistor, EQ_TEMP was calculated using a linear fit of EQ_TEMP - SST ($\text{EqTemp} = 0.8951 * \text{SST} + 2.45$) using the following six cruises: EX0417W, EX0418E, EX0419W, EX0420E, EX0421W and EX0422E.

EX0428E: Due to the broken equilibrator thermistor, EQ_TEMP was calculated using a linear fit of EQ_TEMP - SST ($\text{EqTemp} = 0.8951 * \text{SST} + 2.45$) using the following six cruises: EX0417W, EX0418E, EX0419W, EX0420E, EX0421W and EX0422E.

EX0429W: Due to the broken equilibrator thermistor, EQ_TEMP was calculated using a linear fit of EQ_TEMP - SST ($\text{EqTemp} = 0.8951 * \text{SST} + 2.45$) using the following six cruises: EX0417W, EX0418E, EX0419W, EX0420E, EX0421W and EX0422E.

EX0430E: Due to the broken equilibrator thermistor, EQ_TEMP was calculated using a linear fit of EQ_TEMP - SST ($\text{EqTemp} = 0.8951 * \text{SST} + 2.45$) using the following six cruises: EX0417W, EX0418E, EX0419W, EX0420E, EX0421W and EX0422E.

EX0431W: Due to the broken equilibrator thermistor, EQ_TEMP was calculated using a linear fit of EQ_TEMP - SST ($\text{EqTemp} = 0.8951 * \text{SST} + 2.45$) using the following six cruises: EX0417W, EX0418E, EX0419W, EX0420E, EX0421W and EX0422E.

EX0432E: Due to the broken equilibrator thermistor, EQ_TEMP was calculated using a linear fit of EQ_TEMP - SST ($\text{EqTemp} = 0.8951 * \text{SST} + 2.45$) using the following six cruises: EX0417W, EX0418E, EX0419W, EX0420E, EX0421W and EX0422E.

EX0433W: Due to the broken equilibrator thermistor, EQ_TEMP was calculated using a linear fit of EQ_TEMP - SST ($\text{EqTemp} = 0.8951 * \text{SST} + 2.45$) using the following six cruises: EX0417W, EX0418E, EX0419W, EX0420E, EX0421W and EX0422E. Gas flow problems from 8/21/04 to 8/22/04 - questionable data removed.

EX0434E: Due to the broken equilibrator thermistor, EQ_TEMP was calculated using a linear fit of EQ_TEMP - SST ($\text{EqTemp} = 0.8951 * \text{SST} + 2.45$) using the following six cruises: EX0417W, EX0418E, EX0419W, EX0420E, EX0421W and EX0422E.

EX0435W: Due to the broken equilibrator thermistor, EQ_TEMP was calculated using a linear fit of EQ_TEMP - SST ($\text{EqTemp} = 0.8951 * \text{SST} + 2.45$) using the

following six cruises: EX0417W, EX0418E, EX0419W, EX0420E, EX0421W and EX0422E.

EX0436E: The broken equilibrator thermistor was replaced.

EX0438E: Questionable data removed from 9/24/04 (22:24) to 9/27/04 (7:52). No water flow data - merged water flow from the VIDS Lab Feed Flow subdirectory into the data file. There is also low flow from the shower head.

EX0440E: Air Temperature not available for this cruise. There was a plumbing problem during the beginning of the cruise. When the system came back on line, there was no flow coming from the shower head; the 3-way valve for the seawater connection was clogged. Once the valve was cleaned and reconnected, flow returned from the shower head and data acquisition resumed.

EX0441W: Due to a system leak, the following data was removed: 10/11/04 from 19:47 to 22:16, 10/15/04 from 14:47 to 16:11, and 10/15/04 from 19:49 to 22:59.

EX0442E: Due to a leak in the system, the following data was removed: 10/20/04 from 1:54 to 5:16 and 10/21/04 from 22:11 to 23:59.

EX0443W: Problems with the barometric pressure sensor. Replaced all zeros and bad data (very low values) with -9 in Pres_sealevel_hPa.

EX0444E: Due to a leak in the system, the following data was removed: 11/03/04 from 1:26 to 4:21 and 11/04/04 to 11/05/04 from 22:11 to 00:31.

EX0446E: Due to a water flow problem, the following data was removed: 11/17/04 from 4:24 to 7:36 and 11/18/04 to 11/19/04 from 23:36 to 1:36.

EX0447W: Low gas flow during the water phase; Chip readjusted the gas flow.

EX0448E: Gas flow problems in the water phase - removed the data from 11/29/04 (4:21) to 12/1/04 (23:59).

EX0449W: Gas flow problems in the water phase - removed the data from 12/09/04 (0:02) to 12/11/04 (1:59).

EX0450E: Air temperature data was not available for this cruise. Leak in system, removed data from 12/13/04 (0:11) to 12/14/04 (16:59) - there was an air leak coming out on the side of the fridge where the tubing is connected. Don stopped data collection and pushed the tubing further up the port and anchored it with two tie-wraps.

