

HOT_surface_CO2_readme.pdf

This readme file contains explanatory material, metadata, and notes regarding the Hawaii Ocean Time-series surface CO₂ system data product, HOT_surface_CO2.txt. Both files may be found on the HOT website at: <https://hahana.soest.hawaii.edu/hot/hotco2/hotco2.html>

Created 5 October 2009 by J.E. Dore.

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When using this data product please cite as adapted from:

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Please direct questions or comments regarding this data product to John Dore:

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Background Information:

All data in this product are from Station ALOHA (22°45'N, 158°00'W). HOT program background information and details of sampling strategy may be found in Karl and Lukas (1996) and Karl et al. (2001). Results from the HOT CO₂ measurement program may be found in Winn et al. (1994, 1998) and Dore et al. (2003, 2009, 2014).

The data in this product represent mean surface (0-30 dbar) values for each HOT cruise except where otherwise indicated.

Temperature and salinity data are from a calibrated Seabird CTD (Lukas and Santiago-Mandujano 1996); the individual values to be averaged were determined during the upcast at the time of the bottle trip except where otherwise noted. All seawater samples were collected using a rosette package lowered on a conducting hydrowire except as otherwise noted. Phosphate and silicate were measured colorimetrically via autoanalyzer using standard HOT methodology (Karl and Lukas 1996; Dore et al. 1996). Phosphate and silicate were assumed to be 0.07 and 1.04 $\mu\text{mol kg}^{-1}$ (approximate mean values), respectively, where data were not available.

Dissolved inorganic carbon (DIC; equivalent to total CO₂) and total alkalinity (TA) were measured by coulometry and open cell acid titration, respectively. Since 1993, a semi-automated SOMMA system (Johnson and Wallace 1992) was used for the coulometric DIC measurements. Certified seawater CO₂ reference materials (Dickson 2001) were used to validate DIC and TA

calibrations. The spectrophotometric *m*-cresol purple method was used for direct pH measurements at 25 °C (Clayton & Byrne 1993). The reagent grade dye was sourced commercially and NOT further purified. It has been suggested that the absolute calibration of the *m*-cresol purple pH method may be slightly biased such that a +0.0047 correction to measured pH values is necessary (DeValls & Dickson 1998); we did NOT apply this correction factor to our pH measurements. All pH measurements since 2003 have been made with the same lot of dye (Aldrich Chemicals product# 21176-1, Lot# 01920CX). We have determined the value of ${}_{434}A_{\text{imp}}$ according to Douglas and Byrne (2017) to be 0.003253 but have NOT applied a dye impurity correction to these data.

Sampling, sample storage and analytical protocols for all CO₂ system measurements followed internationally accepted recommendations (Dickson et al. 2007) with only minor modifications. Salinity-normalized values for DIC and TA were calculated as: $n\text{DIC} = 35 * \text{DIC} / \text{salinity}$ and $n\text{TA} = 35 * \text{TA} / \text{salinity}$. CO₂ system calculations were carried out with the CO2SYS software (Excel version 2.1; Pierrot et al 2006), using the Mehrbach et al. (1973) formulations of the apparent dissociation constants of H₂CO₃ in seawater, as refit by Dickson and Millero (1987), and the total boron formulation of Uppström (1974). For all calculations made at in situ conditions a pressure of 10 dbar was assumed. Calcium carbonate saturation state is calculated as (Pierrot et al. 2006): $\Omega = [\text{CO}_3^{2-}] * [\text{Ca}^{2+}] / K_{\text{sp}}$ where the calcium ion concentration is estimated from salinity and K_{sp} is the solubility product for the given carbonate mineral (aragonite or calcite).

A few missing DIC and TA data points during the early years of the time-series have been filled with values from C. D. Keeling's parallel Station ALOHA CO₂ measurement program (Keeling and Guenther 1994; Keeling et al. 2004), as described in Dore et al. (2003, 2009) and noted in the data product file. The HOT and Keeling measurements have been carefully intercompared (Dore et al. 2001). The Keeling dataset (through November 2002) may be found at: <http://cdiac.ess-dive.lbl.gov/ftp/oceans/keeling.data/HAWI.txt>

Data columns:

HOT_surface_CO2.txt is a tab-delimited text file with 22 data columns. Missing data points are indicated by -999. The columns are arranged as follows:

cruise

The integer number of the HOT cruise.

days

The mid-day of the cruise expressed as the number of days from 1 October 1988.

date

The mid-day of the cruise expressed as a calendar date.

temp

The mean in situ seawater temperature, in °C.

sal

The mean seawater salinity, in practical salinity units.

phos

The mean seawater phosphate concentration, in $\mu\text{mol kg}^{-1}$.

sil

The mean seawater silicate concentration, in $\mu\text{mol kg}^{-1}$.

DIC

The mean seawater dissolved inorganic carbon (= total CO_2) concentration, in $\mu\text{mol kg}^{-1}$.

TA

The mean seawater total alkalinity, in $\mu\text{eq kg}^{-1}$.

nDIC

The mean seawater salinity-normalized DIC, in $\mu\text{mol kg}^{-1}$ at salinity = 35.

nTA

The mean seawater salinity-normalized TA, in $\mu\text{eq kg}^{-1}$ at salinity = 35.

pHmeas_25C

The mean measured seawater pH at 25 °C, on the total scale.

pHmeas_insitu

The mean measured seawater pH, adjusted to in situ temperature, on the total scale.

pHcalc_25C

The mean seawater pH, calculated from DIC and TA at 25 °C, on the total scale.

pHcalc_insitu

The mean seawater pH, calculated from DIC and TA at in situ temperature, on the total scale.

pCO2calc_insitu

The mean seawater CO₂ partial pressure, in μatm , calculated from DIC and TA at in situ temperature.

pCO₂calc_20C

The mean seawater CO₂ partial pressure, in μatm , calculated from DIC and TA at 20 °C.

aragsatcalc_insitu

The mean seawater aragonite saturation state (solubility ratio).

calcsatcalc_insitu

The mean seawater calcite saturation state (solubility ratio).

freeCO₂_insitu

The mean seawater free CO₂ concentration, in $\mu\text{mol kg}^{-1}$.

carbonate_insitu

The mean seawater carbonate ion concentration, in $\mu\text{mol kg}^{-1}$.

notes

This column contains pertinent notes about the data used, especially where sampling was different from the HOT standard procedures. The following codes are used to indicate such variations:

- a No HOT DIC data; used Keeling DIC
- b No HOT TA data; used Keeling TA
- c No pH samples collected
- d No TA data; assumed nTA of 2303.2
- e No DIC data in upper 30 dbar; used value from 34.0 dbar
- f No TA data in upper 30 dbar; used value from 51.3 dbar
- g Used temp and sal data from downcast before cable broke
- h No phos data; assumed 0.07
- i No sil data; assumed 1.04
- j Rosette lost; samples collected with Go-flo bottle on Kevlar line
- k No sampling occurred
- l No rosette; samples collected with Niskin bottles on Kevlar line
- m No DIC or TA data in upper 30 dbar; used values from 34.9 dbar
- n No DIC or TA data in upper 30 dbar; used values from 44.9 dbar
- o No DIC, TA or pH sampling occurred in upper 200 dbar
- p No DIC, TA or pH sampling occurred
- q 10-30 dbar averages used due to transient influence of heavy rainfall on 5 dbar sample

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