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ACCSP Heron Island - Wistari CO2 mooring

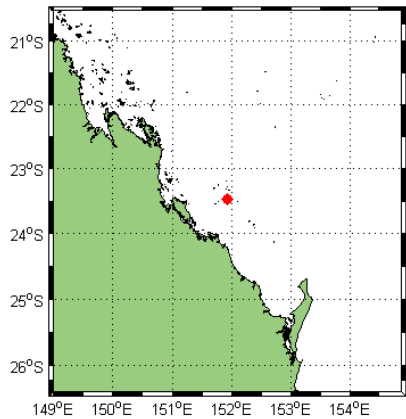
Dataset:

IMOS_ANMN-AM_GST_20231011T060000Z_GBRWIS_FV01_GBRWIS-CO2-2310-delayed_END_20240403T220000Z_C-20240909T125358Z.nc

Deployment information

Location:

Heron Island - Wistari Channel, Queensland;-23.4585,151.9268



Water Depth:

16m

Platform:

IMOS_ANMN-AM_CO2_GST

Platform code:

GBRWIS

Deployment code:

GBRWIS_27

Expocode:

09F520231011

Start date

20231011T060000Z

End date

20240403T220000Z

Mooring Bounds: North West South East

-23.45876 -23.45828 151.9265 151.9271

Data history

Data report submission:

2024-09-11

Most recent report update:

09-09-2024

Investigators:

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Mooring deployment

Deployed

2023/10/11 00:30

Recovered

2024/04/04 01:00

Vessel

Heron Island Mooring

Moored sensors:

Battelle MApCO2 s/n

0192

Seabird SBE 16pus_V2 s/n

01606551

Aanderaa Optode s/n

1614

Field personel

Erik van Ooijen, Gary Curtis, Rick Cuthbertson

Instrumentation

Erik van Ooijen

Quality control

Erik van Ooijen

Data file description:

Variable [Unit] Description =====

TIME [YYYY-MM-DDThh:mm:ssZ] Time and Date, ISO8601

LATITUDE [deg] Latitude

LONGITUDE [deg] Longitude

XCO2_DRY_SW [umol/mol] Mole fraction of CO2 in the equilibrator head space

XCO2_DRY_AIR [umol/mol] Mole fraction of CO2 in the atmosphere

fCO2_WET_SW [uatm] Fugacity of carbon dioxide at surface water, corrected for water vapour at surface water salinity and temperature

dFCO2 [uatm] Delta fCO2 = (fCO2_WET_SW - fCO2_WET_AIR)

ATMOSPHERIC PRESSURE [kPa] Atmospheric pressure

EQUILIBRATOR PRESSURE [kPa] Equilibrator pressure

SEA SURFACE TEMPERATURE [degC] Sea surface temperature

EQUILIBRATOR TEMPERATURE [degC] Equilibrator temperature

SALINITY [PSS] *Sea surface salinity*

DISSOLVED_OXYGEN [μmol/l] *Concentration O₂ in surface sea water*

WOCE QC flag 2=good, 3=questionable, 4=bad

SUB_FLAG 24-bit number, internal QC

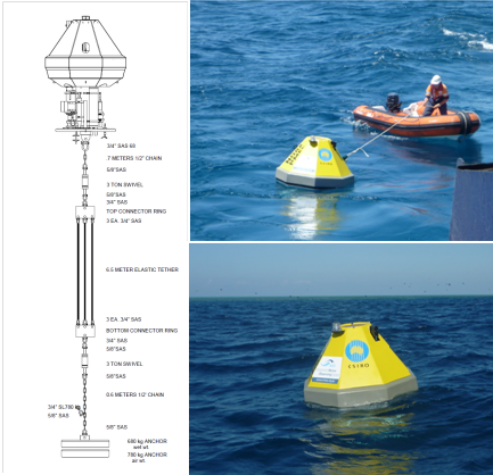
PH Total pH surface water

General system description and procedures

Instrumentation and methods

Measurements are made with a Battelle Seaology pCO₂ monitoring system (MApCO₂), a Seabird SBE16plusV2 CTD, mounted on a surface buoy similar to the system described in Sutton et al. (2014), with an Aanderaa optode used to measure dissolved oxygen concentrations. The seawater sensor intakes for the MapCO₂, SBE16Plus V2 and the optode are located at about 1m water depth. The CO₂ measurement uses a bubble equilibrator (Sutton et al., 2014), where the air from the equilibrator headspace is circulated through a LI-COR 820 non-dispersive infrared detector (NDIR) for measurement of CO₂. The system carries out an automated measurement sequence every 2 or 3 hours, depending on the instrumentation setup. At the beginning of each measurement sequence, the NDIR undergoes a two point calibration with a zero CO₂ gas and a high CO₂ standard span gas (typically 450-550 micromol/mol), which bracket the range of CO₂ mole fractions in seawater and air. The zero CO₂ gas is generated by cycling air through a soda lime chamber and silica gel to remove CO₂ and water vapour, respectively. The CO₂ span gas is prepared by the NOAA Earth Systems Research Laboratory in the USA and calibrated on the WMO X2007 scale with a standard deviation of 0.06 micromol/mol (<http://www.esrl.noaa.gov/gmd/cc/airstandard.html>). Each measurement cycle of zero and span gas, equilibrator headspace, and air takes 20 minutes with the equilibrator headspace measurement occurring at about 17 minutes followed by the air measurement. The pressure measurements are considered the same for the equilibrator headspace gas and air measurements due to the design of the MapCO₂ system (Sutton et al., 2014) as are the temperature and salinity of the surface seawater and the equilibrator measured by the Seabird SBE16PlusV2.

Location and mooring design



The Heron Island Wistari mooring is located on the east side of Heron Island in the Wistari Channel in about 16m water depth. A 700kg anchor holds the mooring buoy in position, which is connected to the surface buoy via a 16.5m bungee used to dampen wave action. As part of regular maintenance and to minimise the effects of biofouling, the mooring is recovered every six months, the mooring line checked and replaced if necessary, and a replacement surface buoy and newly calibrated sensors swapped in.

Testing and calibration procedures

The LI-COR 820 sensor response is checked before and after each deployment using a range of CO₂-in-air reference gases (0, 260, 370, 450 micromol/mol) at CSIRO, Hobart. The sensor measurement using factory calibrations for the LI-CO₂ 820 is typically within 1 micromol/mol of the reference gas value. If the LI-COR 820 measurements and the CO₂-in-air reference gas values are different by more than 2 micromol/mol, a correction is applied to LI-CO₂ 820 output based the reference gas values. A seawater bath operated over a range of temperatures and CO₂ expected in the field is then used to check the MapCO₂ system (equilibrator and LI-COR 820 measurement) against a General Oceanics 8050 CO₂ sensor to ensure the systems agree within 2 micromol/mol. Pressure measurements are made using the LI-COR 820 pressure sensor, checked against a Druck DPI142 pressure indicator and verified to agree within 0.5 kPa before and after each deployment. The air CO₂ values are compared to Globalview CO₂ products, although these can result in some variability due to limited data in Globalview to constrain atmospheric boundary layer CO₂ measurements in coastal regions of the Southern Hemisphere.

A SBE16plus V2 CTD is polled for the temperature, salinity, and dissolved oxygen data for each MapCO₂ measurement sequence, with additional measurements made each hour. The SBE16PlusV2 temperature and salinity measurements use either factory calibrations for initial deployments, or annual calibrations performed at a certified National Australian Testing Authority facility at CSIRO, Hobart. The optodes are calibrated before and after deployments at CSIRO, Hobart, using a purpose built calibration system, referenced to dissolved oxygen measurements made using modified Winkler titrations (Culbertson, 1991). The calibrations cover a range of temperatures and oxygen concentrations that occur in the field and new calibration coefficients are generated to fit a Stern-Volmer equation (Uchida et al., 2008).

The DuraFET-based SeapHet sensor (Satlantic or Scripps design, Martz et al., 2010) obtains a sample hourly. The sensor uses a single pair of bottle samples for DIC and Alkalinity taken on site for calibration, where CO₂SYs is used for the calculation of pH (see next section).

Data reduction and quality control

Fugacity

After recovery of the instrument the data from the MapCO₂ and the SBE16plus is downloaded. The data are recorded at each 2 or 3 hourly measurement interval as blocks of measurements of equilibrator headspace gas, air, zero and span gas values. The data blocks are checked for size and the MApCO₂ data is checked for outliers and corrected using the Thomson Tau method (Thompson, 1985).

The NDIR detection is based on the absorption of infrared light by CO₂. For each measurement cycle, the zero and span gas are analysed immediately before equilibrator air or atmospheric gas measurements to calibrate the LI-COR 820 NDIR response and provide a measurement of the CO₂ mole fraction in the gas stream. The gas stream analysed by the NDIR is only partially dried by flowing the gas through silica gel and the same light absorbed by CO₂ is also absorbed by water vapour present in the gas. A dilution correction is applied to account for the presence of water vapour that is measured in the gas using a humidity sensor (LI-COR Application note 129):

$$xCO_2 = \frac{xCO_2^{raw}}{(1 - w/1000)}$$

where w is calculated water vapour mole fraction and xCO₂raw is the raw data value for the CO₂ mole fraction measured in the gas stream by the LI-COR 820 NDIR.

The partial pressure of CO₂ in the water is calculated by applying a water vapour pressure correction:

$$pCO_2 = xCO_2(P - p[H_2O])$$

with,

$$p[H_2O] = \exp 24.4543 - 67.4509 \frac{100}{T} - 4.8489 \ln \frac{T}{100} - 0.000544S$$

the calculated water vapour pressure of the equilibrator sample at the sea surface temperature, *T* (K), and Salinity, *S* (Weiss and Price, 1980) and *P* is the total pressure in atmospheres.

The partial pressure of CO₂ is converted to fugacity using (Weiss, 1974):

$$fCO_2 = pCO_2 \exp \frac{P(B(CO_2, T) + 2\delta(CO_2, T))}{RT}$$

where, $R = 82.0578 \text{ cm}^3 \text{ mol}^{-1} \text{ K}^{-1}$, $B(\text{CO}_2, T) = -1636.75 + 12.0408T - 3.27957 \cdot 10^{-2}T^2 + 3.16528 \cdot 10^{-5}T^3$ and, $\delta(\text{CO}_2, T) = 57.7 - 0.118T$

Dissolved oxygen

Two voltage signal (V0 and V1) related to the bphase (Bp) and the temperature (Topt, in degrees Celsius) by:

$Bp = 12V0 + 10; Topt = 9V1 - 5$

from the Aanderaa optode are measured and stored by the SBE16plus. From these values a pre- and post-calibrated dissolved oxygen values (DOraw) are calculated using the Stern-Volmer equation (Uchida et al., 2008), and the corresponding pre- and post- calibration coefficients (Appendix 3);

$DO_{raw} = \frac{(c4 + c5Topt)/(c6 + c7Bp) - 1}{c1 + c2Topt + c3Topt^2}$

This value for dissolved oxygen applies to use in fresh water and therefore needs to be compensated for seawater salinity using:

$DO_{sc} = DO_{raw} \exp S(B0 + B1T_S + B2T_S^2 + B3T_S^3) + C0S^2$

With S the salinity obtained by the SBE16plus and

$T_S = \ln \frac{298.15 - T}{273.15 + T}$

With T the temperature obtained in Celsius by the SBE16plus, and B0 = -6.24097e-3, B1 = -6.93498e-3, B2 = -6.90358e-3, B3 = -4.29155e-3, C0 = -3.11680e-7.

Subsequently, a drift correction is calculated and applied from the calibration data for each of the pre- and post-calibrated and salinity compensated values. From these values an average value for the dissolved oxygen (DO) and a standard deviation (SD_DO) is obtained, which is interpolated at the time when the MAPCO2 equilibrator pump off cycle ends.

pH

The raw pH voltage data obtained by the instrument for both the internal as external reference pH values are calibrated using a single DIC and Total Alkalinity sample pair obtained at the site when the sensor is taking a sample. The pH on the total scale (pHt) at in-situ temperature and salinity is calculated using DIC and total alkalinity with CO2SYS (Van Heuven et. al. 2011), using the Lueker et al (2000) K1/K2 dissociation constants, bisulfate (HSO4-) dissociation constant of Dickson (1990), the hydrofluoric acid dissociation constant of Perez and Fraga (1987) and the boron-salinity ratio of Uppstrom (1979). The maximum total phosphate and silicate concentrations measured at the Maria Island site of 0.5 and 1.8 micromol/kg, respectively, cause less than a 0.001 reduction in pHt and are assumed zero for the calculation. The calculated pH value is then used to calibrate the linear response of pH vs the raw voltages and calculated for both internal and external references, where the internal reference pH values are published. The external pH values are used as a QC test for the internal pH data. More details can be found in P.J. Bresnahan et. al. (2014) and T. Martz et. al (2010)

Data report

Automated data quality control report:

For first order quality control, automated checking of value ranges for a number of diagnostic parameters are checked, and subflags assigned to values outside the accepted ranges listed in Appendix 2. The summary results of the automated data checking procedure were:

Flagged data points:

No issues

Delayed mode quality control report:

After automated checking, data are plotted and manually checked in a final delayed mode quality control with WOCE (<http://cchdo.ucsd.edu/formats>) quality flags used, where 2=good, 3=questionable, 4=bad, with the following result:

Reason: Possible drift in D0 due to fouling-> Action: Manually set to questionable:
2024/02/27,02:00:00-2024/03/02,04:00:00
2024/03/02,08:00:00-2024/04/03,22:00:00
Manual set to bad data
Reason:Low Battery pH sensor due to faulty D0 sensor
11-Dec-2023 22:00:00-03-Apr-2024 22:00:00

Low salinity values are verified using NRS data at MAI site (<http://www.csiro.au/tasman/nrsweb/>) and BOM flood history data (http://www.bom.gov.au/tas/flood/flood_history/flood_history.shtml).

Final data quality summary:

Parameter	% flag = 2 good	Number Points
fCO2 sea water	100.000000	2109
XC02 atmosphere	100.000000	2109
Sea Surface Temperature	100.000000	2109
Sea Surface Salinity	100.000000	2109
Dissolved Oxygen	79.042200	1667
Total pH	35.087719	740

Data summary:

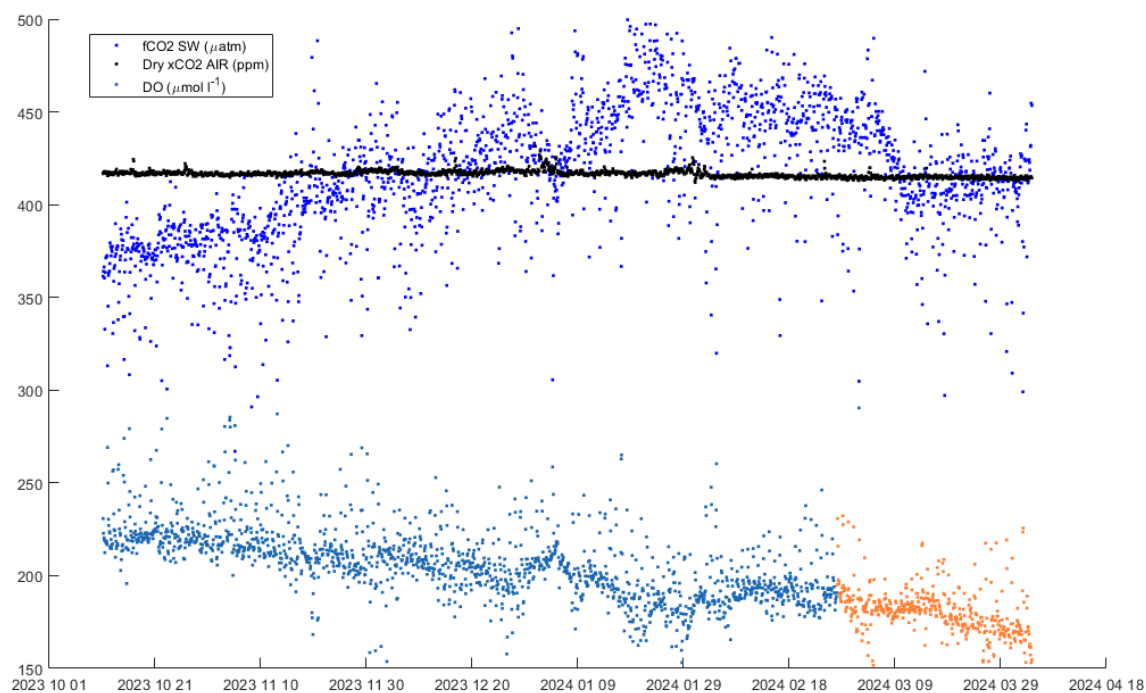


Figure 1: xCO₂ (ppm) for air, fCO₂ (µatm) and Dissolved Oxygen (DO; µmol/l) for sea water. The red and orange data points represent bad (flag =4) and questionable (flag = 3) data, respectively.

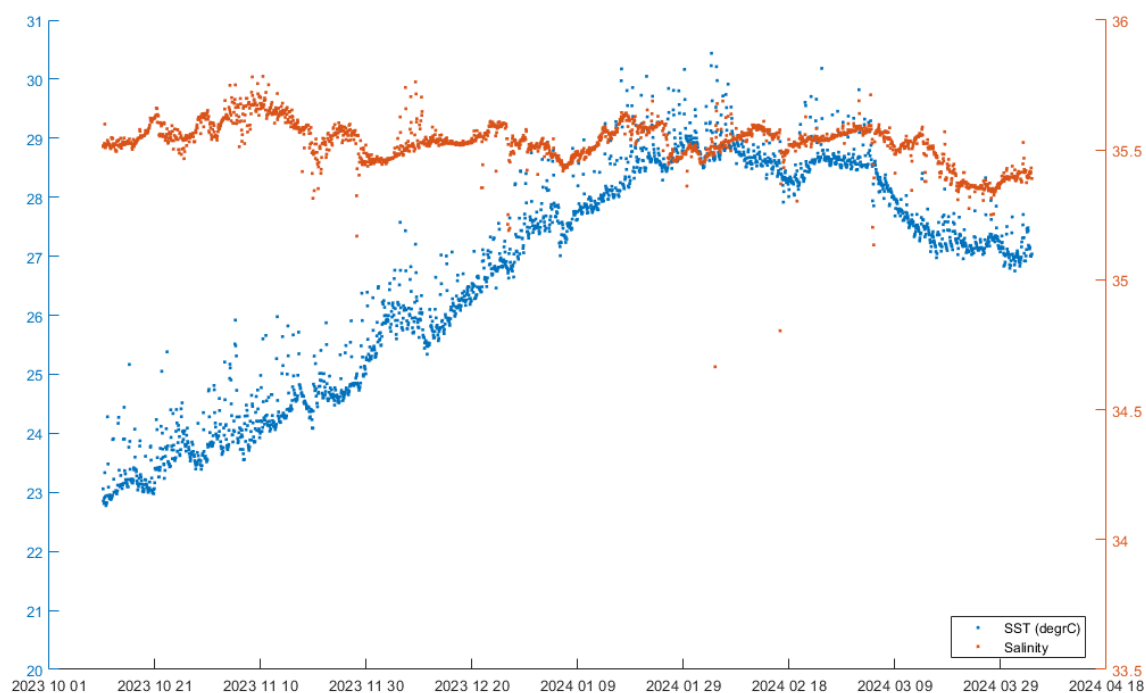


Figure 2: Sea Surface Temperature and Salinity. The red and orange data points represent bad (flag =4) and questionable (flag = 3) data, respectively.

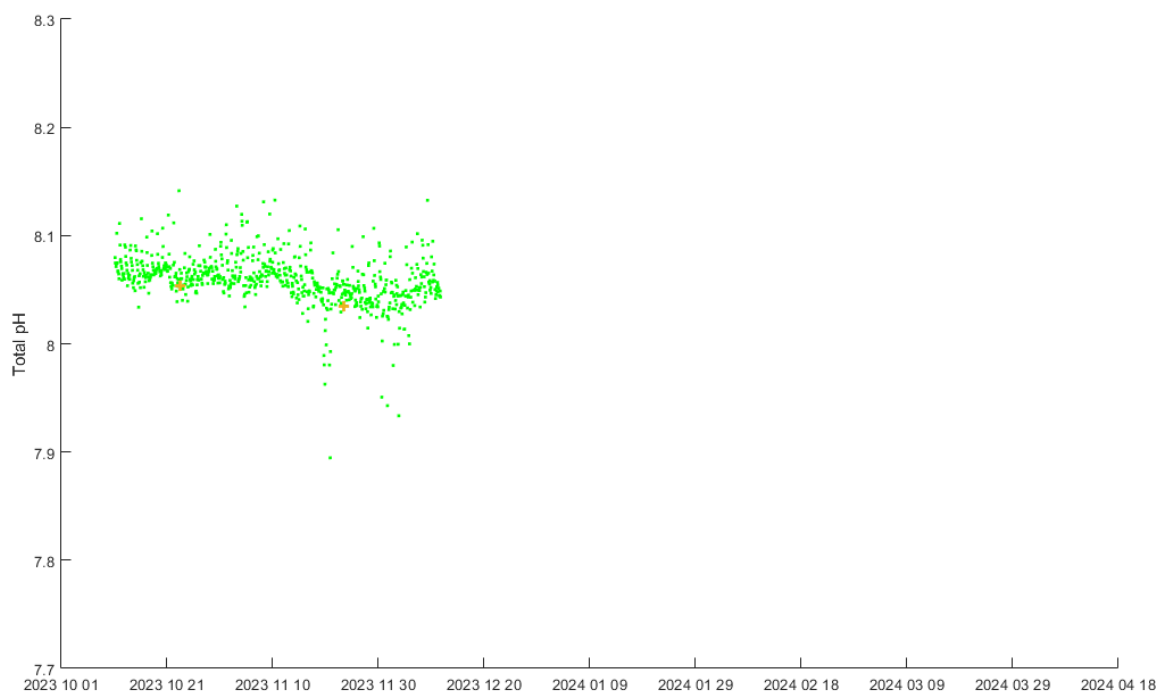


Figure 3: Total pH SeapHox. Bottle samples are indicated in blue.

Appendix 1: Instrumentation specifications

Seaology pCO2

MANUFACTURER: Battelle Memorial Institute, Columbus, Ohio, USA
 WEBSITE: <http://battelle.org/our-work/national-security/maritime-systems>
 MODEL: Seaology
 SERIAL NO: 0192
 FIRMWARE VERSION: 3.18
 EQUILIBRATOR DESIGN: Bubble Equilibrator
 EQUILIBRATOR VOLUME: Less than 100 ml of air equilibrating with an unlimited volume of seawater
 HEADSPACE GAS FLOW RATE: ~600 cc/min
 VENTED: yes
 INTAKE DEPTH: 1m
 MEASUREMENT METHOD: Absolute, non-dispersive infrared (NDIR) gas analyser

CO2 and Equilibrator and Air Pressure Sensor:

MANUFACTURER: LI-COR, Lincoln, Nebraska, USA
 WEBSITE: <http://www.licor.com/env/>
 MODEL: LI-820
 CO2 RESOLUTION: 0.1 $\mu\text{mol/mol}$
 CO2 UNCERTAINTY: < 2 $\mu\text{mol/mol}$ based on comparisons in the laboratory before and after deployment with four WMO X2007 referenced gas standards (0, 260, 370, 450 $\mu\text{mol/mol}$) and < 2 $\mu\text{mol/mol}$ based on pre-deployment comparison in the laboratory with equilibrator headspace measurements of seawater made using a General Oceanics model 8050 pCO2 measurement system (General Oceanics, Miami, Florida, USA).
 PRESSURE RESOLUTION: 0.01 KPa
 PRESSURE UNCERTAINTY: < 0.5 KPa, Based on laboratory comparison against Druck DPI 142 pressure indicator
 CALIBRATION DATE: 2023/04/11

Relative Humidity Sensor:

MANUFACTURER: Sensirion Humidity Sensor, USA
 WEBSITE: <http://www.sensirion.com>
 MODEL: SHT71
 MEASUREMENT RANGE: 0–100%
 ACCURACY: +/- 3% (20–80% RH)
 CALIBRATION: Factory calibration before purchase
 RH CORRECTION: yes

CO2 Span Gas:

MANUFACTURER: NOAA Earth Systems Laboratory, USA
 CYLINDER NUMBER: JB03777
 GAS CYLINDER PRESSURE, PRE-DEPLOYMENT: 1900 psi
 GAS CYLINDER PRESSURE, POST-DEPLOYMENT: 1500 psi
 CO2-IN-AIR CONCENTRATION (WMO X2007): 502.85 PPM
 CALIBRATION DATE: 2021/06/15

O2 Sensor:

MANUFACTURER: Aanderaa, Norway
 WEBSITE: <http://www.aanderaa.com/>
 MODEL:
 SERIAL NO: 1614