Supplementary documents for:

High emissions of carbon dioxide and methane from the coastal Baltic Sea at the end of a summer heat wave

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Method description of Water Equilibration Gas Analyzer System (WEGAS)

Description of the system

The partial pressures of atmospheric and dissolved CO_2 and CH_4 are continuously measured using the Water Equilibration Gas Analyzer System (WEGAS) and cavity ring-down spectrometer (CRDS). This system consists of three major components (Fig. S1):

i) a water handling system comprised of a "Weiss-type" equilibrator (1 L headspace), a pH meter by Sunburst AFT-pH and a thermosalinograph by Seabird TSG 45, all of which are connected through water hoses. The water flow is dialed at ~4.5 L/min by the water pressure controller and passes through the thermosalinograph followed by the pH meter, and thereafter is pressed into the equilibrator. Waterflow and temperature inside the equilibrator are monitored by a flow meter and a thermocouple. To achieve a stable and optimal equilibration, the seawater flows continuously into the equilibrator with two nozzles that maximize the exchange surface between headspace and water by creating a spray of fine droplets, as long as WEGAS is running.

ii) the second component is a gas handling system with circulation pumps for headspace and ambient air from the bow of the ship. The gas stripped into the headspace of the equilibrator in the water handling system is first drawn into a Peltier gas cooler (PKE5, Buehler, Germany) to a dew point of 4 ^{o}C to minimize the risk of corrosion and salt deposition in the gas handling system before it makes its way into CRDS. The gas circulation in the gas handling system and ambient pressure in the headspace is maintained by a metal bellow pump

(MB21, Senior Aerospace Metal Bellows, Sharon, MA) at a flow of 250 ml/min. Due to the loss of the exhaust flow of CRDS, the vent flow of ambient air from a defined location (e.g. stern of the ship to avoid contamination of stack gas from the ship) continuously drawn into the headspace is also monitored by the mass flow controller (MFC, 1179A Mass-Flo, MKS Instruments, Andover, MA). This means that the vent flow rate is equal to the exhaust flow of the CRDS, which is roughly 10% of the normal gas flow of 250 ml/min. To correct this contamination with ambient air in the headspace, a second pump is used to establish a continuous stream of ambient air, in which the CO_2 and CH_4 concentrations is regularly measured by CRDS. This is conducted by continuously switching the gas source between ambient air and headspace measurements. This switching is realized by 3-way solenoid valves (Parker 3-Way valve, Series 9) and performed automatically by the datalogger.

iii) CRDS gas analyzers for CO_2 and CH_4 concentrations (model G2131-i, Picarro Inc. Sunnyvale, CA), it offers a cost-effective and reliable way for monitoring CO_2 and CH_4 concentrations and also has the capability of measuring the concentration of CH_4 and H_2O to compensate for spectroscopic inter-species cross-influence. The analyzer used in this study has an guaranteed specific range of 380 - 2000 ppm and 0 - 500 ppm for CO_2 and CH_4, respectively, which is provided by the manufacturer, and the concentration precision (1σ, 30 s average) is 200 ppb (+ 0.05% of reading) for CO_2 and 50 ppb (+ 0.05% of reading) for CH_4.

The communications and data recording of the three components above are realized by the datalogger (CR1000 Campbell Sci.) connected to a Master PC using a local area network (LAN) established by a router (DLINK). The Master PC records all the data including measurement time, water flow rate, temperature salinity, results from CRDS etc. There is also a graphical user interface (GUI) that allows to monitor the real-time state of the system. In addition, a manual mode is also available to manually control all valves and start/stop the data recording. The CRDS can also be directly accessed from the Master PC using a remote desktop connection.

Gas analyses and data processing

For the CO_2 and CH_4 analysis routine ambient air is measured for 8 minutes followed by the gas in the headspace of the equilibrator for 12 minutes. Hence, one complete analysis cycle is

20 minutes and cycles are performed continuously during the cruise including the station time when Electra is not steaming.

In this study, this analysis routine generated large amount of real-time data that have to be post-processed before any data interpretation. First, the recorded data were filtered by removing data taken during improper functioning of WEGAS (e.g. low water flow, exceptional values due to air contamination by the ship). Second, the transition period between ambient air and water measurements had to be excluded due to the response time of CRDS to sharp changes in concentrations of CO_2 and CH_4. The CO_2 concentrations varied from ~400 ppm in the ambient air to ~1600 ppm in water, while CH_4 ranged from 1.9 ppm up to 42 ppm. Equilibria were observed to be achieved sufficiently within 2 minutes during transitions from one measurement mode to another (Fig. S2). It should be noted that the headspace of the equilibrator may also experience the transition period due to the variation of dissolved CO_2 and CH_4 concentrations in the water column, but this is considered to be negligible in this study because 1) no drastic concentration changes were expected or observed during our cruise given the short 12-minute water measurement and the normal travelling speed of Electra (less than 2 m/s), 2) the response time of the equilibrator for handling small concentration changes were fast and normally less than 1 minute, which was well covered by the response time of CRDS. Third, the remaining data were corrected for the vent flow that is induced into the headspace of the equilibrator using the simultaneously measured ambient air data and vent flow rate. In addition, any remaining data with atmospheric CO_2 concentrations above 450 ppm were also removed. After filtering, atmospheric CO_2 averaged 401.3±2.08 ppm (2σ). As a result of the post-processing, this study presents 15 733 data points for both ambient air and water concentrations of CO_2 and CH_4.

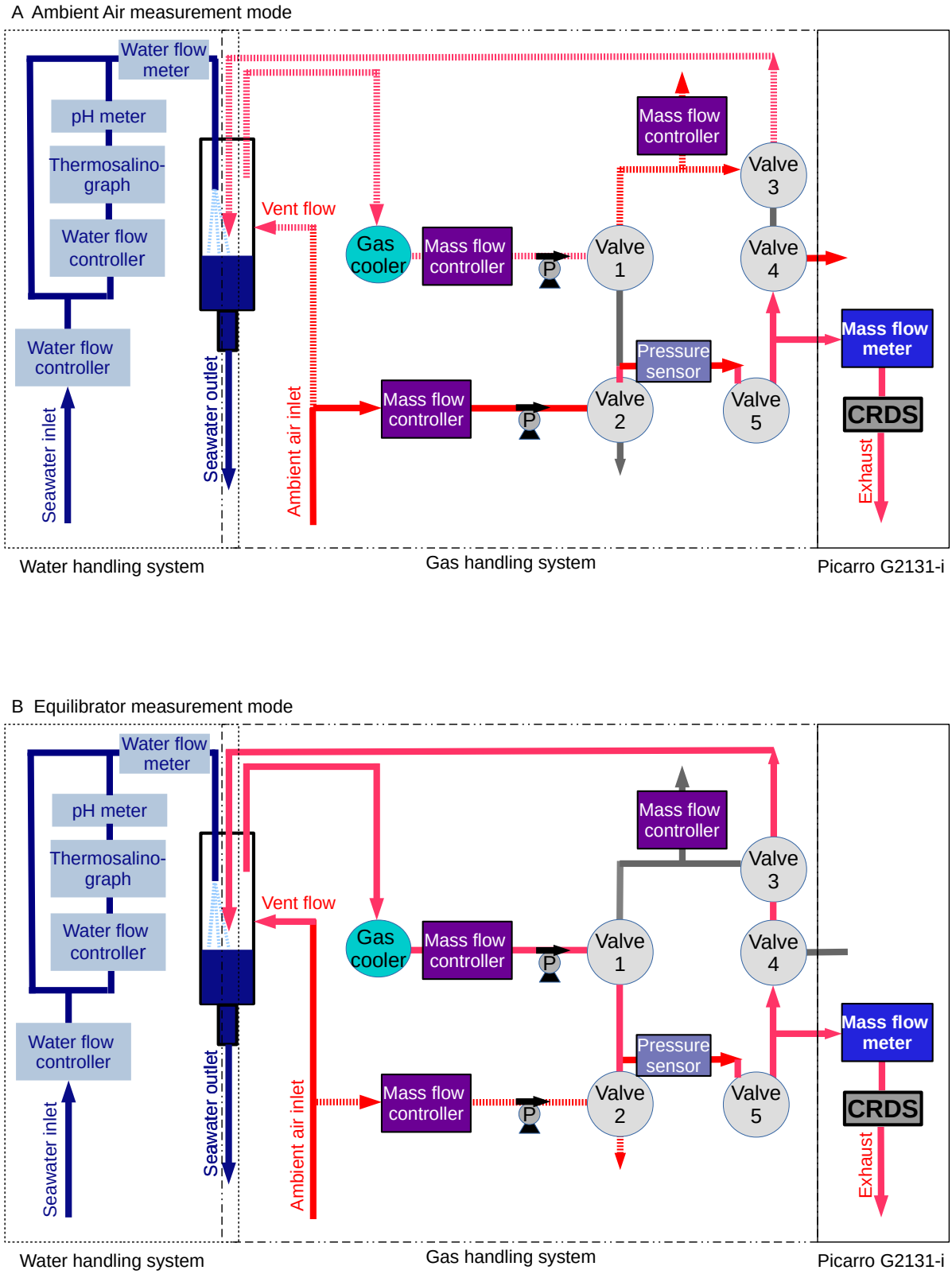

Fig. S1 Schematic overview of WEGAS including its three main components. One complete measurement cycle includes ambient air measured for 8 minutes (A) right after a 12-minute

measurement of the gas from the equilibrator (B). The gas flow in each mode is marked with solid red arrows, while gray solid arrows show the inactive path during one mode and dashed red arrows represent active gas flow paths that are not measured by CRDS in that mode. The datalogger automatically controls the mode switch by switching the open/close positions of five valves.

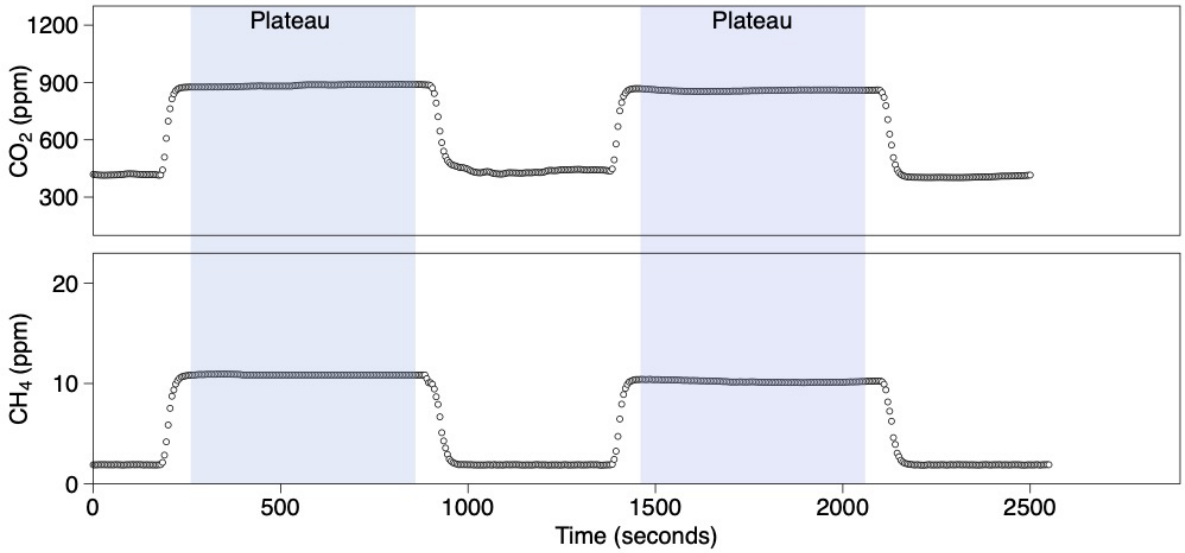

Fig. S2 Examples of 2 cycle measurements of CO_2 and CH_4 that show the equilibrium was sufficiently achieved within 2 minutes in the equilibrator and that only the plateau section was used in calculations.