

InGOS

Integrated non-CO₂ Observing System

Progress report
Annual Meeting
October 2014
Brussels



Overview WP6

Overall objective

- to improve, harmonize and integrate oceanic measurements of N_2O and CH_4 in open ocean and coastal regions

Specific objectives

- Establish a network of oceanic N_2O and CH_4 measurements by using different platforms: time-series stations, hydrographic sections and VOS lines
- Exchange of scientists between laboratories
- Inter-comparison exercises: method (GC-ECD/FID vs. OA-ICOS) and between WP6 partner labs

4 Partners

GEOMAR, Kiel, Germany

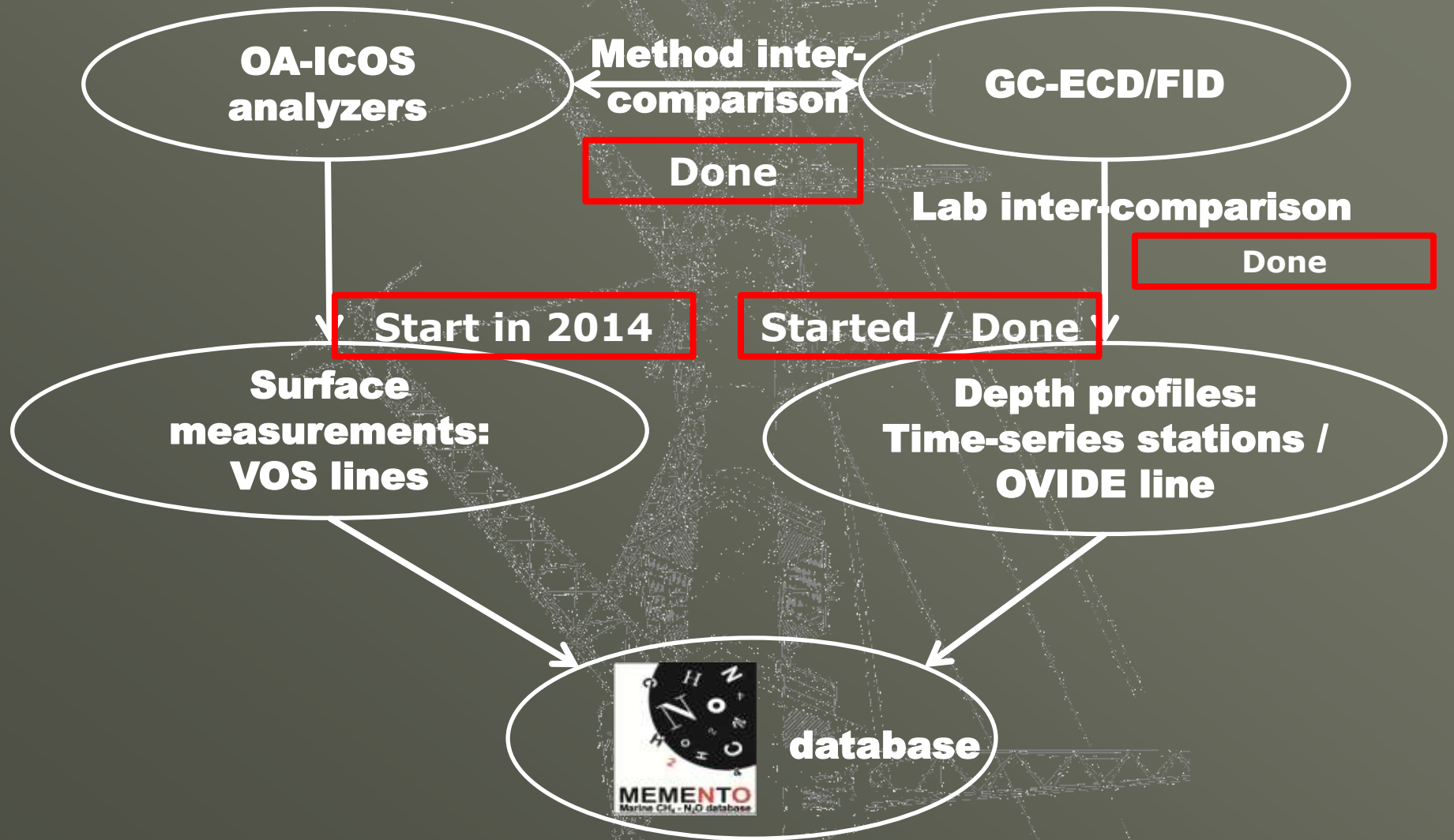
CSIC, Vigo, Spain

U Exeter, UK

UiB, Bergen, Norway



Progress and outlook WP6



Deliverables & Milestones WP6

- ◆ D6.1 - Report: Test of OA-ICOS analyzer (submitted)
- ◆ D6.2 - Report: Inter-comparison (submitted)
- ◆ D6.3 - Report: Time-series data (-> M36)
- ◆ D6.4 - Report: VOS lines (-> M36)
- ◆ D6.5 - Report: Hydrogr. section (-> M36)
- ◆ D6.6 - Report: MEMENTO (-> M42)
- ◆ MS31 - Set-up of OA-ICOS/Equibr. (-> M12)
- ◆ MS32 - Inter-comparison (-> M18)
- ◆ MS33 - Time-series (-> M24)
- ◆ MS34 - VOS lines (-> M24)
- ◆ MS35 - Hydrogr. section (-> M24)
- ◆ MS36 - Data archived (-> M30)

Scientific highlights WP6

Ocean Sci., 9, 1071–1087, 2013
 www.ocean-sci.net/9/1071/2013/
 doi:10.5194/os-9-1071-2013
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A new method for continuous measurements of oceanic and atmospheric N₂O, CO and CO₂: performance of off-axis integrated cavity output spectroscopy (OA-ICOS) coupled to non-dispersive infrared detection (NDIR)

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Received: 20 June 2013 – Published in Ocean Sci. Discuss.: 26 July 2013
 Revised: 6 November 2013 – Accepted: 7 November 2013 – Published: 11 December 2013

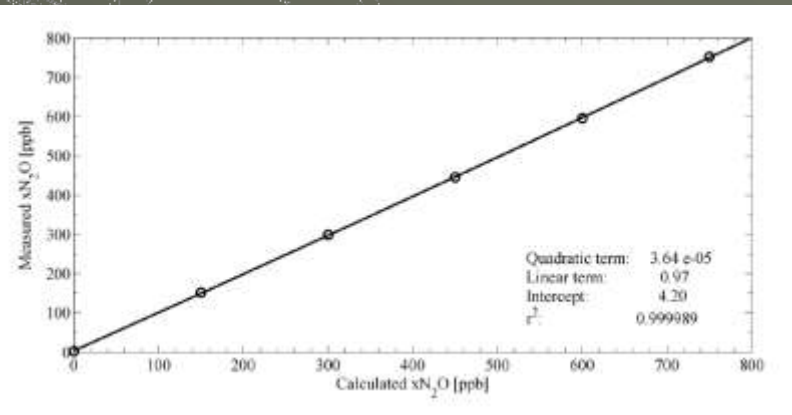
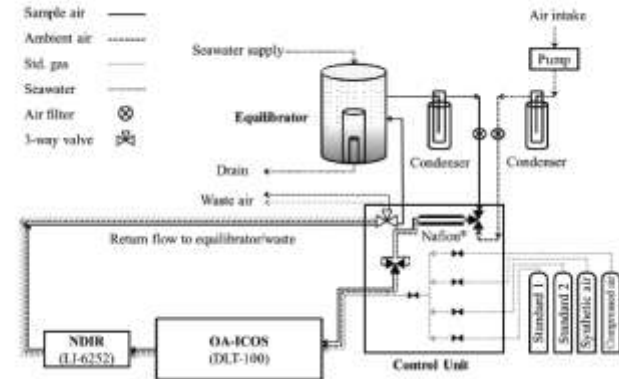
Abstract. A new system for continuous, highly resolved oceanic and atmospheric measurements of N₂O, CO and CO₂ is described. The system is based upon off-axis integrated cavity output spectroscopy (OA-ICOS) and a non-dispersive infrared analyzer (NDIR), both coupled to a Weiss-type equilibrator. Performance of the combined setup was evaluated by testing its precision, accuracy, long-term stability, linearity and response time. Furthermore, the setup was tested during two oceanographic campaigns in the equatorial Atlantic Ocean in order to explore its potential for autonomous deployment onboard voluntary observing ships (VOS). Improved equilibrator response times for N₂O (2.5 min) and CO (45 min) were achieved in comparison to response times from similar chamber designs used by previous studies. High stability of the OA-ICOS analyzer was demonstrated by low optical integration times of 2 and 4 min for N₂O and CO respectively, as well as detection limits of ~40 ppt and precision better than 0.3 ppb Hz^{-1/2}. Results from a direct comparison of the method presented here and well-established discrete methods for oceanic N₂O and CO₂ measurements showed very good consistency. The favorable agreement between underway atmospheric N₂O, CO and CO₂ measurements and monthly means at Ascension Island (7.96° S 14.4° W) further suggests a reliable operation of the underway setup in the field. The potential of the system as an improved platform for measurements of trace gases was explored by using continuous N₂O and CO₂ data to characterize the development of the seasonal equatorial

swelling in the Atlantic Ocean during two R/V *Maria S. Merian* cruises. A similar record of high-resolution CO measurements was simultaneously obtained, offering, for the first time, the possibility of a comprehensive view of the distribution and emissions of these climate-relevant gases in the area studied. The relatively simple underway N₂O-CO-CO₂ setup is suitable for long-term deployment onboard research and commercial vessels although potential sources of drift, such as cavity temperature, and further technical improvements towards automation, still need to be addressed.

1 Introduction

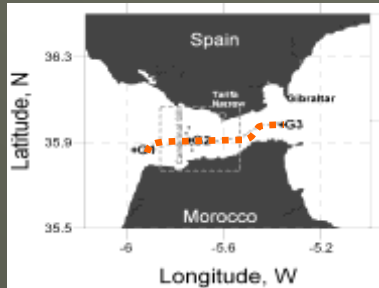
The assessment of marine emissions of climate-relevant gases has become a critical issue in the attempt to improve our current understanding of the impacts of the ocean on atmospheric composition and chemistry and therefore, on climate. Atmospheric concentrations of long-lived greenhouse gases such as nitrous oxide (N₂O) and carbon dioxide (CO₂) have been increasing at unprecedented rates over the last century, mainly in association with human activities, leading to an overall warming of the Earth's climate system (Denman et al., 2007). Both N₂O and CO₂ are strong greenhouse gases (Forster et al., 2007), while carbon monoxide (CO) is considered to be an indirect greenhouse gas that alters the tropospheric photochemistry and enhances the concentrations

Published by Copernicus Publications on behalf of the European Geosciences Union.

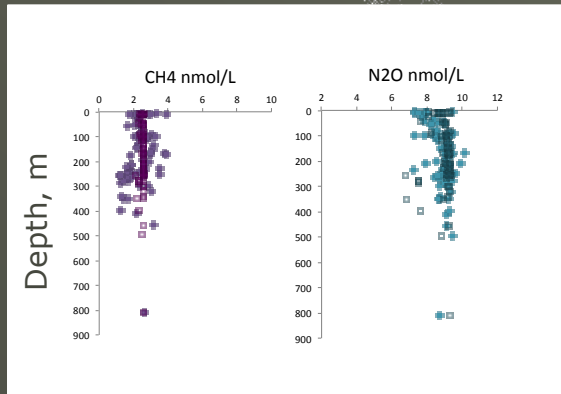


Scientific highlights WP6

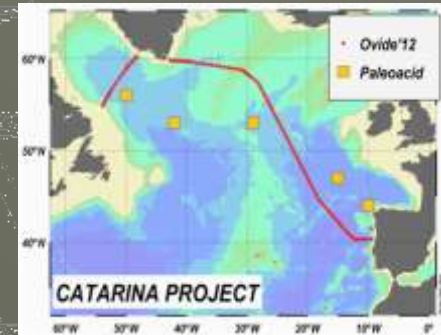
GIFT: Gibraltar Fixed Time-Series Stations



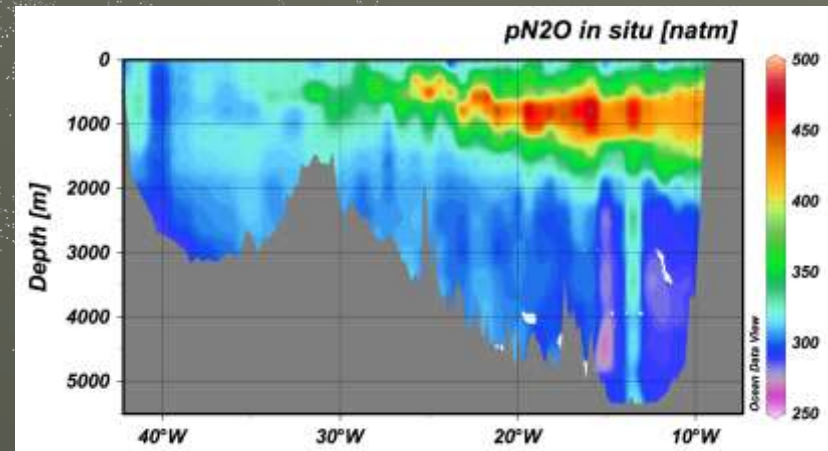
- Sampling cruises in Jul 2011, Aug 2011, Nov 2011, Feb 2012, Mar 2013



OVIDE: Repeated hydrographic Section Lisbon-Greenland



- Bi-annual sampling cruises since 1997
- June/July 2012
- May/June 2014





SCOR WG #143

Dissolved N_2O and CH_4 measurements:
Working towards a global network of ocean time
series measurements of N_2O and CH_4

SCOR WG #143

Dissolved N₂O and CH₄ measurements:
Working towards a global network of ocean time
series measurements of N₂O and CH₄



Major Objectives / Deliverables

- **Intercalibration of oceanic N₂O/CH₄ measurements**
- **Develop recommendation for a standard measurement protocol**
- **Establish N₂O and CH₄ reporting procedures**
- **Establish a framework for an N₂O/CH₄ ocean time series network**

SCOR WG #143

Dissolved N₂O and CH₄ measurements:
Working towards a global network of ocean time
series measurements of N₂O and CH₄



Calendar Year	Key dates
2013	May: Submission of proposal Nov: Decision by SCOR on support 1st Intercalibration Exercise Oct 2013 – May 2014
2014	Feb: WG meeting in Hawaii, (followed by ASLO 2013) 2nd Intercalibration Exercise Winter 2014/2015
2015	Sept: WG meeting in Germany, (followed by SOLAS conf)
2016	Feb: Publish recommendations for analysis and reporting
2017	Feb: 3 year review and Working Group meeting followed by Ocean Sciences Publication of recommendation for N₂O/CH₄ Time Series Station Network

SCOR Funding Period

SCOR WG #143

Dissolved N₂O and CH₄ measurements:
Working towards a global network of ocean time
series measurements of N₂O and CH₄



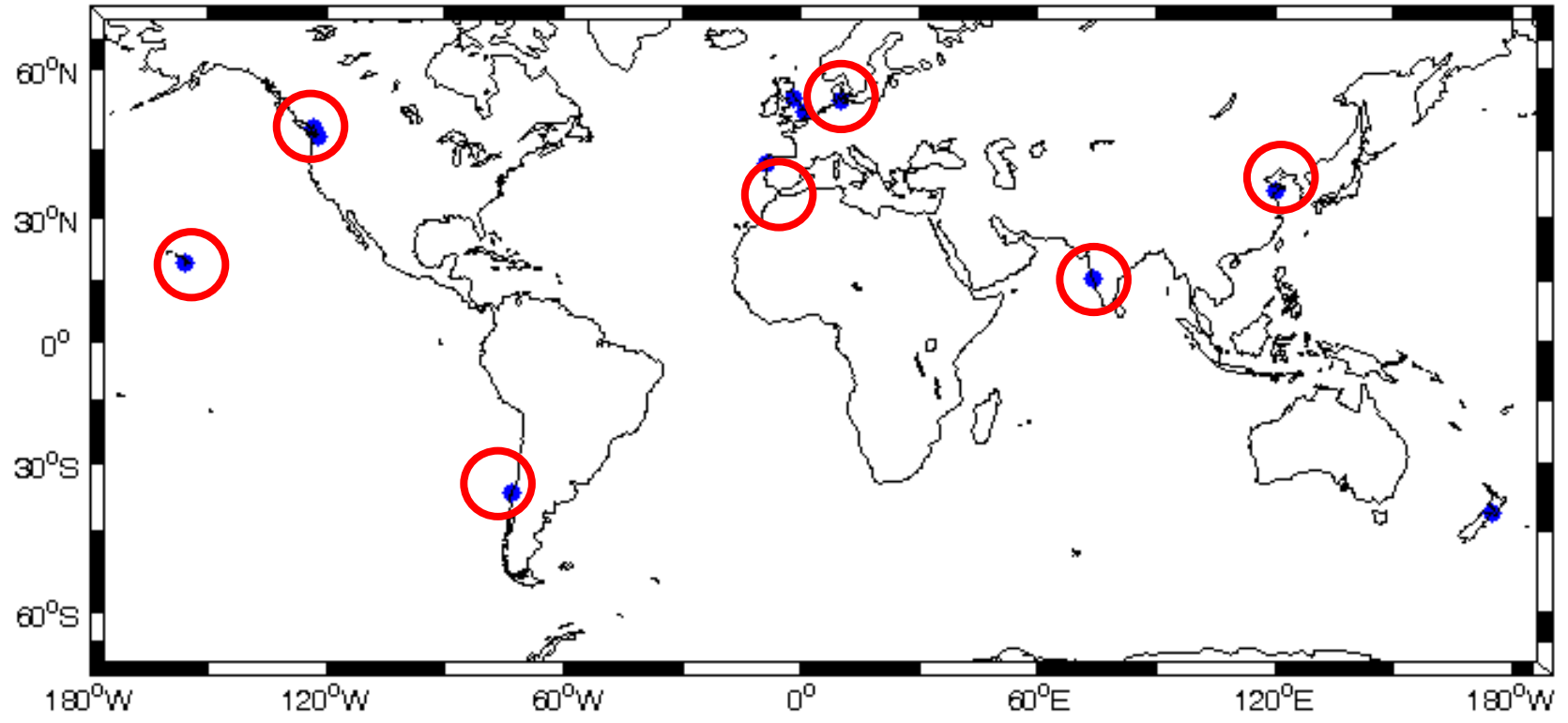
Full members

- Hermann Bange, GEOMAR, Kiel, Germany.
- Mercedes de la Paz Arándiga, IIM-CSIC, Vigo, Spain.
- Laura Farias, COPAS Center, Concepción, Chile.
- Cliff Law, NIWA, Wellington, New Zealand.
- Wajih Naqvi, NIO, Goa, India.
- Gregor Rehder, IOW, Warnemünde, Germany.
- Philippe Tortell, UBC, Vancouver, Canada.
- Rob Upstill-Goddard, U Newcastle; Newcastle, UK.
- Sam Wilson, C-MORE, Hawaii, USA.
- Guiling Zhang, OUC, Qingdao, China.

Associated members

- John Bullister, NOAA-PMEL, Washington, USA.
- Jan Kaiser, UEA, Norwich, UK.
- Annette Kock, MEMENTO, GEOMAR, Kiel, Germany
- Andy Rees, PML, Plymouth, UK
- ...

Locations of the participants and sites of regular N_2O/CH_4 time series measurements





WG #143 ACTIVITIES 2013/2014

- 1st Intercalibration Exercise 2013/2014
- Set up of homepage: <https://portal.geomar.de/web/scor-wg-143/home>
- 2nd Intercalibration Exercise End of 2014

MEETINGS

- 21 February 2014, Honolulu, Hawaii, USA
- 7-11 September 2015: SOLAS Open Science Conference, Kiel, Germany:

<http://solas-int.org/solas-osc-2015.html>

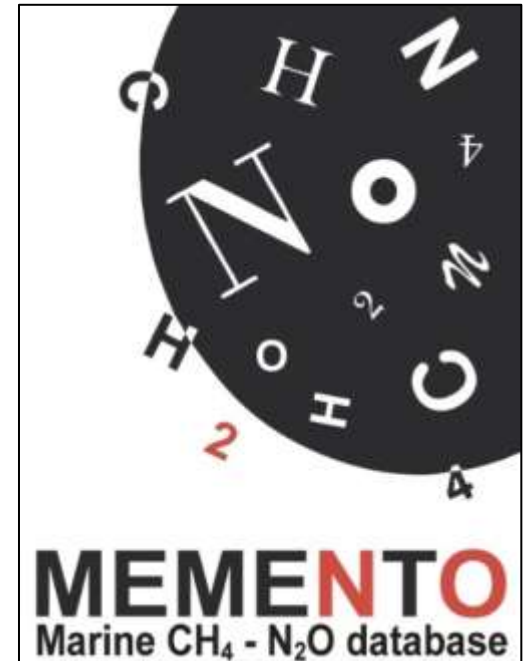


MEMENTO, the **M**arine **M**ethane and **N**itrous **O**xide Database

<https://memento.geomar.de>

Close collaboration between SCOR WG #143 and MEMENTO:

- Recommendations for data analysis and reporting as developed by WG #143 to be used as a quality control criterium for data included in MEMENTO
- Recommendation to archive N_2O and CH_4 data in MEMENTO





**Annette Kock,
Hela Mehrstens,
Hermann W. Bange**



MEMENTO
Marine CH₄ - N₂O database

Why a database for N₂O and CH₄?




Karl Banse , *Frontiers in Marine Science*, 2014:

“How may we know that the ocean has or has not changed on the half-century time scale, if data points through time from *in-situ* measurements are not available because we, the observing scientists, did not and still often do not deposit our observations in data centers?”

frontiers in
MARINE SCIENCE

OPINION ARTICLE
published: 04 August 2014
doi: 10.3389/fmars.2014.00020



Assessing ocean changes without data centers?

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School of Oceanography, University of Washington, Seattle, WA, USA
^{*}Correspondence: banse@ocean.washington.edu

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[†]Present.

Keywords: oceanography, data repositories, climate change

Dear colleagues among water volume oceanographers,

How may we know that the ocean has or has not changed on the half-century time scale, if data points through time

century, few time series can be assembled for studying long-term changes, if any, because the earlier measurements are not at hand. The common reasons are, at best, that many scientists keep their data somewhere in their desks; more serious, forget

however, the dictum about reproducibility cannot be followed in descriptive field studies, because there were just those facts observed during that season and year; at best, the observations were replicated.

Turning to biological temporal changes,

Why a database for N₂O and CH₄?

Geochim. Cosmochim. Acta, 27, 949-955, 1963.

Limnol. Oceanogr., 10 (Suppl.), R185-R201, 1965.

Geochimica et Cosmochimica Acta, 1963, Vol 27, pp. 949 to 955. Pergamon Press Ltd. Printed in Northern Ireland

Nitrous oxide in the ocean and the marine atmosphere

H. CRAIG and L. I. GORDON

Department of Earth Sciences and Scripps Institution of Oceanography
University of California, La Jolla, California

(Received 20 March 1963)

Abstract—Nitrous oxide has been found in surface and deep ocean waters of the S. Pacific. The observed concentrations are lower than expected for solubility equilibrium with concentrations previously reported in the continental atmosphere. Lower atmospheric concentrations than previous continental data have been found in N. Pacific air. These variations indicate that N₂O should be an important tracer gas for atmospheric studies.

SOME CONSEQUENCES OF THE DECOMPOSITION OF ORGANIC MATTER IN LAKE NITINAT, AN ANOXIC FJORD

Francis A. Richards, Joel D. Cline,
William W. Broenkow, and Larry P. Atkinson
Department of Oceanography, University of Washington, Seattle

ABSTRACT

Observations in Lake Nitinat, an anoxic fjord on Vancouver Island, British Columbia, indicate that the large accumulation of ammonium, sulfide, phosphate, silicate, and sulfides in the deep water are the result of anoxic and fermentative decomposition of organic matter of planktonic origin, the reduction of sulfate ions, lyticlytic or other non-oxidative release (in the case of silicates), and the reduction of carbonates (which also increases the alkalinity). Ammonia, sulfides, and silicate accumulate in the middle zone in direct proportion to each other, but some of the phosphate is probably released from the organic matter earlier than the other compounds, and some of the phosphate may be precipitated onto the bottom. Methane was observed in the anoxic water, suggesting that some decomposition takes place by anaerobic fermentation. The concentrations of ferrous and sulfide ions are probably controlled by the solubility of ferrous sulfide. The vertical distribution of sulfides can be described by a mathematical model that can be simplified in one dimension because horizontal advection and diffusive terms can be neglected.

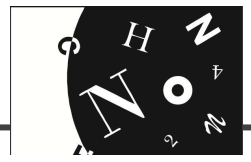


- N₂O and CH₄ measurements available since 1960s
- Original data in old reports and publications, many datasets not archived

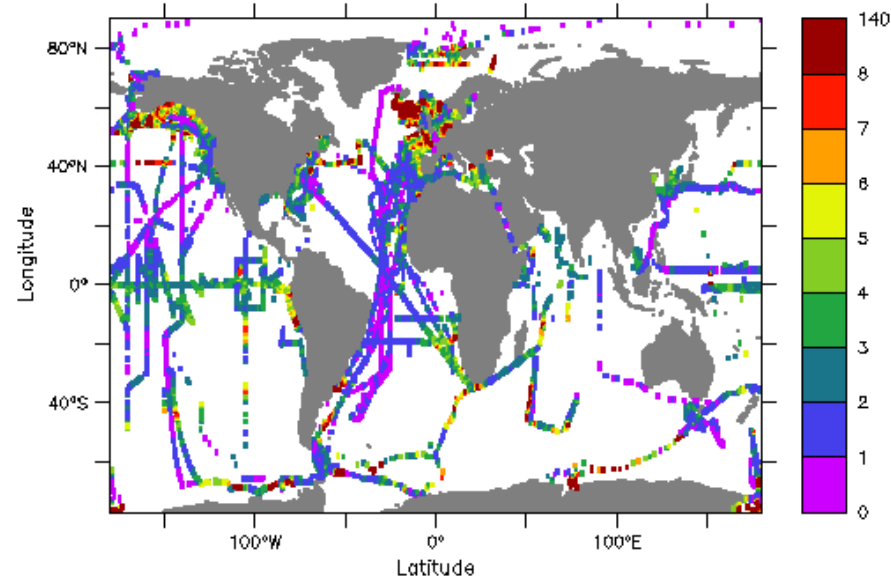
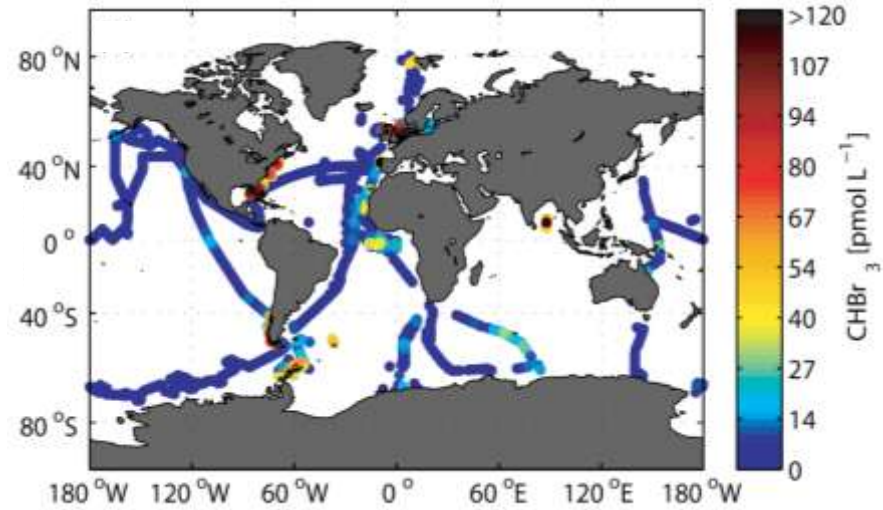
A database serves as:

- Data basis for calculation of global emission estimates
- Assessment of spatial and temporal variability and long-term changes
- Resource for validation of biogeochemical models

Examples



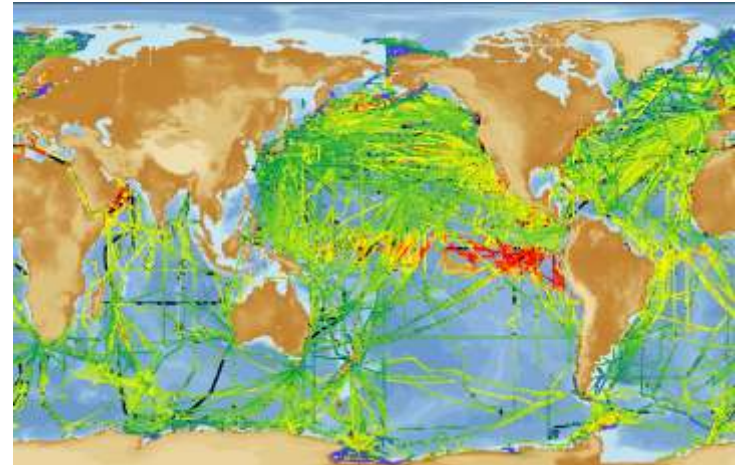
HalOcat



PMEL DMS database:

<http://saga.pmel.noaa.gov/dms/>

SOCAt: <http://www.socat.info/>



MEMENTO - timeline



2004-2012 Maintenance of N₂O database by S. Walter, A. Freing, F. Ziska and H.W. Bange:

Excel files, Matlab workspace file containing all imported datasets (>100 000 data entries!)

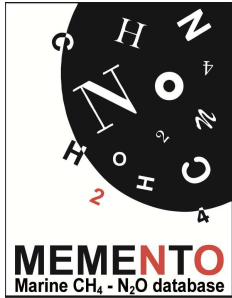
MEMENTO was initiated in 2009 during a COST Action 735 Meeting in Kiel

Feb 2013 - Jan 2016 SOPRAN III: Subproject 1.8 (Annette Kock):

- ✓ Implementation of standard quality control procedure
-> Revision of all data submissions
 - ✓ Data transfer to data portal of Kiel Data Management Team
 - ✓ Setup of website, access to database through website

 - Import of new datasets using standard quality control procedure
 - Calculation of surface N₂O and CH₄ concentration fields and emissions
-

MEMENTO homepage and database



<https://memento.geomar.de/home>



<https://memento.geomar.de/database>

Original datasets

- Can contain oceanic and *corresponding* atm. measurements

Essential data needed for import:

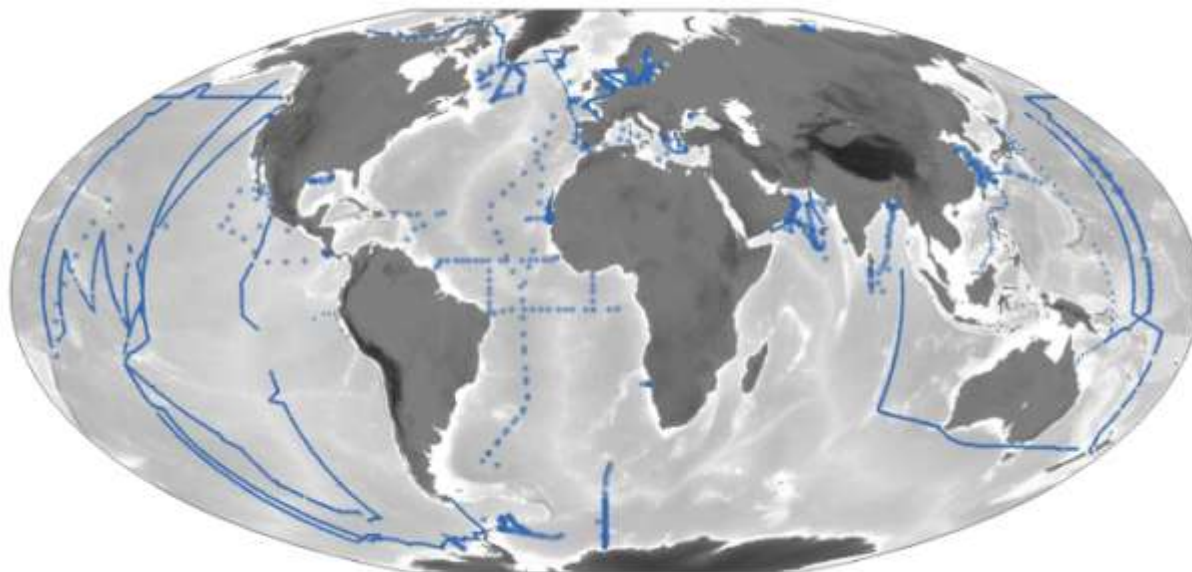
- Position, date/time, sampling depth
- **Data without these parameters is not imported!**
- Additional information: temp, sal, O₂ & nutrients

Range check:

- Date: 1913-now
 - Lat/long: -90 – 90° / -180 – 360°
 - Water temp: -5 – 35°C
 - Air temp: -90 – 60°C
 - Air pressure: 800 – 1100 mbar
 - Nutrients, O₂, CH₄, N₂O, sal: negative concentrations excluded
 - No quality control procedure based on quality criteria (based on e.g. WOCE flags, precision)
-

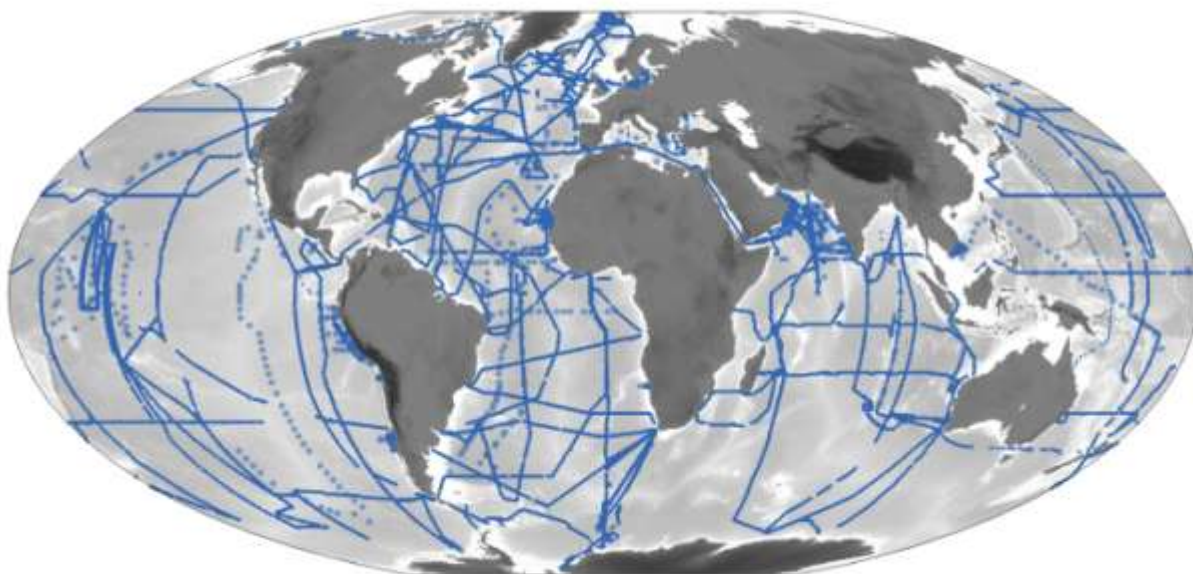


Global data coverage by Sept 2014



CH₄

>20,000 data points



N₂O

>100,000 data points

Next steps



Publications

- IMBER Update, 8, 3-4, 2007.
- Env. Chem., 6, 195-197, 2009.
- Eos Transactions AGU, submitted, 2014.
- Earth System Science Data: detailed description of database

Import of additional datasets into MEMENTO

-> inquiry letter to colleagues

Calculation of 1° x 1° surface concentration fields and emissions

In cooperation with SCOR WG #143: Implementation of standard procedure for N₂O and CH₄ data as quality criterion
