

“DMS measurements in the ocean”

Report about my short-term scientific mission at the Institut de Ciències del Mar in Barcelona, Spain

COST Action Number: 735

Beneficiary's Name and Institution: Mrs Cathleen Zindler, IFM-GEOMAR, Kiel, Germany

Host's Name and Institution: Rafel Simo, Institut de Ciències del Mar, CMIMA-CSIC

Period: from 6/01/2008 to 20/01/2008

Place: Barcelona (ES)

Reference code: COST-STSM-735-03281

Motivation

The topic of my master thesis is to measure dimethylsulfide (DMS) in seawater, especially in the upwelling area off the coast of Mauritania, NW Africa. In order to measure DMS, I am using a purge-and-trap system connected to a gas chromatograph (GC) and a flame photometric detector (FPD).

In order to optimise my analytical system I visited Rafel Simó who is the world-leading expert in measuring sulphur compounds in the ocean.

Summary

During my stay in the group of Rafel Simo at the Institut de Ciències del Mar in Barcelona, I significantly increased my knowledge about the analytical requirements to optimise my DMS method (for details see the Technical Report). Furthermore, I learned how to measure other dissolved and particulate sulphur compounds (such as DMSP and DMSO). Additionally, I was introduced to the field of rate measurements, especially the determination of production and consumption rates of DMS in seawater. Moreover, I had the chance to take part in a day trip to sample DMS at the coastal time series stations off Barcelona.

The visit in Barcelona boosted my knowledge about DMS and the oceanic sulphur cycle and certainly will help to improve my future work on the different aspects of the oceanic DMS cycle.

Outlook

Future collaborations between the Laboratories in Barcelona and Kiel have been arranged: For example, R. Simo was invited to take part in a future R/V Meteor cruise to the eastern tropical North Atlantic Ocean which is currently planned by IFM-GEOMAR for 2010.

Moreover, R. Simo was invited to give an overview presentation in the “Marine Science Kolloquium” at IFM-GEOMAR on 29 June 2008.

Technical Report

Introduction – Scientific background

Dimethylsulfide (DMS) is the most abundant volatile sulphur compound in the ocean. It was identified to mediate the coupling of the sulphur cycle in the ocean and the atmospheric sulphur cycle since DMS is supersaturated in seawater and therefore a continuous flux from the ocean to the atmosphere occurs via DMS. In the atmosphere DMS is rapidly oxidized and forms aerosols which in turn are acting as cloud condensation nuclei (CCN) and thus DMS indirectly influences the Earth albedo. DMS is produced by the enzymatic cleavage of dimethylsulfoniopropionate (DMSP), which is synthesized in phytoplankton. When DMSP is released into seawater it serves as a major organic sulphur source for a number of different bacteria and phytoplankton species and is therefore an important sulphur carrier through the marine food web.

Due to the influence of DMS on global radiation and the complexity of its production and consumption, the oceanic distribution of DMS received an increasing interest by different disciplines such as marine ecology, chemistry and physiology over the last 40 years.

Method - DMS measurement

In order to expel DMS out of the seawater, the seawater sample is purged with helium (He). Gaseous DMS is transported with the helium gas stream into the cryogenic trap, which is filled with liquid nitrogen in order to cryofocus DMS. After purging the trapped DMS is heated up and transferred onto the gas chromatography column where it is separated from other gaseous compound and burned in the FPD at the end of the column. The emissions of the containing-containing fragments are converted into a signal, which can be analysed. For detailed information about the set up please see Figure 1.

Method - Calibration

In order to calibrate the device a known concentration of DMS has to be measured to correlate the concentration to the measured signal. Pure DMS is gravimetrically weighted into ethylenglycol and well mixed. For the secondary standard a few μL of the primary standard is weighted in ethylenglycol. The secondary standard should have a concentration in the range from 7 –to 15 μM . The standard is mixed with water and measured like a sample.

Potential sources of error in the DMS measurement device

Due to the small diameter of the GC-capillary column compared to the diameter of the tubing in the purge-and-trap system the gas stream on the GC recognize a higher resistance when it is transferred onto the GC column. Hence higher pressure than the atmosphere pressure is necessary to maintain a continuous gas stream through the column. But high pressure causes a higher risk of occurrence of leaks and the disappearance of DMS within the purge and trap system due to leaks. The sensitivity of the FPD is dependent on the mixture of synthetic air and hydrogen, which fuel the flame. But the optimal mixture has to be tested for each individual FPD.

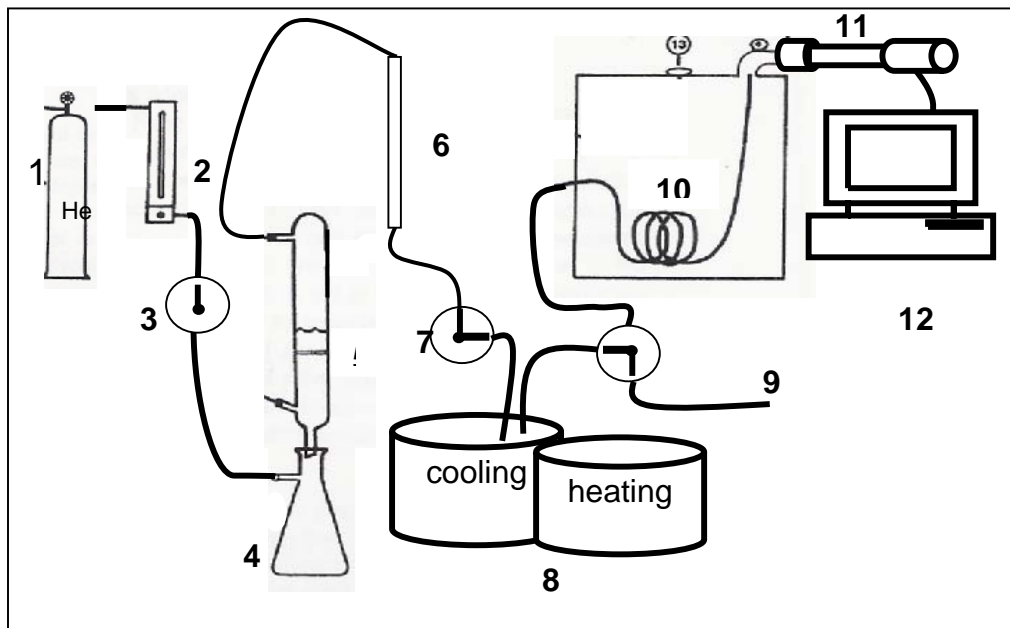


Figure 1: Set-up of the DMS measurement device. The elements are not true to scale. 1 gas bottle, 2 flow meter, 3 one way valve, 4 sample flask, 5 purge chamber, 6 drying column filled with K_2CO_3 , 7 two way valve, 8 Dewar flask (filled with liquid nitrogen) and heater, 9 bleed valve, 10 gas chromatograph, 11 flame photometric detector, 12 computer

The purging time of the sample is dependent on the sample volume. Therefore the purging time has to be tested in order to efficiently purge DMS from seawater. Further on the gas stream has to be dried after purging otherwise the sensitivity of the FPD is decreasing. I use a column filled with potassium carbonate (K_2CO_3). The K_2CO_3 is fast saturated with water and has to be replaced after around 20 samples.

These problems mentioned above occurred when I reconstructed and optimised my DMS measurement device. Thus I visited Rafel Simó at the Institut de Ciències del Mar, CMIMA-CSIC in Barcelona to learn more about how to measure DMS, to solve the problems described above and to obtain more information about the complexity of the sulphur cycle in the ocean.

Methods applied at the Institute de Ciències del Mar

Method to measure DMS

At the CSIC, DMS is also measured with a purge-and-trap system, which is connected to a GC/FPD (Fig. 2). But in this case the GC column is a packed column with the same diameter as the purge-and-trap tubings. Thus, pressure effects do not influence the analytical system.

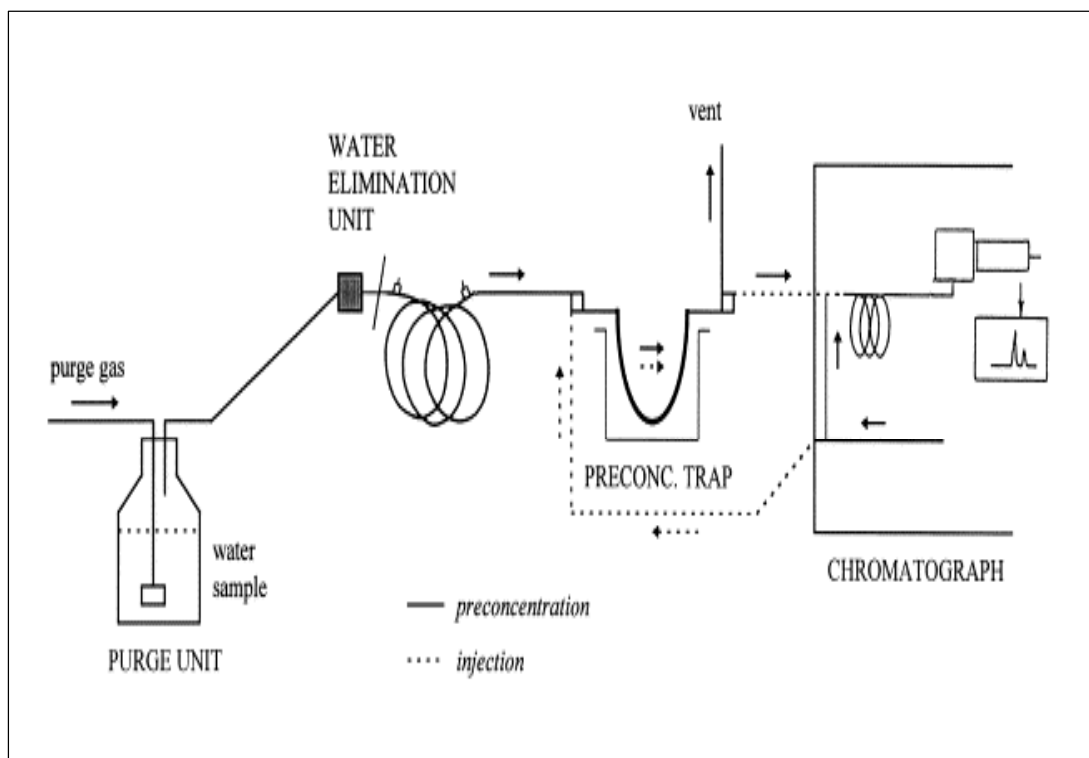


Fig. 2: Schematic diagram of the basic instrumental configuration for the analysis of DMS in water (Simo, 1998)

The seawater sample volume range between 3 and 5 ml therefore the purging time is only 3 min. Thus a fast measuring of the samples is possible. The sample is already purged in the sample vial, thus an extra purging chamber is not necessary making the purge-and-trap system simpler.

The gas stream was dried with a Nafion membrane, which is enclosed by Teflon tubing. The gas stream is flowing through the Nafion tube while the water is passed the membrane following a gradient. This gradient is produced due to a counter flow of dry air through the Teflon tube. The counter flow rate should be twice as high the DMS/He gas stream is.

Calibration

With the aim of fast calibration a gaseous DMS standard is injected with a syringe directly into the tube after the purge-and-trap system before the gas stream is transferred onto the GC column. The DMS standard is gained by using a device, which contained a permeation tube. This tube is filled with liquid DMS and is closed at both sides with a membrane. The tube is heated in order to bring a certain amount of DMS to diffuse into a continuous helium flow passing the tube. Hence the DMS concentration used for calibration depends on temperature and the He flow rate.

Sampling and sample filtration

Water can be sampled either using a CTD rosette or directly from the surface by submerging a bottle gently to avoiding bubbles. For sampling dark brown bottles are recommendable to eliminate photolysis. The sampling bottles should be filled completely in order to prevent a headspace.

Before measuring the seawater sample it should be filtered to remove big particles and to avoid a breakdown of plankton cells containing DMSP, which in turn enhances DMS concentrations when it is released during purging. Water samples are taken by using a

syringe. A filter holder is attached to the syringe and the water sample is gently pushed through the filter directly into a purging vial.

Determination of dissolved DMSP, DMSO and particulate DMSP, DMSO

A filtered sample is measured for background DMS $[DMS]^0$. Then a new filtered sample taken from the same sample bottle is alkalinised with sodium hydroxide pellets. Dissolved DMSP $[DMSP]_d$ is converted rapidly into DMS, which in turn is measured. Subsequently dissolved DMSP can be calculated as $[DMSP]_d = [DMS] - [DMS]^0$. Dissolved DMSO $[DMSO]$ can be converted into DMS by adding sodium borohydride pellets into the same sample after measuring $[DMSP]_d$.

In order to determine particulate DMSP $[DMSP]_p$ total DMSP $[DMSP]_t$ has to be measured. Again the background DMS concentration $[DMS]^0$ has to be determined first. An unfiltered seawater sample is alkalinized in a 50 ml vial assuming that this seawater sample is a representative random sample with a natural distribution of particles. To obtain a complete conversion of $[DMSP]_t$ to $[DMS]$ the sample should be allowed to react for several hours. Again $[DMS]$ is measured and $[DMSP]_t$ is calculated as follows: $[DMSP]_t = [DMS] - [DMS]^0$. Particulate $[DMSP]_p$ is calculated according $[DMSP]_p = [DMSP]_t - [DMSP]_d$. After measuring total DMSP the same sample can be prepared with sodium borohydride to convert particulate DMSO into DMS.

DMS production and consumption rate

For measuring both the consumption and production rates, two dark brown glass bottles have to fill with surface seawater. Each bottle should contain 2.5 l in order to adequately representing the natural micro community. To measure the DMS production rates, dimethyldisulfide (DMDS) is added to one bottle to inhibit DMS consumption. The second bottle serves as a control where both consumption and production occur. After several time steps the DMS concentrations are measured in both bottles. Microbial consumption rates can be calculated by subtracting the slope (DMS vs time) of the control bottle from the slope of the DMDS inhibited bottle.

To obtain the DMS yield DMS production has to be divided by DMSP consumption times hundred.

$[DMSP]_t$ consumption rate by the whole community

It is recommended to sample before sunrise because the plankton community is then still adapted to low light. The sample should be stored in dark brown glass bottles to eliminate photosynthesis and DMSP production. After several time steps the total DMSP content is measured.

Determination of photolysis rate

For calculating the photolysis rate, samples have to be taken at the same location at different times (normally at two consecutive days). Out of the first sample the DMS_i concentration, the DMS consumption and production rates and also the DMS ventilation rate have to be measured. $DMS_{(i+1)}$ concentration has to be detected in the second sample at the time step $(i+1)$.

The photolysis rate is calculated as follows:

$$DMS_{(photolysis)} = DMS_{(production)} - DMS_{(consumption)} - DMS_{(ventilation)}$$

The photolysis rate can also be measured in the laboratory. The water sample has to be filtered (0.22 μ m pore width) to eliminate DMS production/consumption by plankton and bacteria. One bottle with filtered seawater is stored in light while the other one is stored in

dark. After several time steps the DMS concentrations are determined. The difference of the slope (DMS vs time) of the dark sample and the slope of the sample in light shows the DMS loss due to photolysis.

DMS flux

The sea-to-air gas exchange of DMS is calculated using the formula suggested by Nightingale et al. (2000). The DMS Schmidt number is calculated with the relationship proposed by Saltzmann et al. (1993).

Topics to investigate the complexity of the DMS, DMSP and DMSO cycle:

- Determination of bacteria and plankton species which take up DMSP and/or DMS
- Determination of the amount of DMSP/DMS which is consumed by bacteria and algae and how fast it is consumed
- Which species have a selective advantage during times with a high DMSP availability?
- Determination of the annual variability of DMS concentration in different oceanic regions
- Which factors are responsible for the loss of DMS, which of them is the most powerful sink for DMS and when?
- Light effect on the uptake of DMSP/DMS
- How does grazing effect the DMS production?
- Following the way of DMSP through the food web
- Which atmospheric components are potentially affected by DMS?
- Influence of CO₂/pH on DMS concentration in seawater