2013-018

CCGS *JP Tully*

Dimethylsulfide (DMS) & Dimethylsulfoniopropionate (DMSP) Report

August 20 to September 5, 2013

Prepared by Michael Arychuk

1. Sample Collection

Samples were collected from all major stations (P2, P4, P12, P16, P20, P26) for DMS, $DMSP_{D\ (dissolved)}$ & $DMSP_{T\ (total)}$.

1.1 DMS

Fourteen water samples from various depths (300m, 200m, 175m, 100m, 75m, 50m, 40m, 30m, 25m, 20m, 15m, 10m, 5m, surface) were collected at each of the stations P4, P12, P16, P20 & P26. At P2 there were eleven samples collected (100m, 75m, 50m, 40m, 30m, 25m, 20m, 15m, 10m, 5m, surface). In all cases, samples were collected in 250 ml ground glass stoppered bottles and stored in a fridge, in the dark and removed one at a time before analysis.

1.2 DMSP

Six samples for both $DMSP_D$ and $DMSP_T$ were collected at each station; two at the surface (0m, 5m), one in the mixed layer (100m), one in the deep chlorophyll max (20m) and two in the salinity mix layer (175m, 200m). The only exception to this was P2 where there were no 175m or 200m samples, hence, only 4 samples were collected.

2. Analysis

2.1 DMS & Université Laval Samples

A sample was loaded onto the stripper and purged with UHP Nitrogen for 10 minutes at ~100 ml/min. The DMS was extracted from the water and absorbed onto a Tenax TA trap kept at -80°C. The trap was subsequently desorbed at 100°C (with a Dewar containing boiling water) onto a Chromasorb 330 column which eluted onto a Flame Photometric Detector (FPD). All samples were run as soon as possible after being collected.

2.2 $DMSP_D$

Approximately 50-75 ml of seawater were allowed to flow directly from the Niskin into a filtration funnel containing a 0.7 μm GF/F filter. The first 3.5 ml were collected in a polypropylene tube (15 ml) containing 50 μl of a 50% sulphuric acid solution. The sample was then stored in the dark and at 4˚C where it would be analysed back at IOS at a later date.

2.3 $DMSP_T$

3.5 ml of seawater were collected directly from the Niskin into a polypropylene tube (15 ml) containing 50 μl of a 50% sulphuric acid solution. The sample was then stored in the dark and at 4˚C where it would be analysed back at IOS at a later date.

2.4 Université Laval

Nine incubated water samples were run for eleven consecutive days. These samples were treated as a DMS sample and were run as described in 2.1 above. Samples were analysed within an hour of receiving them.

3. Calibration

3.1 DMS & Université Laval Samples

A four to six level calibration table was used for calculating the concentrations of DMS. The standards were prepared in water and run under the same conditions, as described above, for the samples. A calibration curve was valid for 12 hours. If analysis exceeded 12 hours, a continuing calibration standard was run to ensure the calibration curve was still within acceptable limits.

4. Quality Control

4.1 DMS & Université Laval Samples

System blanks and duplicates were run approximately every 13 samples to ensure the system remained free of contamination and had acceptable reproducibility. Stripping efficiency was evaluated at the beginning of the cruise and was proven to be acceptable at over 97%.

4.2 DMSP

Blanks and duplicates were collected at every station. Blanks were done by simply treating MQ water as an actual sample. For example, in the case of $DMSP_D$ it was put through a separate funnel and for $DMSP_T$ it was added directly to the polypropylene tube.

5. Data & Results

5.1 DMS

There were some very high levels detected on this cruise. Specifically at P12 there were levels of DMS that were some of the highest ever seen in 10 years. There were also a lot of blank problems for the first half of the cruise but they were later resolved. See the "Conclusions" part of this report for more detail.

5.2 DMSP

Samples were not run due to blank contamination.

5.3 Université Laval

Samples were run under same conditions and parameters as DMS. A separate report was provided to Université Laval with their data.

6. Conclusions

6.1 DMS & Université Laval Samples

As mentioned above there were once again issues with obtaining a clean, DMS free blank. This blank is very important as it demonstrates to the analyst that their system is free of any background or residual DMS that would adversely elevate the DMS concentration levels in standards and samples. For this reason no standards or samples are run on the system until a clean blank is obtained. Under normal conditions the procedure takes no more than a few runs (60 minutes) but for the first half of the cruise it was taking between two and four hours.

In the end it was discovered that the MQ water system on the ship which provides the water for the blanks, had not been serviced in over a year and the filter's subsequently needed to be replaced. Once the filters were replaced the blank problem was alleviated. To prevent this problem in the future there will be more attention paid to the service schedule of the system and some pre cruise tests will be run prior to the cruise to demonstrate the system is free of contamination that could otherwise affect the analyses being done on the cruise.

6.2 DMSP

Samples were not run due to blank contamination. These blanks were run over a year after being collected and although they should have remained stable during this time it is possible they became contaminated from the storage process or while being collected.