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CCGS *JP Tully*

Dimethylsulfide (DMS) Report

May 30, 2007 to June 19, 2007

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1. Sample Collection

Samples were collected from all major stations (P4, P12, P16, P20, P26) for DMS. Thirteen water samples from various depths (200 m, 175 m, 100 m, 75 m, 50 m, 40 m, 30 m, 25 m, 20 m, 15 m, 10 m, 5 m, surface) were collected at each station in 250 ml ground glass stoppered bottles. On some stations a 300 m sample was taken. Samples were stored in the dark and removed one at a time before analysis.

2. Analysis

A sample was pre-filtered under gravity with GF/F filters prior to being loaded under vacuum into the 20 ml calibration vessel. From there it was transferred to 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^{o}C. The trap was subsequently desorbed at 100^{o}C (with a dewar containing boiling water) onto a Chromasorb 330 column which eluted to a Flame Photometric Detector (FPD). All samples were run immediately after being collected.

3. Calibration

A four to five 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. Normally a continuing calibration standard is run after all samples from a station have been run or every 12 hours, which ever comes first, to ensure the calibration curve is still within acceptable limits.

4. Quality Control

System blanks and duplicates were run approximately every 13 samples to ensure the system remained free of contamination and had acceptable reproducibility. All blanks were non-detectable and duplicates did not differ by more than 10% (well within the acceptable limits of 20%). Stripping efficiency was evaluated at the beginning of the cruise and was proven to be acceptable at over 95%.

5. Data & Results

This cruise involved collaboration between IOS and University Laval with respect to DMS and DMSP analysis. Our DMS results were provided to U Laval so that they would be able to do their DMSP analysis as well as additional samples were run from additional stations to meet their profile requirements. These additional DMS data are not included in this final report but is available from the original data file if needed.

The two previous cruises have shown trace DMS at levels below 100 m. This was also evident on this cruise, but at a greater frequency. Stations P16, P20 & P26 all showed detectable DMS at 200 m and 300 m (300 m samples were taken at most stations to try and resolve the issue of contamination versus a true hit). Although blank runs did indeed show no detectable DMS I still would exercise caution towards concluding the hits at 200 and 300 m are indeed valid DMS results. One has to truly question a DMS hit at 300 m especially when 300 m, 200 m and 175 m samples all gave the same amount of DMS. If DMS was indeed present at the 300 m depth then one would expect the value to increase (and not stay steady) at the 200 m and 175 m levels. In one instance (P20) the 300 meter sample is actually higher than the 200 m sample. This simply does not make sense and one subsequently has to call into question the validity of these hits and all of the deep water hits. A possible explanation for these deep water hits is contamination of the sample bottle. Ideally it would've been preferable to either replace the samples bottles with clean bottles or to acid wash the bottles. Unfortunately there were no extra bottles to spare and no provisions available on board the ship to acid wash glassware.

6. Conclusions

This is the third cruise where there is questionable data at depths below 100 m. It has now become necessary to take additional supplies which will aide in the investigative process of determining whether or not the hits are valid should it happen once again on the next cruise. This will have to be undertaken while at sea and hopefully can be resolved by the next cruise.

Martine Lizotte of University Laval was very surprised we were filtering our DMS samples prior to analysis. Based on her experience this is only required if one is also doing a DMSP analysis. She suggested that we were probably losing accuracy on samples that were close to the detection limit due to the added air exposure. Since there was obviously some question as to the validity of our procedure I ran a mini-experiment. Two low level samples in duplicate (around 0.5 nM) and two high level (4 nM) samples in duplicate were run. One duplicate from each was filtered and the other was not. Results showed that indeed we were losing some DMS in the low level analysis (0.5 nM DMS in the unfiltered sample and non detectable on the filtered). The higher samples, however, were less affected (4.2 nM in the unfiltered and 3.8 nM in the filtered). In other words exactly what Dr. Lizotte had claimed. Based on the findings it is now preferable to run the samples without filtering unless we are going to proceed with DMSP analysis. This new procedural note will be incorporated for the next cruise.