REPORT ON THE SHORT TERM SCIENTIFIC MISSION (STSM): COST-STSM-735-6337

Knowledge exchange of Oxygenated Volatile Organic Compound (OVOC) research between PML & IFM-GEOMAR

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03- 07/05/2010

MOTIVATION:

Oxygenated Volatile Organic Compounds (OVOCs), which consist of alcohols, aldehydes, and ketones, play an important role in atmospheric chemistry by influencing levels of both hydroxyl radicals and ozone. In addition, both acetone and acetaldehyde are precursors to the stable trace gas PeroxyAcetyl Nitrate (PAN). PAN is able to sequester reactive nitrogen and transport it long range where it can be released in cleaner areas of the troposphere. The role of the ocean in the cycling of these compounds remains largely unknown due to the difficulty in extracting and measuring these soluble gases in sea water samples.

I have developed two systems at PML; (i) Purge and Trap – Gas Chromatography / Flame Ionisation Detection (P&T-GC/FID) for the analysis of acetone, acetaldehyde, ethanol, 1-propanol, 2-propanol and propanal and (ii) Membrane Inlet – Proton Transfer Reaction / Mass Spectrometry (MI-PTR/MS) for quantification of methanol, acetone and acetaldehyde. These two techniques differ from the method being used at IFM-GEOMAR with Dr. Marandino, who uses purge and trap coupled to a Gas Chromatograph / Mass Spectrometer (GC/MS). The main motivation for this short term science mission (STSM) was to exchange knowledge on our current research progress within the OVOC projects, paying particular attention to the differences in analytical techniques being used.

Dr. Marandino also used a separate technique prior to her association with IFM-GEOMAR that consisted of Atmospheric Pressure Chemical Ionisation Mass Spectrometry (API-CIMS) to measure acetone in sea water. This method, similar to PTR/MS, utilized an internal standard to calibrate and monitor the sampling setup and instrumental drift. I believe that incorporating a similar internal standard technique is a way to improve our methods at PML. Her expert knowledge in this field will enable a similar system to be implemented much faster at PML.

One of the challenges associated with analysing sea water trace gas concentrations is efficient sample analysis, especially when a large number of measurements are required. The ability to store samples for later measurement would be an asset for discrete measurement techniques, such as GC/FID or GC/MS. However, it is unclear if OVOCS in seawater are stable when stored. Hudson et al. (2007) mentions freezing samples prior to acetone analysis but does not present details about the freezing technique. A second motivation for this joint work was to conduct a preliminary sample freezing experiment to investigate whether OVOC concentrations are compromised during the freezing procedure and subsequent storage.

SUMMARY OF ACTIVITIES:

The freezing experiments were conducted to answer 2 separate questions; (i) Do OVOC concentrations fluctuate when stored?, (ii) Does the act of freezing alter OVOC levels in water?

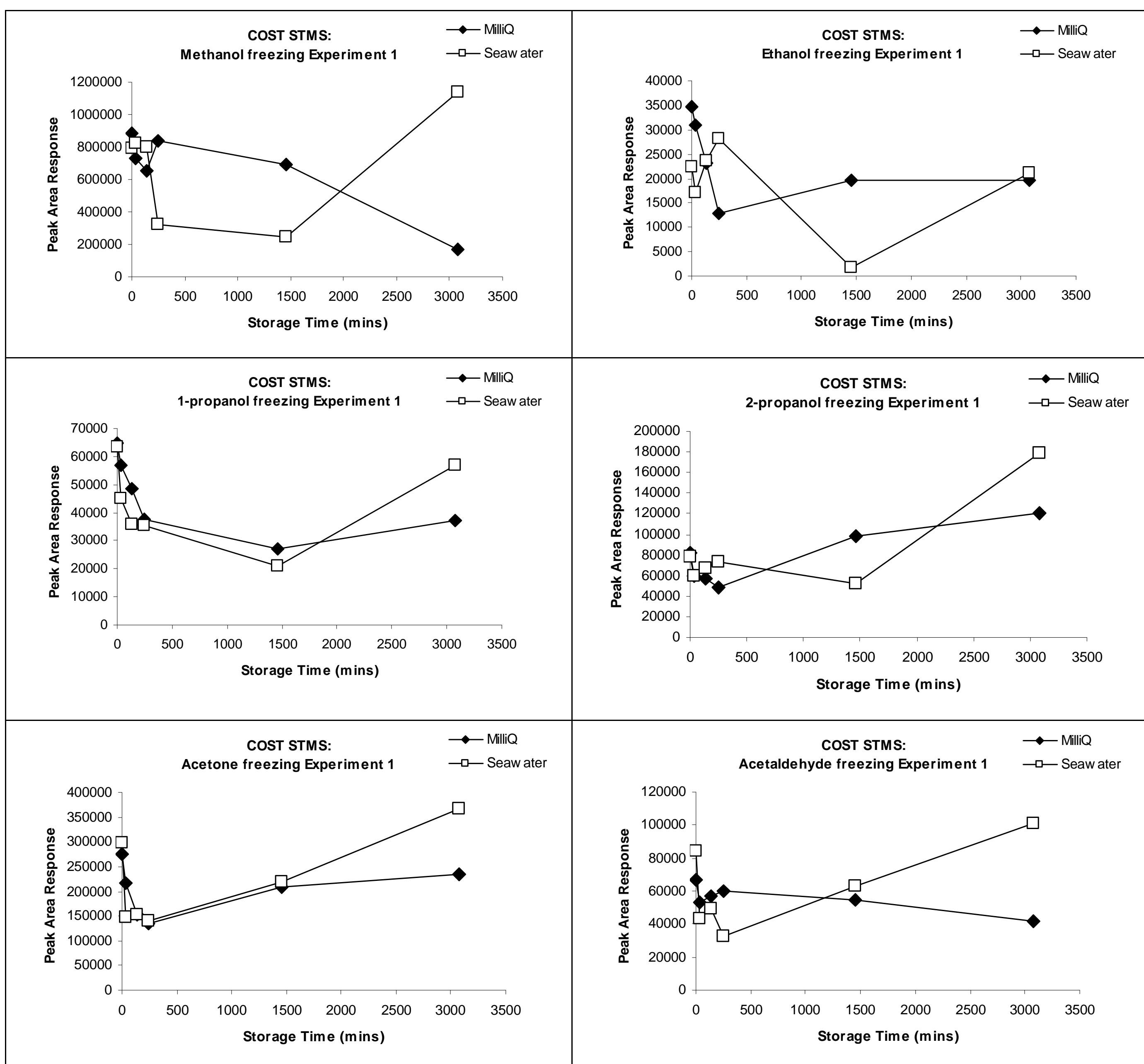
The first question was addressed by freezing multiple liquid standards, made in both milliQ and sea water for comparison, and removing them from the freezer over the course of hours to days to monitor the OVOC levels.

The freezing process could cause the oxidation of organics in the water, leading to altered OVOC concentrations, or could rupture biological cells, potentially releasing OVOCs into solution. The second experiment compared results from two different freezing methods in order to investigate this further.

(1) The first experiment utilized both milliQ water and samples of sea water that were collected from the fjord outside IFM-GEOMAR. 25 mL amber glass vials with crimped caps were flushed with helium and filled with either 10 mL of milliQ or 10 mL fjord water. Each was spiked separately with methanol, ethanol, acetaldehyde, 1-propanol, 2-propanol, acetone, dimethylsulphide (DMS) and propanal. All were frozen cryogenically by inserting into liquid nitrogen for approximately 2 minutes. After this period the samples were inserted into a -80°C freezer until analysis. Blank solutions of these samples were first analysed followed by unfrozen standards in both milliQ and sea water. All subsequent frozen samples were then blank corrected and compared to the response of these standards on the mass

spectrometer. Approximately 30 minutes prior to analysis, samples were removed from the freezer and allowed to defrost naturally.

In each case (blanks, unfrozen and previously frozen standards) 5 mL of headspace was removed from the vial with a gas-tight syringe and injected into a flow of helium gas. OVOCs present in this headspace were then cryogenically trapped with liquid nitrogen in a section of capillary column for 5 minutes. The sample was injected into the GC/MS for separation and detection by removing the liquid nitrogen. The results from this experiment are displayed in figure 1.



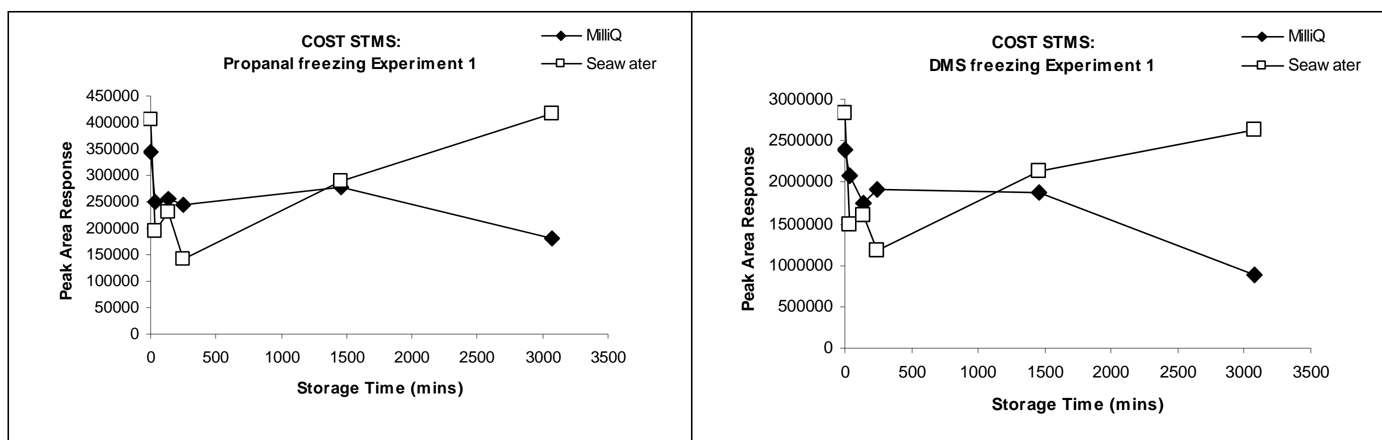
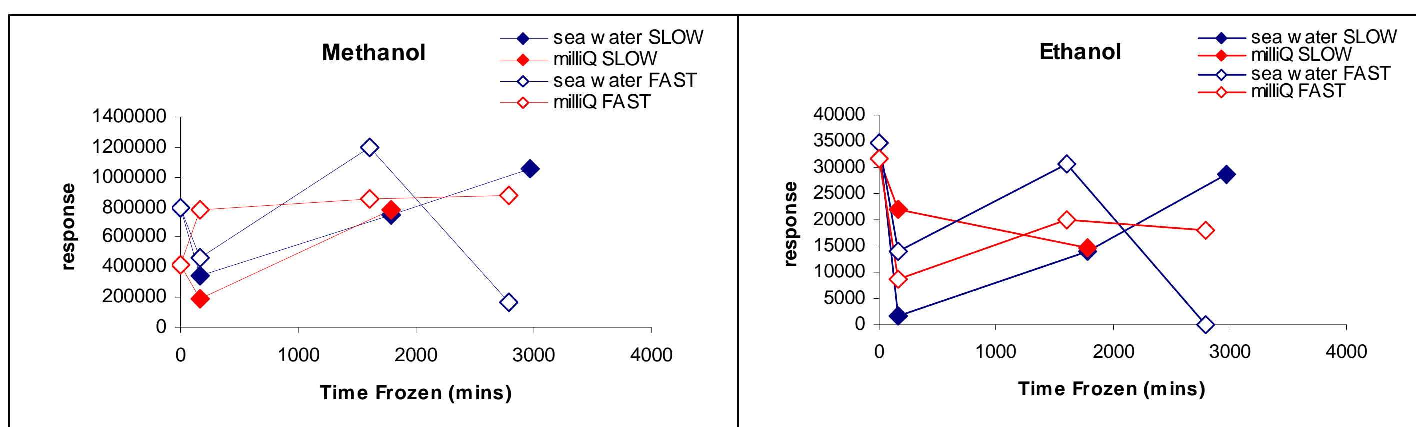


Figure 1: OVOC responses after cryogenic freezing and storage in -80°C freezer.

It can be seen that nearly all OVOC responses undergo a decrease from the initial unfrozen standard response (time zero) in the first few hours, regardless of water type. In seawater samples, the initial OVOC decrease was largely followed by an increase towards the end of the experiment. The milliQ standards often exhibited different trends than the sea water samples, suggesting that biology present in the fjord may have caused OVOC levels to fluctuate. Unfrozen standards were run at the beginning of each consecutive day to show the response of the instrument. These were relatively stable indicating that the change in response was a true reflection of OVOC level in the frozen standards and not instrument drift.

(2) In the second experiment, milliQ and seawater samples were frozen in liquid nitrogen or in a -10°C freezer and fluctuations in their respective levels were measured over time. We hypothesized that fast 'flash' freezing with liquid nitrogen may have been too harsh so this was compared to a slower freezing technique. The samples for this experiment were produced in bulk. Aliquots were syringed into pre-flushed, crimped vials in the same manner as experiment 1. It was suspected that spiking each standard individually may have caused some of the fluctuation observed in OVOC response during experiment 1. Headspace sampling and injection to GC/MS were carried out in the same way. The results are presented in figure 2.



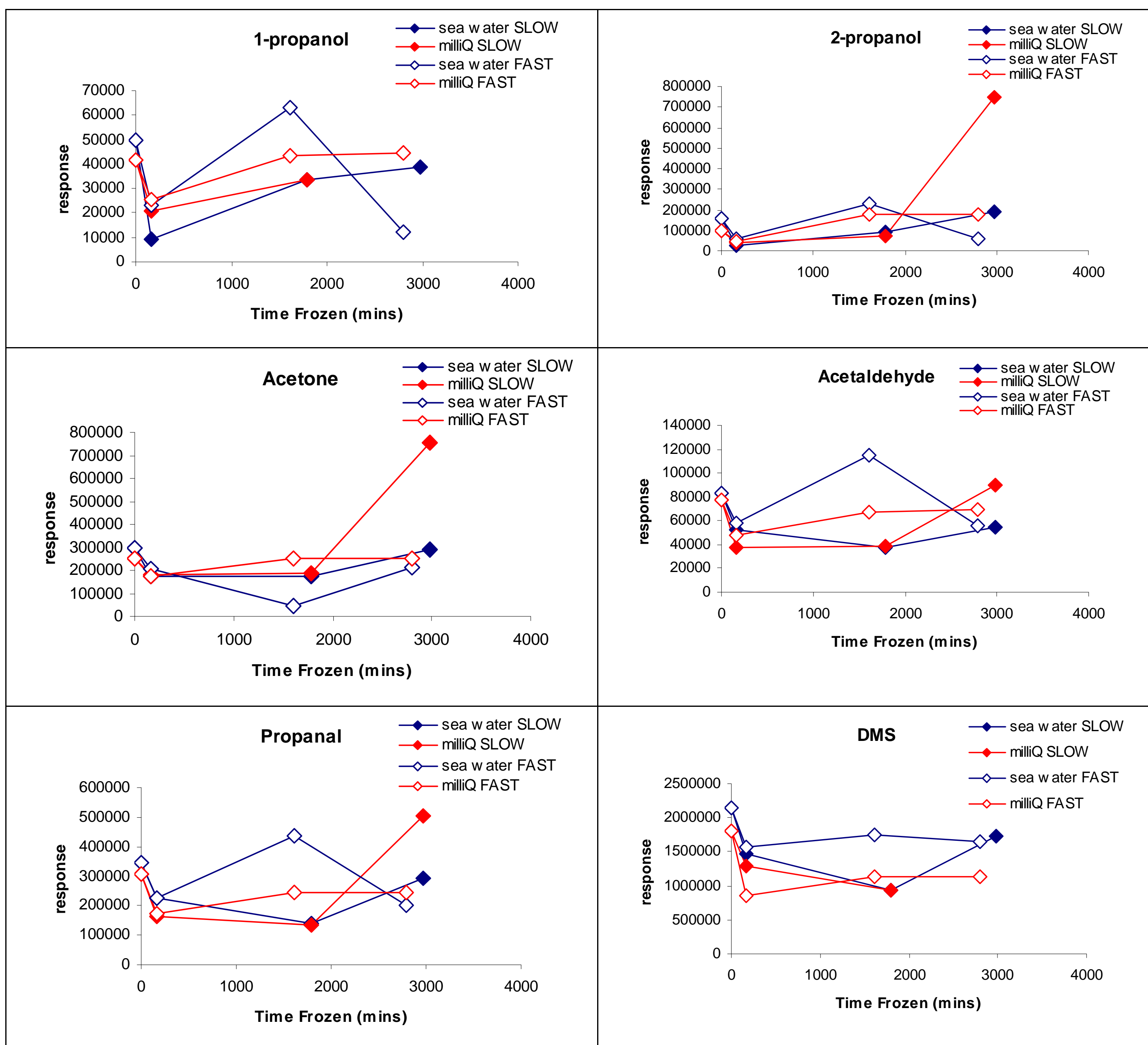


Figure 2: OVOC responses in fast cryogenically frozen standards compared to slow -10°C frozen standards in milliQ and seawater samples. NB: Plots for methanol, ethanol and 1-propanol have had the last point for milliq, slow standard removed. Response was high and the necessary rescaling distorted the other points.

Although there appears to be more stability in the responses seen during experiment 2, there is still an initial period of OVOC decrease during the first hours of storing. This seems to occur in both types of water and for both types of freezing techniques used.

In addition to these experiments, we conducted one last experiment. A sample of fjord water was added to a pre-flushed vial, without being spiked with standard solution, and sampled using headspace injection like those above. It was then flash frozen in liquid nitrogen and allowed to defrost immediately. We re-injected to see if OVOC response had altered. This was mainly to see if flash freezing caused an 'explosion' of cells in biological material found in the fjord water that may release OVOC into solution. No difference was observed but this may have been due to the low sensitivity encountered with headspace injection. This experiment may be repeated when the purge and trap method is working.

OUTCOMES:

This STSM allowed us to observe that levels of OVOCs in frozen samples do not seem to show sufficient stability when frozen and stored for later analysis. During the experiments we were able to gain more knowledge about the analytical techniques used at both institutions by means of direct observations, hands-on experience with the IFM-GEOMAR kit, and through a seminar of my work given during my visit. I gained useful information on the use of ^{13}C labelled acetone as an internal standard and saw data from its use on previous field experiments from Dr Marandino's work.

FUTURE COLLABORATION:

We discussed the application for joint funding between the two institutes for a period of 2 years. This money would potentially fund the inter-calibration of our three individual methods and the performance of culturing experiments to investigate the biological controls on surface seawater OVOC levels.

References:

Hudson, E. D., Okuda, K., Ariya, P. A. (2007). "*Determination of Acetone in seawater using derivatization solid-phase microextraction*." Analytical & Bioanalytical Chemistry **388**: 1275-1282.