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Cruise Report for Sulfur Hexafluoride dosing and analysis aboard R/V Revelle

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The tracer gas, sulfur hexafluoride (SF₆), was released concurrent with the first iron fertilization of the two patches. The procedure for the SF₆ dosing will be briefly described, and estimates of the amount released will be provided. The analytical systems used for measuring the SF₆ concentrations will be described. Comments about the results are listed in a separate file to assist researchers utilizing the results.

Two tanks (steel tank coated with white epoxy paint from MLML, and an unpainted aluminum tank from AOML) were fabricated to the same dimensions. Each tank contained approximately 4840 liters of seawater that was enriched with SF₆. The opening at the top of each tank was covered with either a dosing chamber or a dispensing plate.

The dosing chamber enclosed a gas volume of approximately one liter, and attempts were made to keep the water level at the perforated bottom of this chamber. The gas was removed from the top of the chamber and was returned through a 2 meter long aeration tube at the bottom of the tank at a rate of several liters per minute (see figure #1). The gas being recirculated through the tank was constantly being augmented with SF₆ at a rate of 200-300 ml/min. There was a vent of the top of the chamber to relieve any overpressure.

The dispensing plate allowed a weather balloon to be inflated with water inside the tank as the SF₆-enriched seawater flowed out. To reduce the potential loss of dissolved SF₆ into the gas phase, the dosing chamber was replaced quickly with the dispensing top and all gas bubbles trapped under the dispensing top were removed. The flow out of the tank was maintained by gravity without active pumping. The water that inflated the balloon came from a carboy, or header tank, about two meters above the dispensing plate. The water level in the carboy was maintained at an overflow tap, which ensured a constant head pressure.

Prior to the first fertilization, the seawater in both tanks was enriched. The SF₆ gas cylinder, which contained liquefied SF₆, had been weighed before and after this use. During shipment to New Zealand, the gas cylinder had probably leaked. This resulted in contamination of the analytical equipment. The amount of tracer gas left for use on the southern patch was a concern, so only one tank of seawater was released on the northern patch.

The SF₆-enriched water was released at a rate to ensure complete coverage of the intended patch. It was felt that leaving some water in the tank was better than running out of enriched water before the iron fertilization was finished. After about 41 hours of fertilization the weather balloon in the tank burst instantly diluting the enriched seawater.

The source of the tracer-enriched water was quickly switched to a dynamic dosing arrangement. This arrangement consisted of water and fine bubbles flowing through a 30 meter coil of tubing before release. The dynamic dosing system yielded a lower and more variable SF₆ dosing rate. For the last 15% of the fertilization, the concentration in the stream leaving the ship was about one-third of that during the previous 41 hours. The total amount of SF₆ released in the northern patch was estimated at 28 liters.

During the transit to the southern site, the remains of the burst balloon were removed from the aluminum tank, the tank was refilled with seawater, and the seawater was enriched with SF₆. The simultaneous release of both tanks of enriched seawater proceeded without problems in the southern patch. During the 42 hours of fertilization, an estimated 43 liters of SF₆ were released. A second tracer gas, helium-3, was released along with the SF₆. The helium-3 dosing rate was approximately 10% of that for SF₆. Samples were collected from the casts in the southern patch for later helium analyses.

Approximately 4 liters of SF₆ dissolved in seawater remained in the two tanks after Revelle left the southern patch. This last parcel of enriched seawater was released without the use of the dosing plates during the refertilization during Revelle's reoccupation of the northern patch. The release was done to aid the analysts on the Melville in finding the northern patch with little intention of doing a mass balance.

The amount of SF₆ dissolved in the dosing tank and dosing stream was measured with glass syringes and a gas chromatograph (GC) equipped with a thermal conductivity detector (TCD). A 30-40 ml aliquot of seawater was drawn into the syringe. The remaining 50 ml volume was filled with nitrogen gas. The syringe was shaken for at least 10 minutes, and the headspace gas was pushed through a 0.34 ml gas sample loop. The loop was injected onto a 1/8" by 9' column of molecular sieve 5A with a carrier gas flow of a 15-17 ml hydrogen/min. The TCD had a positive deflection for the SF₆ and oxygen. The chromatograms for all three analytical systems were digitally saved and manually re-integrated. The peak heights of samples, standards, and blanks were used to quantitate the results from the TCD. Peak areas were used with the other instruments.

The SF₆ concentration in the ocean was measured with two instruments employing molecular sieve 5A columns, nitrogen carrier gas, and electron capture detectors (ECD). Some or all five gaseous standards, ranging from 6 to 1109 parts per trillion SF₆, were analyzed periodically to provide a complete calibration curve. One standard was run often to track any changes in the response of the ECD. The analytical blanks for both instruments were initially very high. The blanks decreased to workable levels before the completion of the first fertilization and eventually reached less than twice the ambient concentration of SF₆.

The underway instrument had a LiquiCel gas exchange cartridge through which seawater and nitrogen continuously flowed. The SF₆ migrated through the porous membranes that separated the water and nitrogen streams. The underway instrument provided a measurement automatically nearly every two minutes. The response of the underway

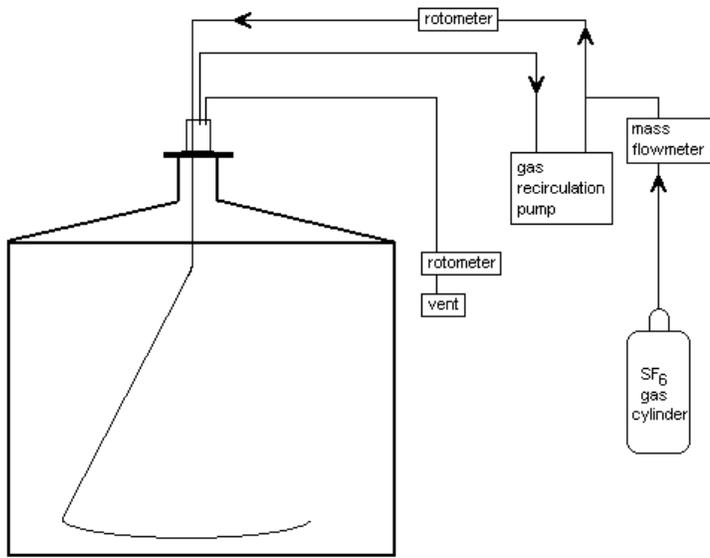
instrument was dependent upon the water and gas flow rates and the exchange efficiency of the cartridge.

The results from the underway instrument were regularly checked versus discrete samples analyzed on the second instrument, a purge-and-trap GC. The dissolved gases in a 264 ml sample were purged and then collected on Carboxen 1000 trap at -50 celsius. Subsequently, the trap was heated and the trapped gases swept through the column and detector. Periodic specific analyses (restrips, replicates) were done to ensure accurate and precise results for discrete samples collected manually from the casts or from the underway seawater stream.

For the reoccupation of the northern patch, it was thought that the underway instrument was not sensitive enough to measure the SF₆ remaining from the first occupation. The discrete instrument was configured to automatically sample the underway seawater supply every six minutes. The results showed that the underway instrument would not have detected the very small residual signal from the first SF₆ release.

Over 6300 measurements were made with the underway instrument. The limit of detection was 2 femtomoles (fM) SF₆. The precision was approximately 1.7 fM or 5% for the LiquiCel underway instrument. The discrete instrument analyzed more than 210 samples collected on 18 casts and more than 360 samples collected from the underway seawater stream. The limit of detection was 0.2 fM. The precision was approximately 0.4 fM or 3%. The ambient SF₆ concentration was measured as 2 fM/liter in surface waters, though smaller values were observed below the mixed layer.

Substantial effort was made to find any systematic biases between the SF₆ results from the Revelle and the Melville. The trends in the highest measurements in both data sets were compared. Specific measurements separated by relatively small intervals of time (6 hours) and distance (0.25 km) were compared. The conclusion was that spatial and temporal variability substantially exceeds any bias that may exist between data sets. From the best match of specific measurements (UTC morning of 4 February), any difference between data sets is less than three times the background SF₆ concentration (~ 2 fM/liter). Any correlation to the SF₆ concentration should be made with the data set for the specific ship



Figure#1 SF₆ Dosing Tank