Methods Development

Pull an aliquot of CH2Cl2 (99.9% Purity) into micro-syringe and weighed on analytical balance.

Flow ~3 L/min high purity N2 through glass-T into standard gas cylinder (Figure 1). Inject CH2Cl2 into glass-T after ~5 minutes of flow. Re-weigh micro-syringe after injection.

Rolled cylinders to ensure CH2Cl2 is well mixed throughout entire cylinder.

Sampled cylinder with Shimdzu GC-14B with 63Ni Electron Capture Detector (Figure 3).

Two columns used: between March and July, a Supel-Q PLOT Column (Column 1, 30 m x 0.32 mm) and after August, a Rtx-1701 Column (Column 2, 30 m x 0.53 mm).

The columns were held isothermically.

The sample loop was ~0.62-mL.

A vent between the standard gas cylinder and the 6-port valve was used to ensure build of pressure did not occur

The decrease in concentration is not fully understood. It is possible that the cylinders are not well mixed; however, this would then yield results that are low. Similarly, losses of the analyte during the injection process, or during sampling from the cylinder would yield results that are low.

There was a larger change of concentration over time and percent difference in calculated versus measured than literature [1-9]; however, in those references, most of the analytes are hydrocarbons instead of halogenated organic compound. Also, the cylinders were analyzed over longer time periods (~2 years minimum), which could result in a more stable average (Figure 4 versus Figure 5).

The percent difference between calculated and measured concentrations is unclear. Contamination from the glass-T and transfer lines were tested and found to be negligible. Also, the analytical balances were carefully calibrated.

There is a 4% and 8% (1 standard deviation) uncertainty with cylinders 1 and 2, respectively. This corresponds well with G. C. Rhoderick’s [7] results; however, lower than the theoretical percent uncertainty from propagation of error from balances (~0.3%).

Future Work

We are working to understand the difference in the calculated and observed concentrations. Future tests will include trying multiple approaches in parallel and trying different polarity compounds.

This work is necessary in order to accurately calibrate instruments to measure low concentrations species in the atmosphere. The drifts currently observed would cause an over estimation of the gases.

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References