

Improving the Sampling and Analysis of Atmospheric Carbonyl Sulfide (OCS) in the GMD Networks

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Recent experimental work in GMD has revealed a number of significant issues regarding the sampling and the GCMS analysis of ambient atmospheric samples for carbonyl sulfide (OCS). Here we detail our current understanding and tentative conclusions as part of our efforts to produce an accurate, artifact-free global OCS dataset. There are currently two GCMS instruments, “M3” and “PR1” in GMD that measure OCS in ambient air, and each instrument has used a slightly different subset of the same suite of NOAA OCS standards to create their respective (and potentially instrument-dependent) OCS calibration scales. Our goal is to reconcile all OCS data to one calibration scale.

To begin with, a recent attempt was made to replicate the NOAA 2004 OCS absolute calibration scale, this time using a new “high purity 99%” starting material from Synquest Labs. Using the same methodology as previously, gravimetrically prepared mixtures of this new OCS were diluted to ambient mole fractions (~ 500 ppt) in zero air, which is a synthetic blend of pure oxygen in nitrogen at ambient ratios. Analyses of three of these new standards on M3 and PR1 yielded an excellent agreement of 0.05% between the two instruments. However, the results of both instruments indicated a ~9% higher response relative to the 2004 scale standards, consistent with the hypothesis that the older standards were prepared from OCS starting material that was considerably lower in purity than the 99+% specified by the manufacturer.

Second, we observed a site-weighted average ~2.1% discrepancy between the M3 and PR1 OCS measurements, with PR1 higher, of the same air samples over the past ~5 years in GMD Halocarbons & other Trace Species (HATS) steel and glass flasks taken at remote global sites. This discrepancy, when considered with the excellent agreement noted above for the very ‘simple’ gravimetric mixtures, suggests that one or both instruments suffer an artifact in analyses of the ‘complex’ mixtures of real air from field sites.

Third, we have recently discovered that Essex Cryogenics, Inc. cylinders purchased in the last few years, and that have been used to prepare OCS standards, can exhibit significant apparent “growth” in OCS mole fraction during storage. While the mechanism for this growth is still under investigation, such drift is carefully monitored and accounted in the ambient OCS datasets.

Fourth and finally, we discovered in 2018 that a suite of Programmable Flask Packages (PFPs) used to sample aboard some aircraft campaigns, such as during portions of the Atmospheric Carbon and Transport (ACT) campaign, were contaminating the sample stream, with some PFPs as much as doubling the ambient OCS mole fraction. Exhaustive searching revealed that the fourteen Viton o-rings used to create the glass-to-metal seals within these PFPs were outgassing OCS. Replacement of those o-rings with non-contaminating Viton o-rings has reduced this issue to less than a 9 ppt (95% C.I.) positive bias.

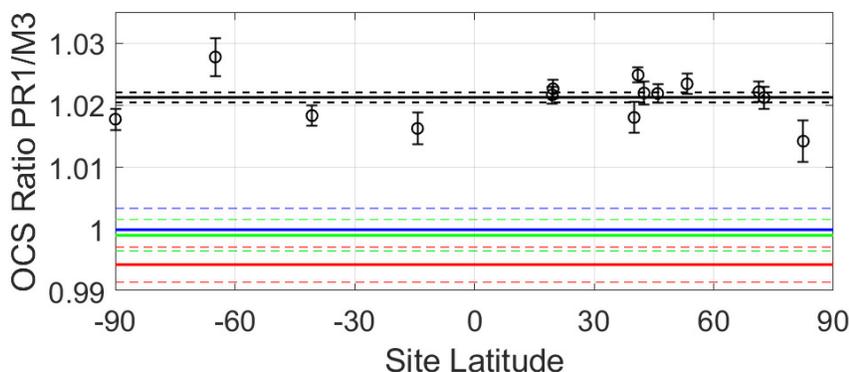


Figure 1. Measured OCS ratios PR1/M3 from two distinctly different sample types. Black circles with 1- σ standard deviation bars represent the remote field site means (weighted by number of samples) for these complex, real air samples. In contrast, the green, blue and red solid lines, with dashed lines of 1- σ standard deviation, represent the much better agreement for PR1/M3 ratios in the relatively simple mixtures of gravimetric OCS standards (tanks SX-3503, SX-3506B and SX-3594, respectively).