Calibration Stability of the SGP ACSM and Total Mass Comparison with UHSAS Measurements

Thomas B. Watson (twatson@bnl.gov), Chongai Kuang, Robert Bullard, Stephen R. Springston
Biological, Environmental, and Climate Science Department/Brookhaven National Laboratory

Introduction

The Aerosol Chemical Species Monitor (ACSM) at the Southern Great Plains site is an instrument that is used to make continuous measurements of the composition of non-refractory aerosol particles using a quadrupole mass spectrometer. The ACSM measures particulate sulfate, nitrate, chloride, ammonium, and organic species with half hour time resolution.

There have been discrepancies identified in SGP ACSM data by several investigators including Jerome Fast, Ann Jefferson, and most recently Qi Zhang. I have been working on methods to evaluate the data in collaboration with Allison McComiskey and others including identification of closure evaluations using aerosol number and size measurements from instruments such as the SMPS and UHSAS and optical measurements such as those made with the Nephelometer.

The first step in addressing these issues was to institute regular calibrations of the instrument

Examples of calibration results are shown in Figure 1.

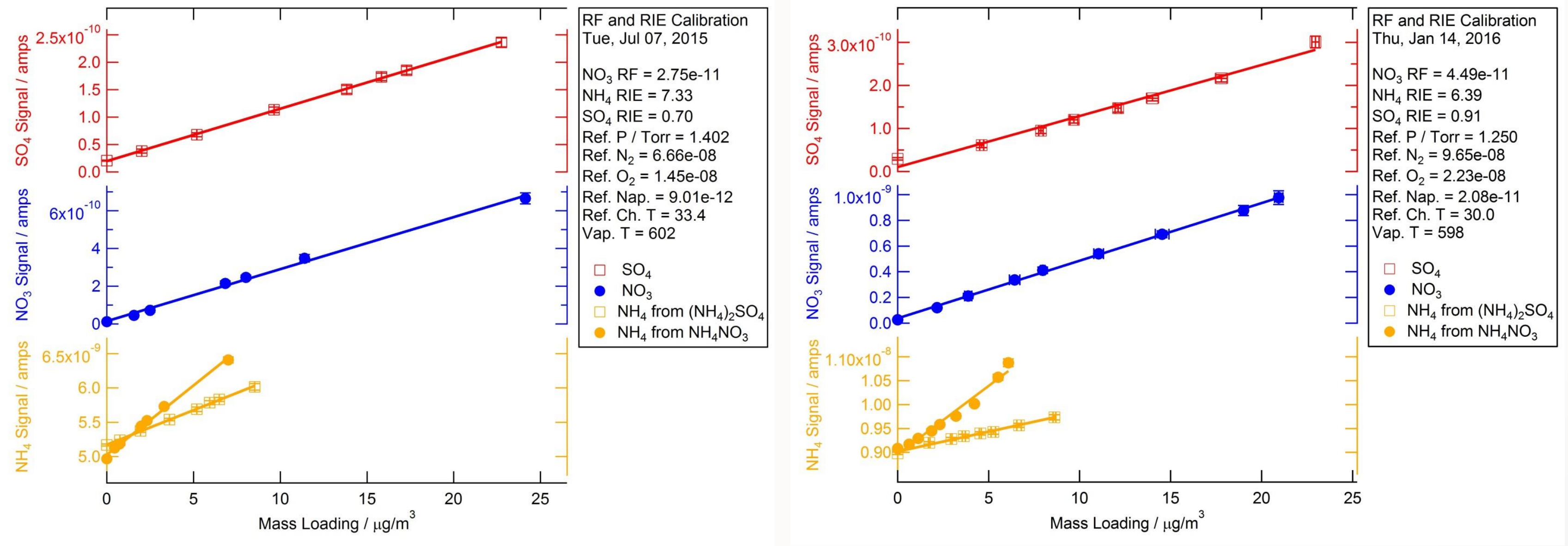


Figure 1: July 7, 2015 and January 14, 2016 ACSM calibration plots.

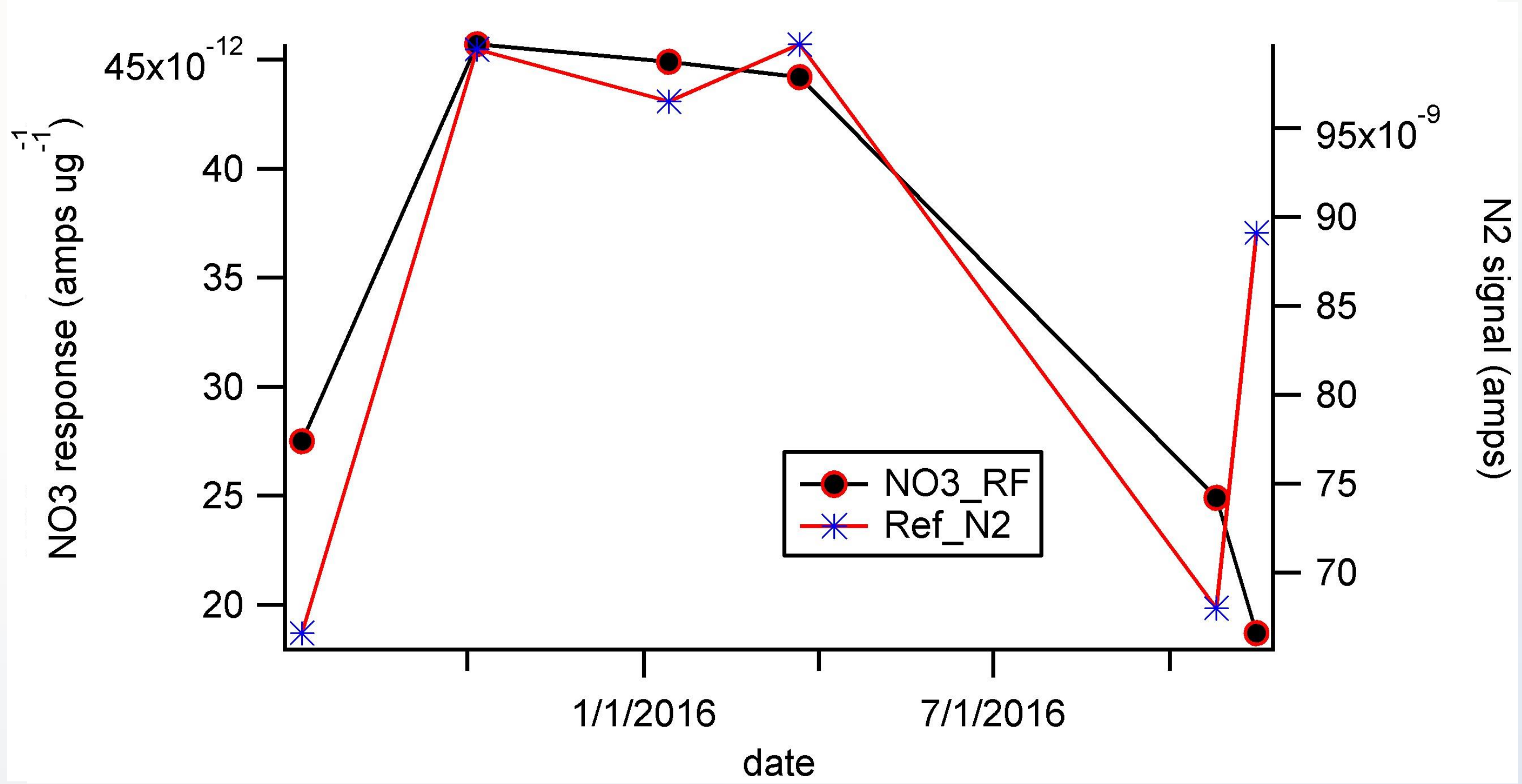
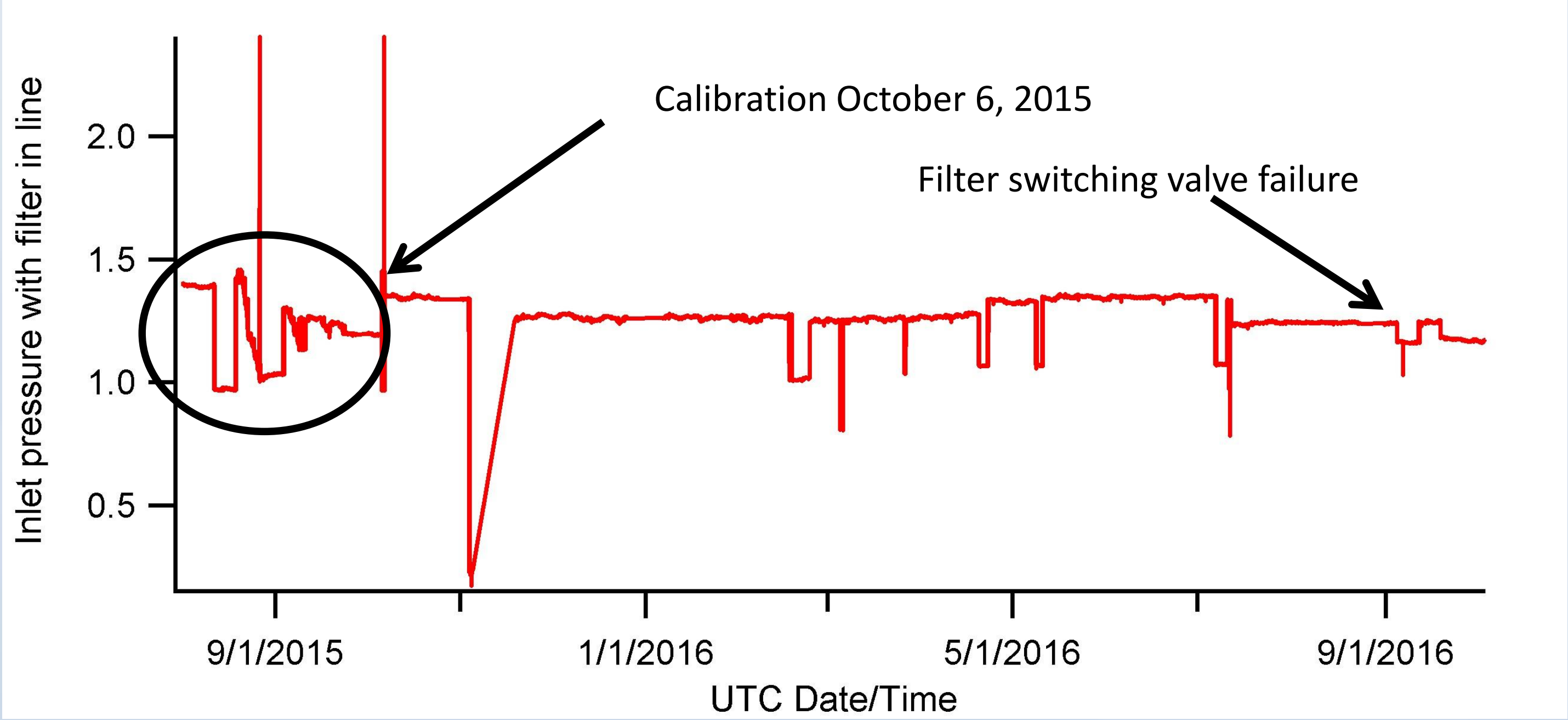


Figure 2: October 15 ACSM NO3 response factor and reference Air beam over 6 calibrations

The SGP ACSM has been calibrated quarterly starting in July 2015. The stability of the instrument of the instrument over the over a year and half and six calibrations is shown in Figure 2. There are three distinct regimes in the NO$_3$ response factor and the N$_2$ response.

- July 2015 to October, 2015
- A very stable period from October 2015 through March 2016
- Changes in August and September 2016

The changes in calibration represented by the jumps in the NO$_3$ response factor and the reference air beam are the result issues with the instrument that changed the instrument response. This can be seen in the inlet pressure (Figure 3) and in the time series of m/z 18, the water signal, and m/x 28, the molecular nitrogen signal (Figure 4).



Calibration October 6, 2015

Filter switching valve failure

Figure 3: Inlet pressure over the test calibration period

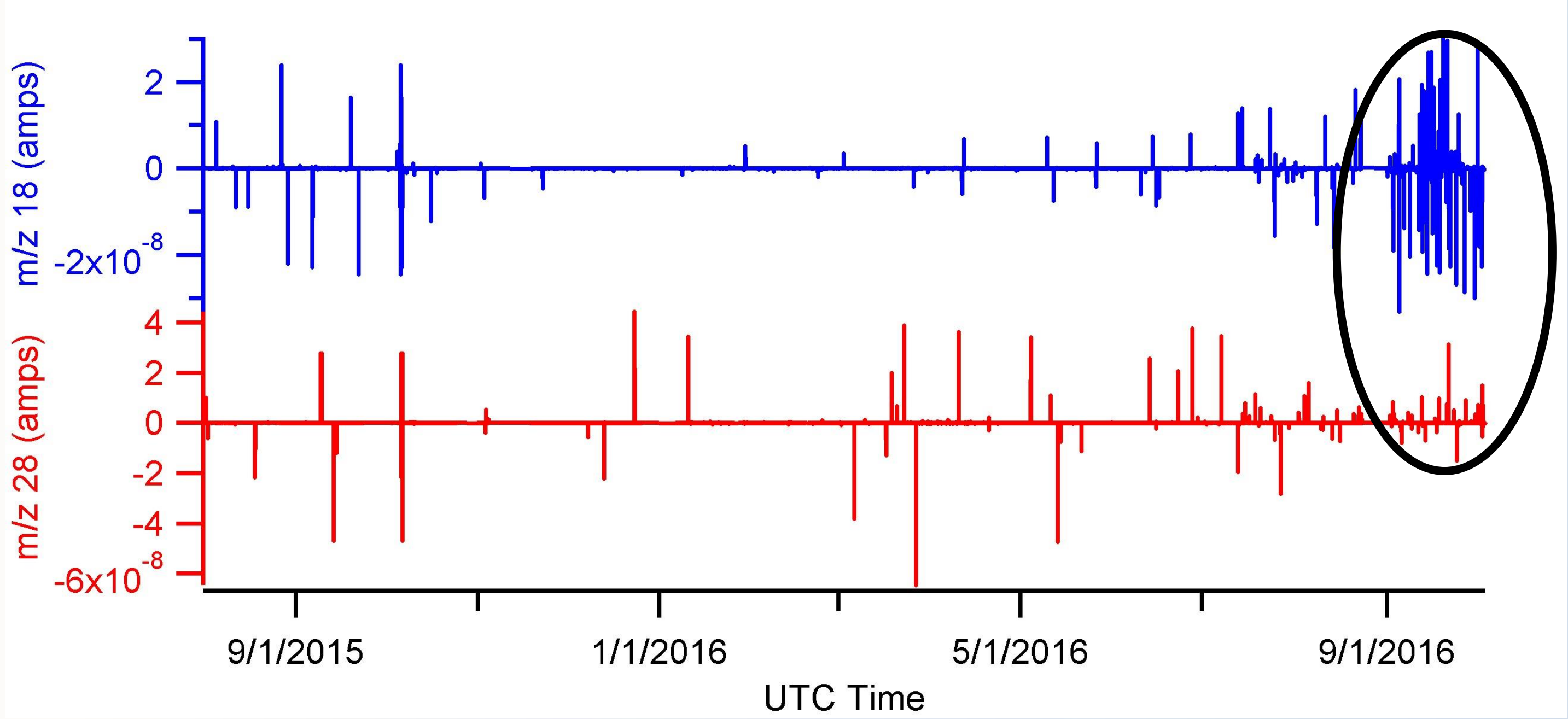


Figure 4: time series of raw signal oat m/z 28 and m/z 18 for September 2015 to October 2016

The problems with the instrument in the August time frame were caused by a change in the configuration of the sample collection system. A critical orifice was inadvertently removed from the line providing ambient air to the inlet of the instrument. This caused a vacuum in the ambient supply line that reduced pressure in the instrument inlet. Little if any aerosol was being introduced into the instrument. This can be seen in Figure 3 where the inlet pressure is low and erratic during August through October, 2015 (black circle). I made a site visit for calibration on October 6, 2015 and installed a new sampling pump that fixed the problem (**DQPR 4839**). The black oval in Figure 4 shows a period when the filter switching valve failed.

Figure 5 shows the water peak, m/z 18, and the N$_2$ peak, m/z 28 immediately after the November 15, 2016 calibration. This calibration was performed after the instrument had been off line for several weeks and the vacuum chamber had been at ambient pressure for part of that time. It is obvious that the signal took several weeks to stabilize

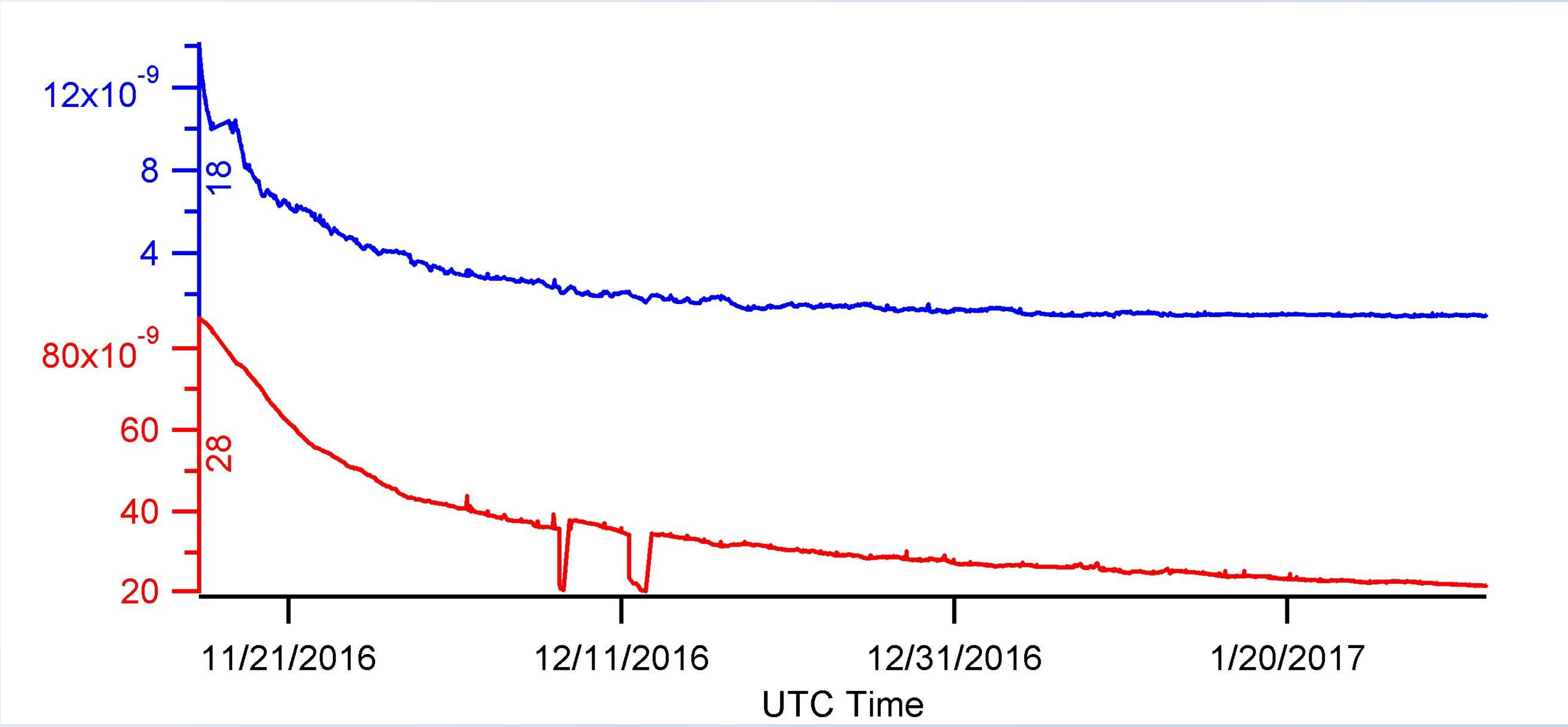


Figure 5: Stability of the water signal (m/z 18) and the N2 signal (m/z 28) over time after venting of the vacuum chamber.

An important test of the ACSM data is a comparison of the total aerosol mass directly measured by the ACSM with the aerosol mass calculated from the instruments that measure aerosol size such as the SMPS and UHSAS. These instruments measure the size distribution of aerosol particles. A mass can be calculated by determining the total aerosol volume and using an aerosol density to get a value for the total mass. I did this calculation with the UHSAS because it covers a size range comparable to the ACSM. I used a density of 1.2 g cm^{-3} for the aerosol density and calculated mass loadings from SGP for the period 2016-11-17 through 2017-01-31. A time series is presented in Figure 6 and a correlation plot in Figure 7.

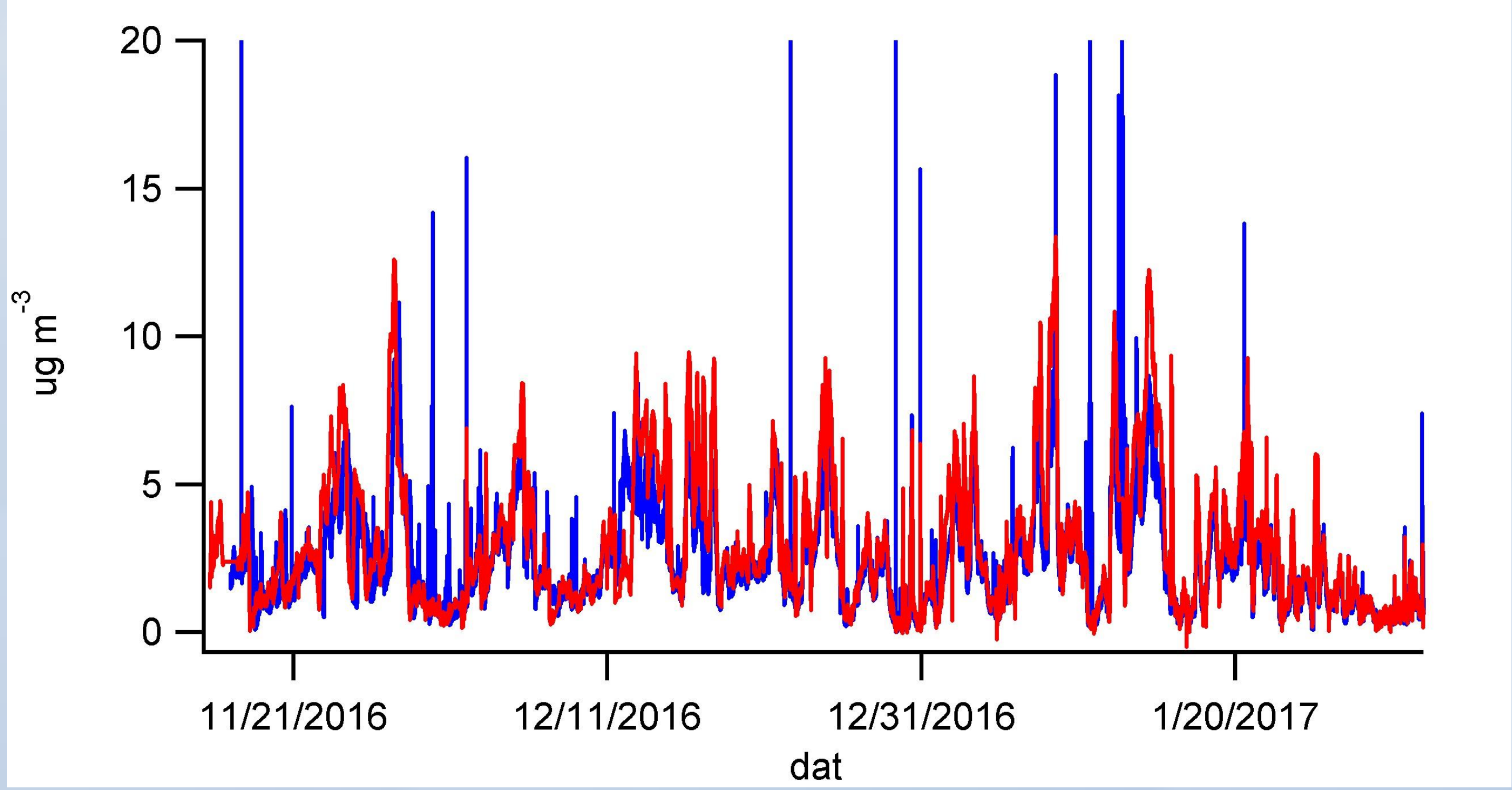


Figure 6: SMPS Mass loading (red). Mass loading calculated from the UHSAS number size distribution (blue).

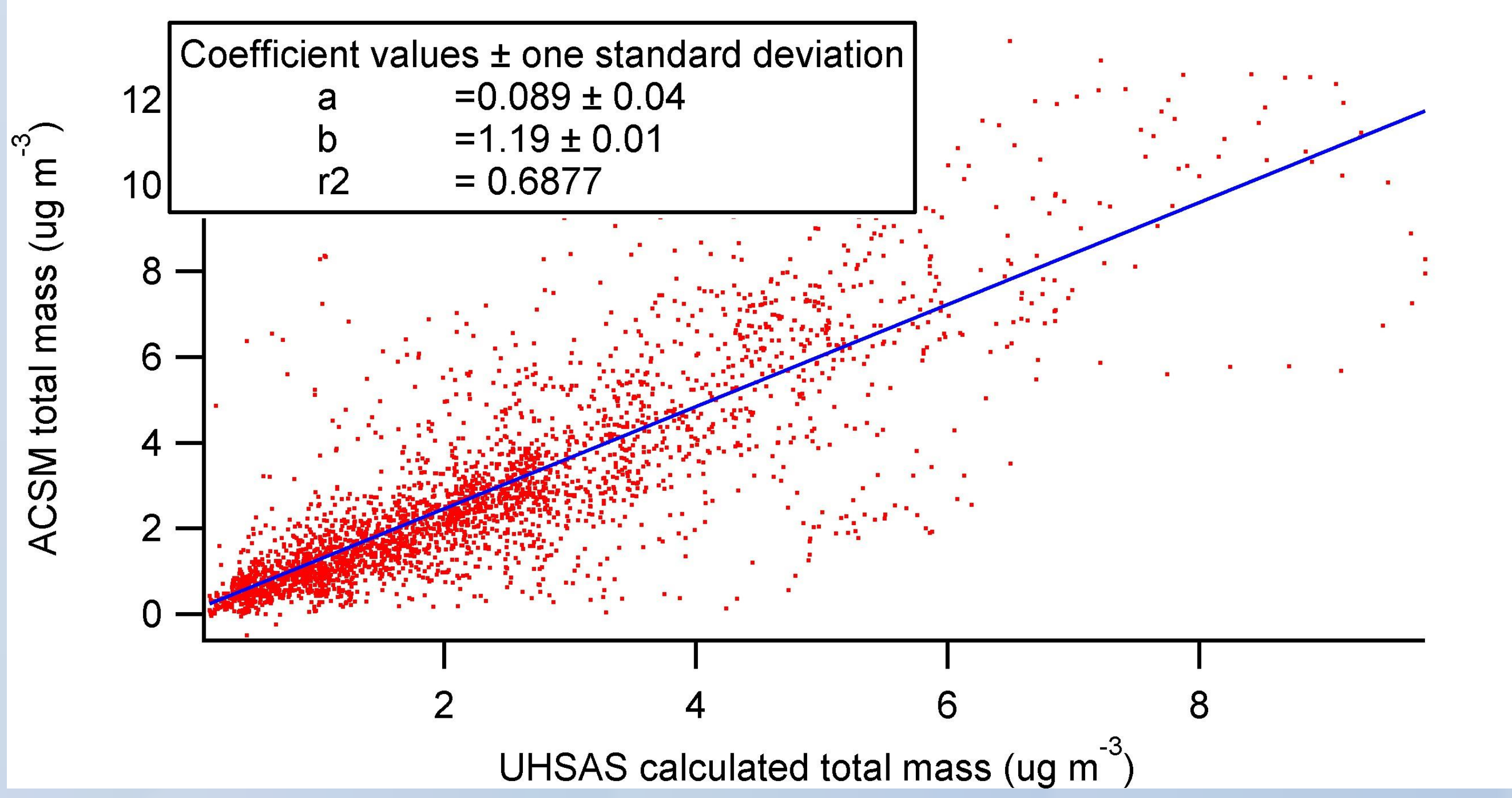


Figure 7: October 24 ACSM and SMPS mass loading time series.

The data are in good agreement with the ACSM total mass about 20% higher than the UHSAS calculated mass. There is a great deal of scatter and the correlation coefficient is low at 0.7, but this is to be expected because of the assumption of a constant density as well as the uncertainties associated with both measurements.

The points raised by Qi are related to the earlier issues, but are also concerned with some errors which may be caused by basic assumptions in the way the data are processed using the Aerodyne software. Concentration of a species is calculated using the equation:

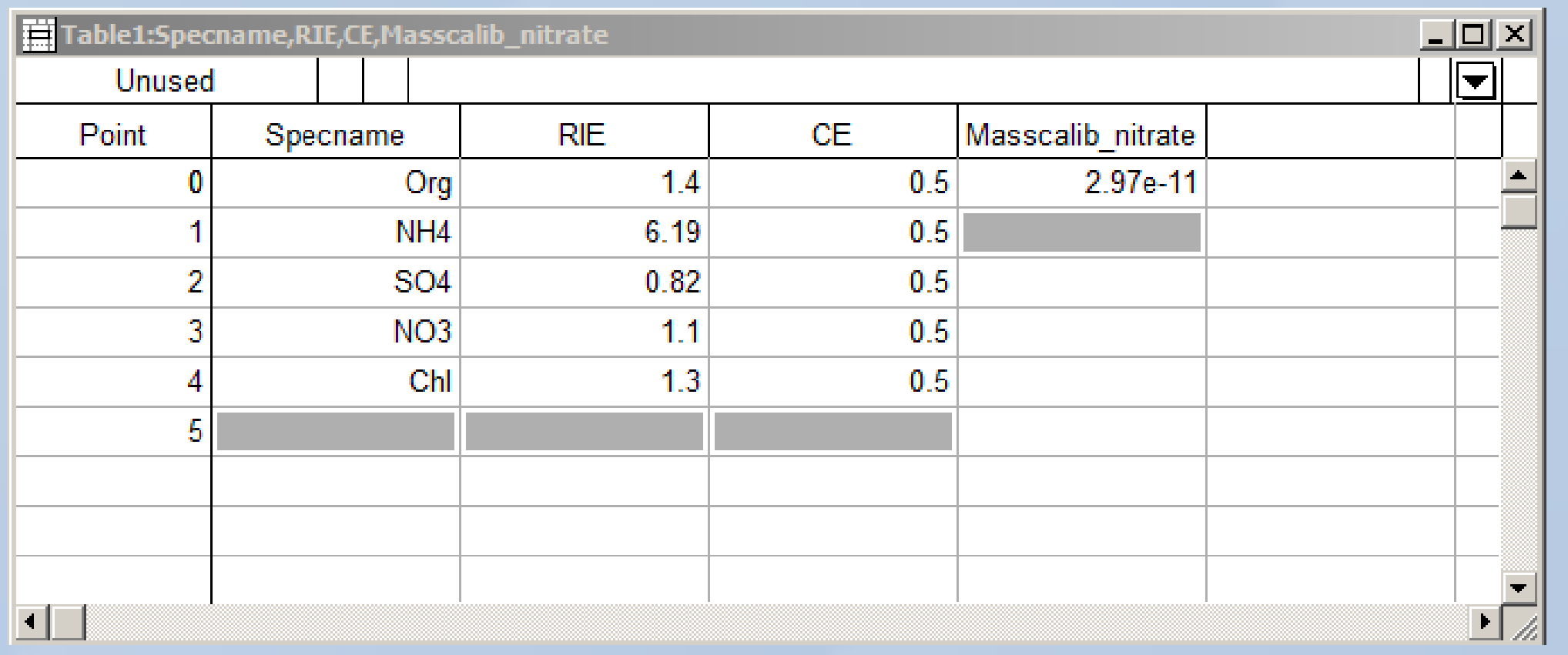
$$C_s = \left(\frac{CE}{T_{m/z}}\right)\left(\frac{10^{12}}{RIE_s}\right)\left(\frac{1}{RF_{NO_3}}\right)\sum_{all\ i} IC_{s,i}$$

Where

$C_s \equiv$ The concentration of species s (µgm^{-3})
$CE \equiv$ The collection efficiency of aerosol mass
$RIE_s \equiv$ The relative ionization efficiency of species s($ions/molecule$)
$RF_{NO_3} \equiv$ the response factor to nitrate(amps of NO3 signal/$\mu g m^{-3}$)
$IC_{s,i} \equiv$ The sum of the ion currents for each of the molecular fragments formed be species s
$T_{m/z} \equiv$ Mass dependent transmission efficiency

There are uncertainties and assumptions associated with most of these terms. The Nitrate response factor (*RF_{N03}*), the relative ionization efficiency of ammonium (*RIE_{NH4}*), and *)*, the relative ionization efficiency of sulfate (*RIE_{SO4}*) are measured directly. Other ionization relative ionization efficiencies are determined based in experience with the precursor of the ACSM, the Aerosol Mass Spectrometer (AMS). The mass dependent transmission efficiency (*$T_{m/z}$*) is measured and value or the theoretical transmission efficiency can be used in the data processing. The default is to use the theoretical value. Collection efficiency *(CE)* is also derived from experience with the AMS.

Finally, and significant for the issues raised by Qi Zhang, is the summation $\sum_{all\ i} IC_{s,i}$ term. This is a sum of all the fragments that correspond to a particular species. It is determined from AMS experiments and has corrections built in to subtract some fragments that may be present in more than one species. Adjustments to this process in response to Qi's findings will be discussed with Aerodyne.



Point	Specname	RIE	CE	Masscalib_nitrate
0	Org	1.4	0.5	2.97e-11
1	NH4	6.19	0.5	
2	SO4	0.82	0.5	
3	NO3	1.1	0.5	
4	Chl	1.3	0.5	
5				

Figure 8: Table of terms used in calculating ACSM mass concentrations.

Conclusions:

- ACSM should be calibrated after the Vacuum chamber is open to atmosphere. There are significant changes in response characteristics of the detector when exposed to oxygen and moisture in ambient air.
- Reference N2 should be set when the instrument is stabilized. This may be several weeks after the vacuum chamber is at atmospheric pressure.
- Ideally, tuning and calibration should be done when the air signal is stabilized, otherwise a reference period should be selected after the instrument has stabilized. This may be require several weeks after the vacuum chamber is at ambient pressure.
- The air beam should be monitored as part of routine diagnostics.
- Mass closure should be made with UHSAS, ASD, and/or SMPS volume to mass conversions as part of routine diagnostics.