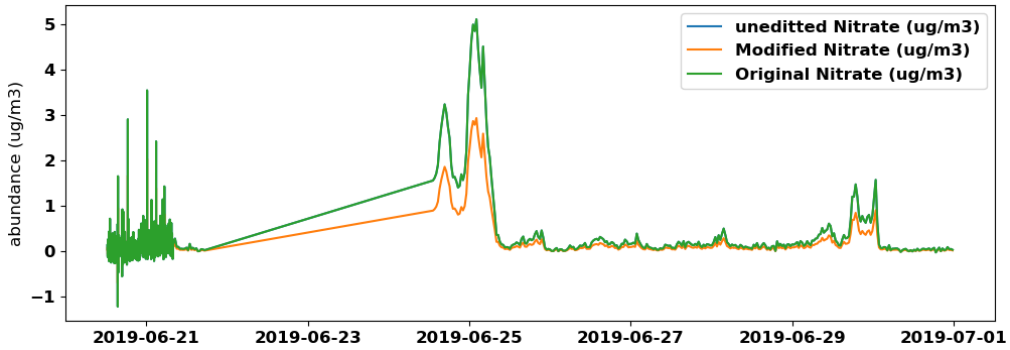
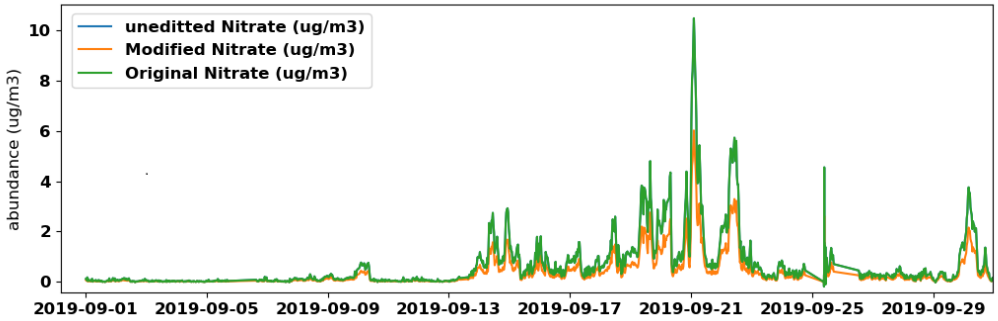
<u>Report on ACSM data</u>:

Date prior to 13th September:

- Note from Firs log book: 13/9/19 9:27 Interrupt SMPS and ACSM monitoring for ACSM alignment and calibration.
    - As the alignment was off before an no calibrations exist for it, any calibrations applied would presumably be guesses.
    - Data from this time is displayed below:





Note: As seen the “original” and unedited data yield the same results

Conclusion: Data from before 13th September is unreliable.

Solution is: excluding Data from before 13th September.

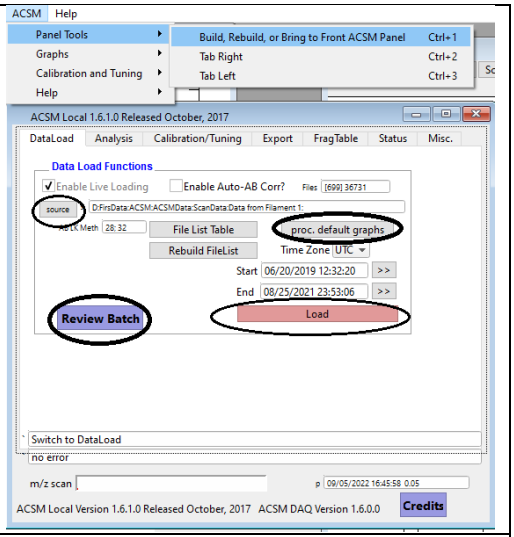
Alternative: Flag data from before 13th September.

How to process the data:

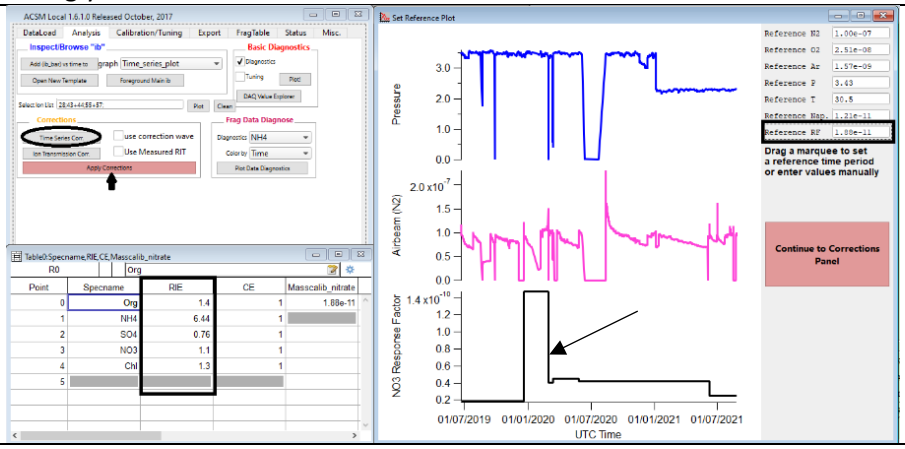
How to change the nitrate mIE factor or the RIE values for the ammonium, sulphate, nitrate, organics and chlorides?

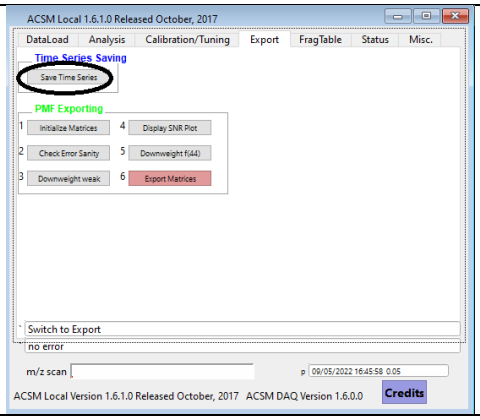
When the data is being taken, just after the calibration is taken, the mIE factor or the RIE values are automatically put in and loaded, as shown below but if these need to be changed retrospectively when the data is being processed, it is uncertain how to do this.

1. To start processing data load using the ACSM function in igor, selecting the "Build, Rebuild or Bring to Front ACSM Panel" function under the Panel Tools.
2. When ACSM local function is opened click source and select folder in which the data you wish to load is present.
3. Check dates are correct for start and end and then click the red load button seen in adjacent figure. Data often takes a while to load if there is lots of data.
4. When files are fully loaded click *proc. default graphs* and data time series should be loaded.



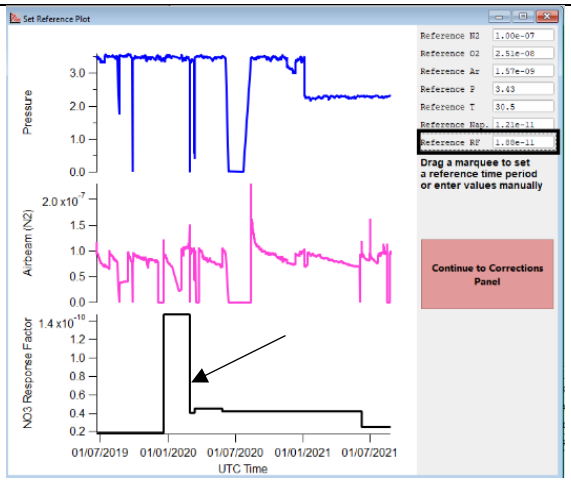
5. Open Analysis tab, and once data is checked for veracity (using various diagnostic plots), click *Time Series Corrections*.
6. Review NO_3 response factor graph and nitrate mIE factor (referred to as *Response RF* value as shown in figure below). Edit RF value using the general average between calibration factors and click *Apply Corrections*. Time Series graph should alter accordingly.
7. Go back to *DataLoad* tab and click Review Batch (circled in Figure above) and locate the ammonium, sulphate, nitrate, organics and chlorides RIE values.
8. Alter ammonium & sulphate RIE values to the general average of each value across calibrations and click *Apply Corrections* in *Analysis* tab. Time Series graph should alter accordingly.



9. Go to *Export* tab and click *Save Time Series* and data file should be generated in *ACSM time series* folder.	

However, what is critical to know is what *nitrate mIE factors* and *what RIE values* should be applied.

What nitrate mIE factor needs to be applied and how should these be applied?

<table>
<tr>
<td>Problem: When data is loaded into the system collectively, it only displays one changeable response factor, the nitrate mIE factor, even though the graph shows several. And the same might also apply for the RIE values for the ammonium, sulphate, nitrate, organics and chlorides.
It is unknown whether, when generating the Time Series Values, whether just of the one RF values is applied, whether the NO_3 response factors are applied from the dates given (as implied by the graph given) or whether these values are applied after an interpolation of these factors.</td>
<td> 
</td>
</tr>
<tr>
<td colspan="2">Furthermore, it is not known given this knowledge, what approach would be best.
Also the MAQS preliminary data is produced live to put on the website, and it is also unknown whether corrections to the response factors are applied automatically.</td>
</tr>
</table>

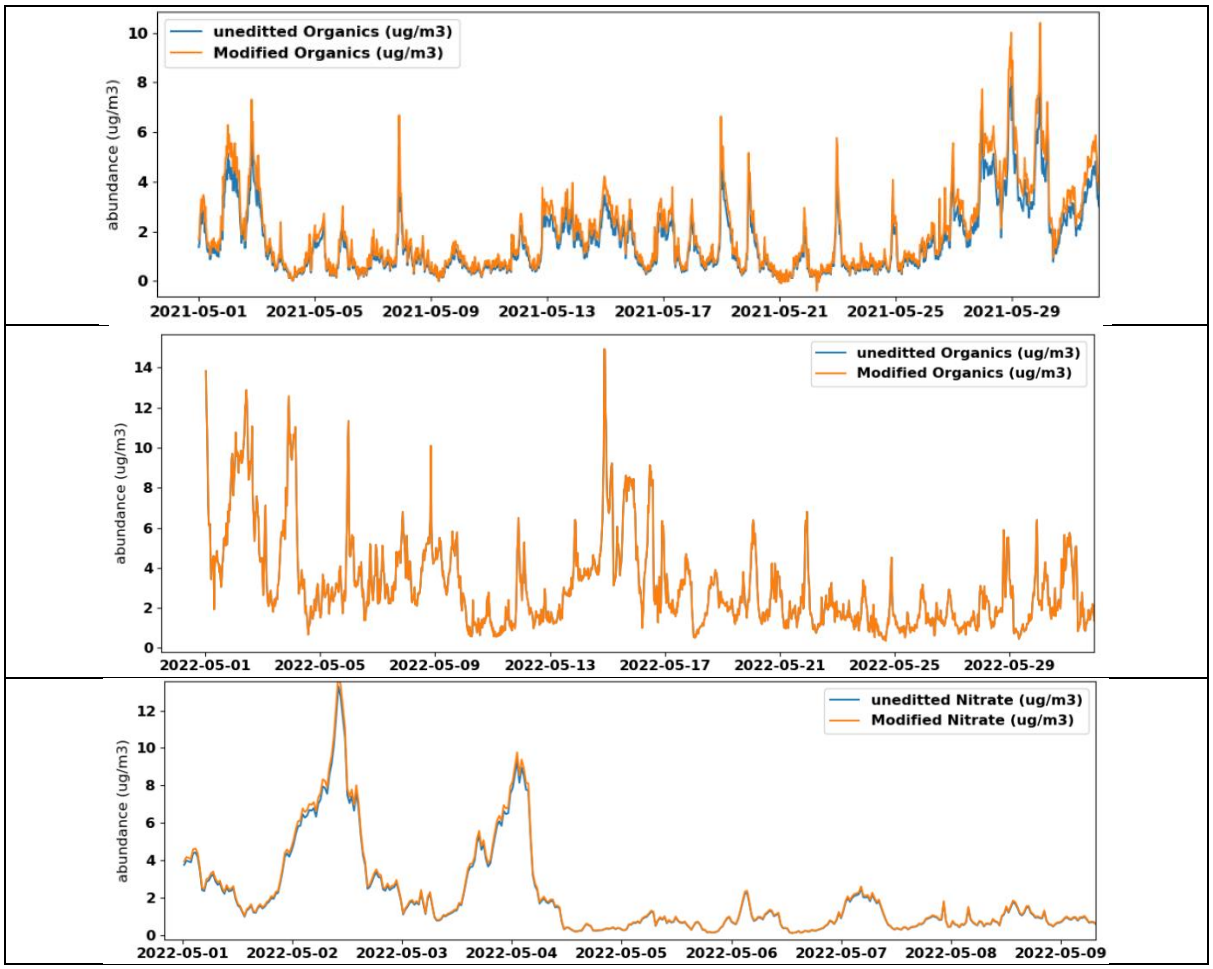
One observation noted by the author is that when a new value is written into the *Reference RF* value and the “apply corrections” button is clicked for the total file is data is altered.

The data for the ACSM spreads from June 2019, with two different points of alignment and 8 different “calibration periods”. To analyse the problems laid out above the data is studied using 4 different ways of processing outlined below:

- The MAQS preliminary data, which the author did not know how is processed initially (only from June 2020).
- The “original data” is where I have divided the data into the period prior to the filament change: Data prior to 23/08/2021 and Data after 23/08/2021
- The “unedited data” in which the data is loaded into the sections where the software says there are calibrations divided by both filament change and calibration but no further changes. Here the software automatically displays the data using the calibrations typed in previously:
    - Filament 1:
        - Cal 1: 20/06/2019 12:32 — 19/12/2019 10:13 – nitrate mIE of 1.88×10^{-11}
        - Cal 2: 19/12/2019 18:40 — 27/02/2020 14:55 – nitrate mIE of 1.47×10^{-10}
        - Cal 3: 28/02/2020 15:30 — 12/03/2020 17:09 – nitrate mIE of 4.08×10^{-11}
        - Cal 4: 12/03/2020 17:10 — 26/05/2020 09:50 – nitrate mIE of 4.53×10^{-11}
        - Cal 5: 26/05/2020 17:09 — 08/06/2020 11:09 – nitrate mIE of 4.18×10^{-11}
        - Cal 6: 08/06/2020 16:11 — 23/08/2021 15:11 – nitrate mIE of 2.49×10^{-11}
    - Filament 2:
        - Cal 7: 23/08/2021 15:40 — 17/09/2021 09:58 – nitrate mIE of 2.49×10^{-11}
        - Cal 8: 17/09/2021 09:58 — present – nitrate mIE of 3.53×10^{-11}
- The modified data – this is where the data divisions given above are also used but new nitrate mIE factors and RIE factors are put inplace. These new values are the averages of all calibrations within that filament – excluding calibration measurements where the nitrate mIE factors are unreliable (see appendix for full details).
  Filiament 1: 3.43×10^{-11} Filament 2: 3.53×10^{-11}

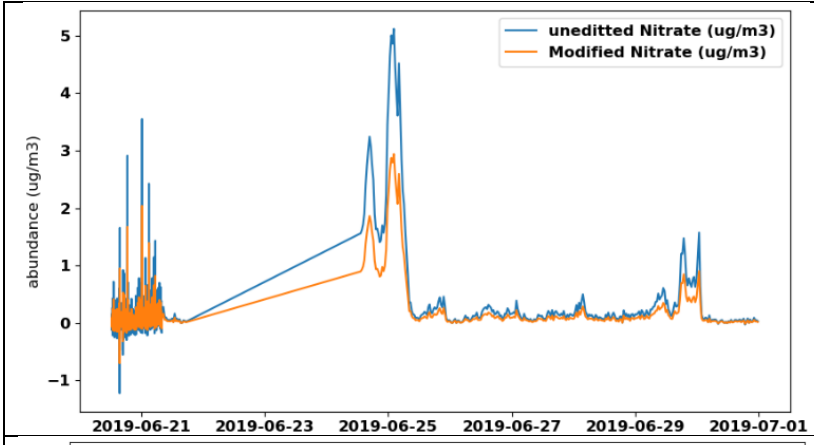
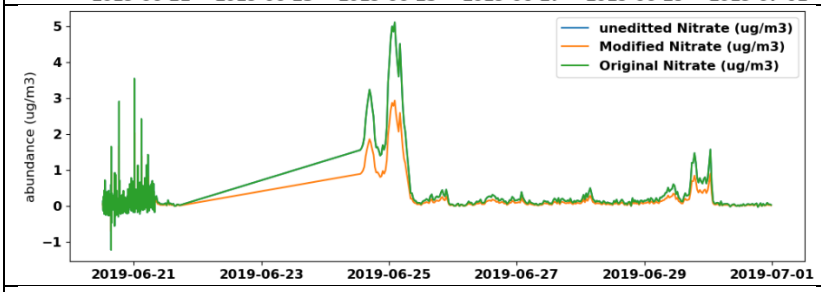
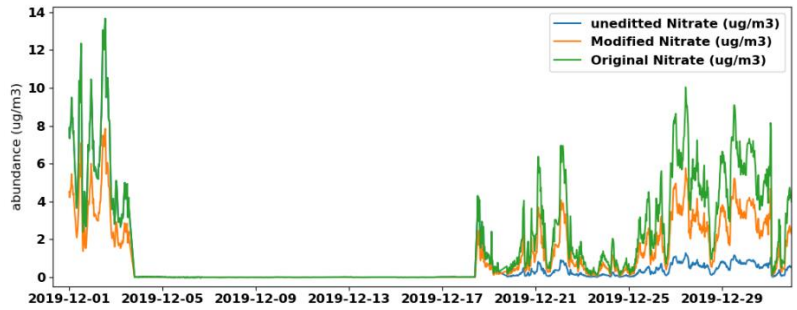
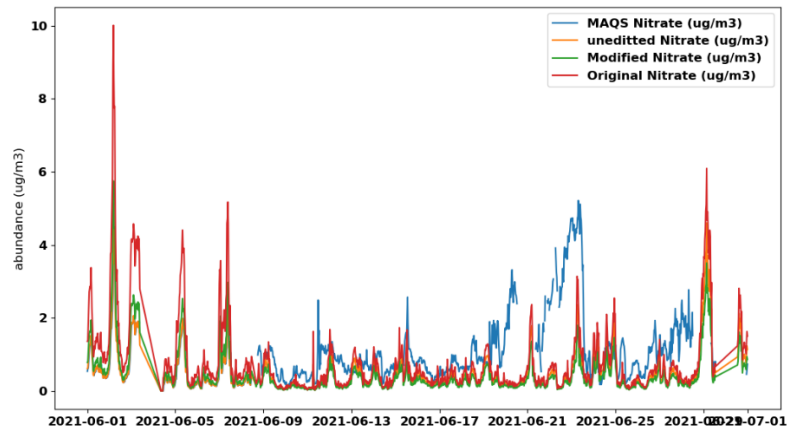
First impressions from Compare the Uneditted and Modified Data?

The main important point to note between the *unedited data* and the *modified data* file is that it proves that by manually altering the response factor and clicking “apply correction” the appropriate data change occurs. This nitrate response factor also has a knock-on effect on the other species mainly below seen in the time series for organics for May 2021.
This is compared to the organics for May 2022, where both the organic RIE and the nitrate response factor are the same for both the *unedited data* and the *modified data* file.
The nitrate RIE was altered here for the purpose of displaying that the changes in RIE does also changes the time series is seen for May 2022 (is minor in third figure below).



Compare the Original Data with the Unedited and Modified data.

By comparing the early Original Data with these other two data sets, it can be seen whether this data applies the calibrations across the board, interpolates the calibrations or does something else.

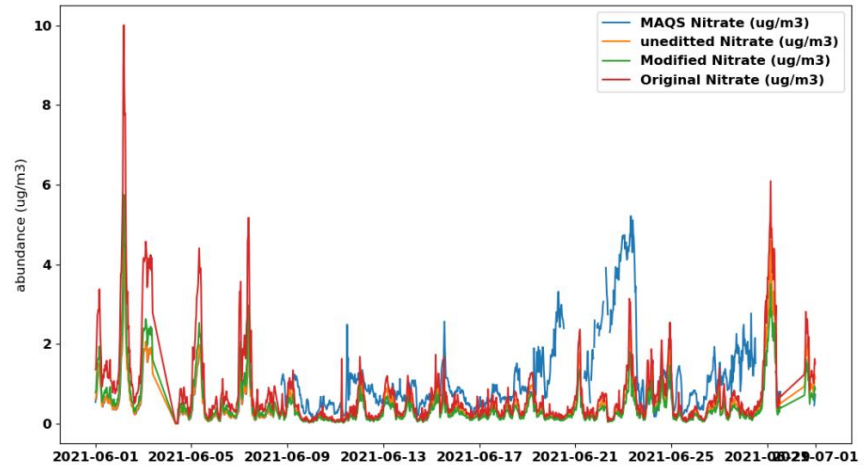
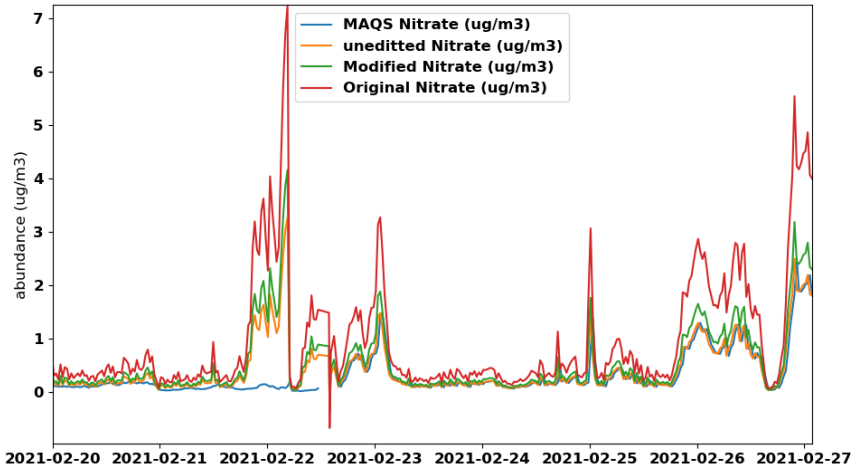
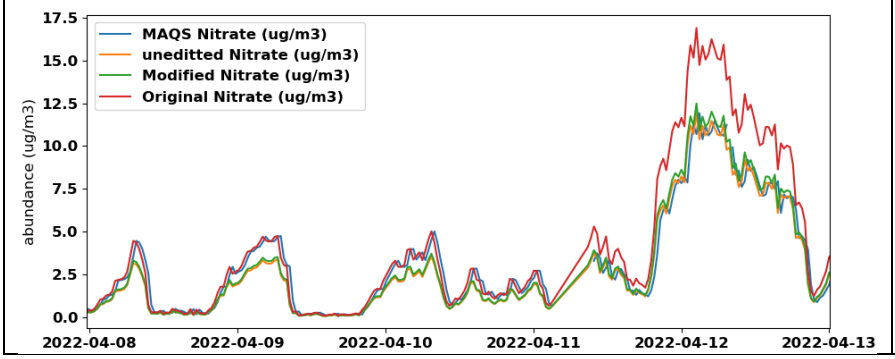
	- Here the Figure shows that there is a clear divergence between the "unedited data" and the "modified data" for the time of June 2019 as the difference in the nitrate mIE factor (the individual mIE and the average mIE values) bears out in the data.
	- However, when the original data is included for June 2019, it is found to be the same time series as the "unedited" nitrate
	- This continues however only till September, where in theory both the unedited data and the original nitrate data should have a new response factor, but the divergence shows this is not true. And the "unedited data" is lower than both *modified* and *original* data
	Later on however the "modified" data becomes lower than that of the "unedited" data. Whereas, the original data stays equally high.

Whereas the nitrate mIE factor for the modified data stays at 3.43×10^{-11} throughout the period of late Sep 2019 to June 2021, the unedited data sees a fall in the nitrate mIE factor from 1.47×10^{-10}, which is above that of the modified data, to 2.49×10^{-11}, which is below that of the modified data. At the same time the nitrate abundance in the unedited data as starts out very low in September 2019

but rises to exceed that of the modified data by June 2021. This shows that there is an inverse relationship between the nitrate response factor and the nitrate abundances (as well as the abundance of the other species measured).

Furthermore, the lowest nitrate mIE measured of this period was that measured during the first calibration, 1.88×10^{-11}, and therefore this would produces the highest nitrate abundances. As the "original data" stays equally high throughout, it is thought that the first calibrations, that with the lowest nitrate mIE was applied across this data. So, when all the data is grouped together, regardless of whether there are different response factors built into the software it appears that the response factor applied in the processed data is the first response factor put in. However, as this has not been fully proved, it is the author's view that each "calibration period" where these calibrations have been put into the software should be separated out, when processing so that if changes needed to be made they can be altered on a "set by set" basis.

Compare all data with the MAQS preliminary data

	The MAQS measurements look odd at first because they seem not to fall into the pattern of any of the previous types of adjusted data types (see figure for July 2021).
	However, there are points where the MAQS data falls in line with the data. In late 02/2021 this happens where it is very out of sync then suddenly matches the “unedited data” This occurs on 22/02/21 when ACSM system restarted, new calibration likely applied
	This is further seen in April 2022, when MAQS starts in sync with the original Nitrate and then moves into the unedited nitrate. 11th April also sees a software crash

Conclusion: it appears that the preliminary data loads directly from the first calibration that was seen on that software launch period and when the software crashes this is reloaded

Follow-up: relaunch software when calibrations apply?

What does the literature say about the Nitrate Response Factor and the RIE factors:

An Aerosol Chemical Speciation Monitor (ACSM) for Routine Monitoring of the Composition and Mass Concentrations of Ambient Aerosol by ***N. L. Ng***:
Experiments conducted at shorter time intervals have demonstrated that the instrument response drift is negligible during the typical ambient and particle free modes. Thus, in practice, calibration of the ACSM is based on determining an instrument response factor, *RF*, using NH_4NO_3 calibration aerosol

Sources and processes that control the submicron organic aerosol composition in an urban Mediterranean environment (Athens) by **Iasonas Stavroulas**:
The average calibration across the history of the ACSM should be used in the data processing. Calibration is remarkably stable and calibration every six months is adequate

Variations in the chemical composition of the submicron aerosol and in the sources of the organic fraction at a regional background site of the Po Valley (Italy) by Michael Bressi:
Thus, for several-months campaigns with an ACSM, we suggest using an average nitrate response factor determined by the slope of all plotted calibration points, independently of the calibration
We also suggest using an average ammonium RIE, which can be calculated as the average of every seasonal calibration (variation larger than ours see below)

Table 2. Calibration history of SGP ACSM collected over seven years of operation. The missing values on 7/3/2013 and 11/15/2016 are because of documented problems with the calibrations. "Stdev" is standard deviation. "rel stdev" is relative standard deviation.

Date	RF NO_3	RIE NH_4	RIE SO_4	Ref N_2	Ref NO_3/Ref N_2
4/14/2010	4.40E-11	5.60		9.90E-08	4.44E-04
7/3/2013					
8/1/2014	2.97E-11	6.19	0.82	5.95E-08	4.99E-04
9/3/2014	4.08E-11	7.09	1.07	8.11E-08	5.03E-04
7/7/2015	2.75E-11	7.33	0.70	6.66E-08	4.13E-04
10/6/2015	4.57E-11	5.77	1.03	9.94E-08	4.60E-04
1/14/2016	4.49E-11	6.39	0.91	9.65E-08	4.65E-04
3/22/2016	4.42E-11	7.76	1.05	9.97E-08	4.43E-04
10/25/2016	2.49E-11	4.28	0.65	6.80E-08	3.66E-04
11/15/2016					
8/24/2017	2.81E-11	5.13	0.60	8.86E-08	3.17E-04
2/5/2018	2.27E-11	5.40	0.52	5.74E-08	3.95E-04
Average	3.53E-11	6.09	0.82	8.16E-08	4.29E-04
Stdev	9.41E-12	1.08	0.21	1.73E-08	5.86E-05
rel stdev	0.27	0.18	0.26	0.21	0.14

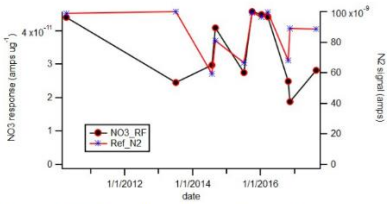


Figure 3. The nitrate response factor (RF_{NO3}) and reference air beam (Ref_N_2) versus time.

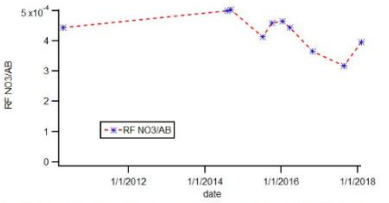


Figure 4. (RF_{NO3})/AB versus time. The values collected on 7/3/2013 and 11/15/2016 have been removed because of documented problems.

First ARM Aerosol Chemical Speciation Monitor Users' Meeting Report by T. Watson: The average calibration across the history of the ACSM should be used in the data processing. Calibration is remarkably stable and calibration every six months is adequate. Deviation from the average should be, used to assess the quality of the calibration.

Conclusions to this report:

- Exclude data prior to September 2019
- Processing should occur in a calibration by calibration set while separating out the filament changeovers too
- All RIE and mIE values should be general averages of those measured over the lifetime of the filament. (provided there is now drift)
- Manually insert flags where data appears to have pressure and voltage and leak problems
- Below 0.2 um/m^3 the measurements are below detection limits
- Software should be relaunched for every calibration to adjust the preliminary data (old prelim data should be warned off)

Averages used for Current Data (v 2.0)

The current averages that are used for ACSM data version 2.0 are displayed below

Data set for Filament 1:

Calibration Date/Time	Nitrate mIE	Organic RIE	NH_4 RIE	SO_4 RIE	NO_3^- RIE	Chl RIE
13/09/2019 15:30	1.88×10^{-11}	1.40	6.44	0.76	1.10	1.30
*19/12/2019 18:40**	*1.47×10^{-10}*	*1.40*	*4.60*	*1.36*	*1.10*	*1.30*
28/02/2020 15:30	4.08×10^{-11}	1.40	3.84	1.10	1.10	1.30
12/03/2020 17:10	4.53×10^{-11}	1.40	4.20	1.42	1.10	1.30
26/05/2020 17:09	4.18×10^{-11}	1.40	4.18	1.03	1.10	1.30
08/06/2021 16:11	2.49×10^{-11}	1.40	3.20	1.52	1.10	1.30
Average	**3.43×10^{-11}**	**1.40**	**4.37**	**1.17**	**1.10**	**1.30**

*note – the calibration values from 19/12/2019 have been found to be faulty and so is excluded from the calculation of these averages

Data set for Filament 2

Calibration Date/Time	Nitrate mIE	Organic RIE	NH_4 RIE	SO_4 RIE	NO_3^- RIE	Chl RIE
17/09/2021 09:58	3.53×10^{-11}	1.40	5.23	1.60	1.05	1.30
04/10/2022 09:58						
Average						