Last Updated: 4/4/2023

This readme is R1 for GC-Vocus data collected during the Aerosol Growth in the Eastern North Atlantic (AGENA) campaign at ARM ENA site on Graciosa Island, Azores.

Site: 39.0916°N, 28.0257°W (<https://www.arm.gov/capabilities/observatories/ena/locations/c1>)

Dates: June 1, 2022 – July 15, 2022

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Anyone accessing or using the data (including for proposals, presentations, or publications) must contact authors prior to access and use. Data cannot be utilized for proposals, presentations, or publications by anyone not involved in the AGENA study until summer 2024.

Data Collection and Quantification:

All VOC data was collected with an Aerodyne/Tofwerk Vocus PTR-ToF-MS with a coupled GC thermal desorption preconcentration system. Data reported here include quantified measurements of 12 VOCs at 5 minute time resolution measured with the RT-Vocus and quantified measurements of isoprene measured by the GC-Vocus.

Dimethyl sulfide was calibrated in field every few days with an isotopically labeled dimethyl sulfide standard (D3-DMS). All other VOCs reported here were calibrated in lab post-field and scaled based on the ratio of in-field and post-field D3-DMS calibration factors. For isomers, the calibration factor for one of the isomers was applied to determine the concentration of all isomers; the isomer used for each is noted in the table below. Information on the calibration standard for each molecule is listed in the table next to the molecule. Uncertainties are reported as the uncertainties in the calibration standard.

The ratio of GC-Vocus sensitivity to isoprene to RT-Vocus sensitivity to isoprene was determined in lab post-field. We assumed this ratio was constant and used this ratio with the in-field RT-Vocus sensitivity to isoprene calculated above to determine the in-field GC-Vocus sensitivity to isoprene.

All RT-Vocus and GC-Vocus data are background subtracted. RT-Vocus zeros were collected for four minutes every 30 minutes by overflowing the full inlet with zero air from a zero air generator. Background subtracted RT-Vocus signals are calculated by subtracting the linear interpolation of the average zero signal during the last three minutes of each zero from the RT data. GC-Vocus zeros were collected in the chromatogram immediately prior to the ambient sample chromatogram and used for background subtraction of the ambient sample after.

RT-Vocus limits of detection (LOD) are calculated according to Eq. 1 in Bertram et al. (2011) for a 5 minute averaging time at a signal-to-noise ratio of 3. The LOD lowered by roughly a factor of 2-3 from the beginning to end of the study due to the calibration factor of D3-DMS increasing during the study. As such, the LOD reported below is the average LOD at 5 minute averaging time for the study.

GC-Vocus LODs are calculated as the full width half maximum of the chromatographic peak multiplied by three times the standard deviation of the baseline divided by the sensitivity, as done in Claflin et al. (2021). GC samples were collected by preconcentrating a volume of air, either 1.5 L or 3 L, during the study. LODs are reported for each configuration.

Flags:

Flags are derived from RT-Vocus data collected during AGENA. RT-Vocus sampled at 1 Hz for the majority of the day, but was down for ambient sampling during instrument zeros, calibrations, and when collecting chromatograms with the GC-Vocus. We used the 5-minute averaged RT-Vocus data to derive these flags and so do not have flag information for the periods when the RT-Vocus was not ambient sampling currently.

Pollution Flag:

This flag aims to capture pollution from airplane landing and departures, airplane idling, and any car pollution on the airport runway or near the site. A large set of VOCs, including alkanes, alkenes, carbonyls, and aromatics, have been shown to be tracers for airplane and airport activity, with total VOC higher during airplane idling compared to departure or landings (Mokalled et al. (2019)). We use three ions in the RT-Vocus data, C9H12H+, C8H10H+, and C7H8H+, corresponding to C9 aromatics, C8 aromatics, and toluene, respectively, since these three molecules should only have an anthropogenic source. Using the 5-minute averaged data, any time point when any of the three ions’ signals was greater than 1.5 times their baseline signal was flagged as polluted. This resulted in removing 14% of the 5-minute averaged time points.

Grass-Cutting Flag:

This flag captures the grass-cutting events that happened at and near the site. Hexenal is released during grass-cutting and drying (de Gouw et al. (1999)). Using the 5-minute averaged ambient data, any time point when the C6H10OH+ ion, representing hexenal, was greater than 1.6 times its baseline signal was flagged as a grass-cutting event. This method was validated using three documented observations of grass-cutting during AGENA on June 14, June 26, and July 4.

Data Included:

A. RT-Vocus Dataset

1. Datenum time stamp in Matlab serial time in UTC-0 local Azores time. Data was saved at 1 Hz and the datenum time stamp corresponds to the middle point of the measurements for the 5 minute down-averaging.
2. Fractional day of year time stamp (DOY) corresponding to datenum.
3. RT-Vocus measurements of VOC in parts per trillion (ppt) at a 5 minute averaging time. Time points with no available RT-Vocus ambient data or data that failed QA/QC are reported with NaN. Time points where the ambient signal is below the background are left as negative values. Provided molecules in the dataset are listed in the table below.
4. Pollution flag derived from RT-Vocus 5 minute averaged measurements.
	1. NaN = RT-Vocus ambient data is not available
	2. 0 = Not polluted
	3. 1 = Polluted
5. Grass-cutting flag derived from RT-Vocus 5 minute averaged measurements.
	1. NaN = RT-Vocus ambient data is not available
	2. 0 = No grass-cutting
	3. 1 = Grass-cutting

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| **Molecule** | **Header** | **Ion** | **LOD (ppt) at 5 min. averaging time** | **Uncertainty** | **Calibrated with:** |
| Dimethyl sulfide | DMS | C2H6SH+ | 1.75 | ±5% | D3-DMS4 |
| Acetonitrile | Acetonitrile | C2H3NH+ | 8.74 | ±5% | Acetonitrile1 |
| Ethanol | Ethanol | C2H6OH+ | 58.4 | ±5% | Ethanol1 |
| Acetone | Acetone | C3H6OH+ | 9.27 | ±10% | Acetone1 |
| Benzene | Benzene | C6H6H+ | 12.5 | ±5% | Benzene1 |
| Methane thiol | MeSH | CH4SH+ | 5.14 | ±7% | MeSH2 |
| Methanol | MeOH | CH4OH+ | 97.3 | ±3% | Methanol3 |
| Monoterpenes | SumMT | C10H16H+ | 2.48 | ±5% | α-pinene1 |
| C4H6O Isomers | SumC4H6O | C4H6OH+ | 8.24 | ±5% | Methyl vinyl ketone1 |
| C4H8O Isomers | SumC4H8O | C4H8OH+ | 5.27 | ±5% | Methyl ethyl ketone1 |
| C8 Aromatics | SumC8H10 | C8H10H+ | 2.10 | ±5% | m-xylene1 |
| C9 Aromatics | SumC9H12 | C9H12H+ | 3.36 | ±5% | 1,2,4-trimethylbenzene1 |

1Calibrated with NMVOC standard (Apel-Riemer Environmental, Inc.; 1 ppm in N2). 2Calibrated with MeSH standard (Airgas, 6.11 ppm in N2). 3Calibrated with syringe injection of pure molecule in humidified zero air flow. 4Calibrated with D3-DMS standard (Airgas, 1.14 ppm in N2).

B. GC-Vocus Dataset

1. Datenum time stamp in Matlab serial time in UTC-0 local Azores time corresponding to the start time of the chromatogram file.
2. Fractional day of year time stamp (DOY) corresponding to datenum.
3. Volume trapped in cm3.
4. Isoprene calibrated in parts per trillion.

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| --- | --- | --- | --- | --- | --- |
| **Molecule** | **Header** | **Ion** | **LOD (ppt)** | **Uncertainty** | **Calibrated with:** |
| Isoprene | Isoprene | C5H8H+ | 6.8 ppt for trapping 1500 cm32.0 ppt for trapping 3000 cm3 | ±5% | Isoprene1 |

1Calibrated with NMVOC standard (Apel-Riemer Environmental, Inc.; 1 ppm in N2).

References

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