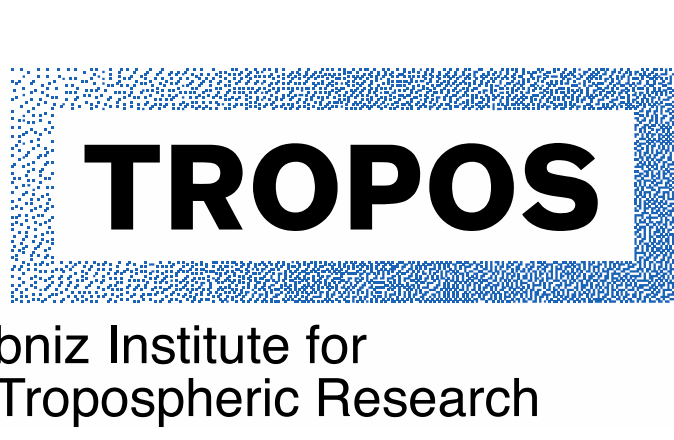


Comparison of automated GC instruments for continuous time-resolved measurements of ozone precursor VOCs in Borna, Germany

Max Hell¹, Dominik van Pinxteren¹, Susanne Bastian², and Hartmut Herrmann¹

¹Leibniz Institute for Tropospheric Research (TROPOS), Atmospheric Chemistry Department (ACD), Permoserstraße 15, 04318, Leipzig, Germany
²Saxon State Office for the Environment, Agriculture and Geology (LfULG), Dresden-Pillnitz, Germany

contact: hell@tropos.de



Introduction

Volatile organic compounds (VOCs) are important precursor substances for the formation of ground-level ozone (O_3) through complex reaction chains involving NO_x and HO_x . Biogenic sources for VOCs can be plant messenger substances or vegetation fires. The use of solvents or the combustion of fossil fuels are typical anthropogenic sources of VOCs. Currently, there are relatively low regulatory requirements for VOC measurements in the EU (e.g. Directive 2008/50/EC on ambient air quality), therefore VOCs are only sparsely recorded in air quality monitoring networks in Germany and Europe. However, in order to determine trends, check the effectiveness of emission reduction strategies, the correctness of emission inventories, allocate emission sources and better understand ozone formation and the spread of its precursors, it is necessary to carry out long-term measurements of ozone precursors with a high temporal resolution.

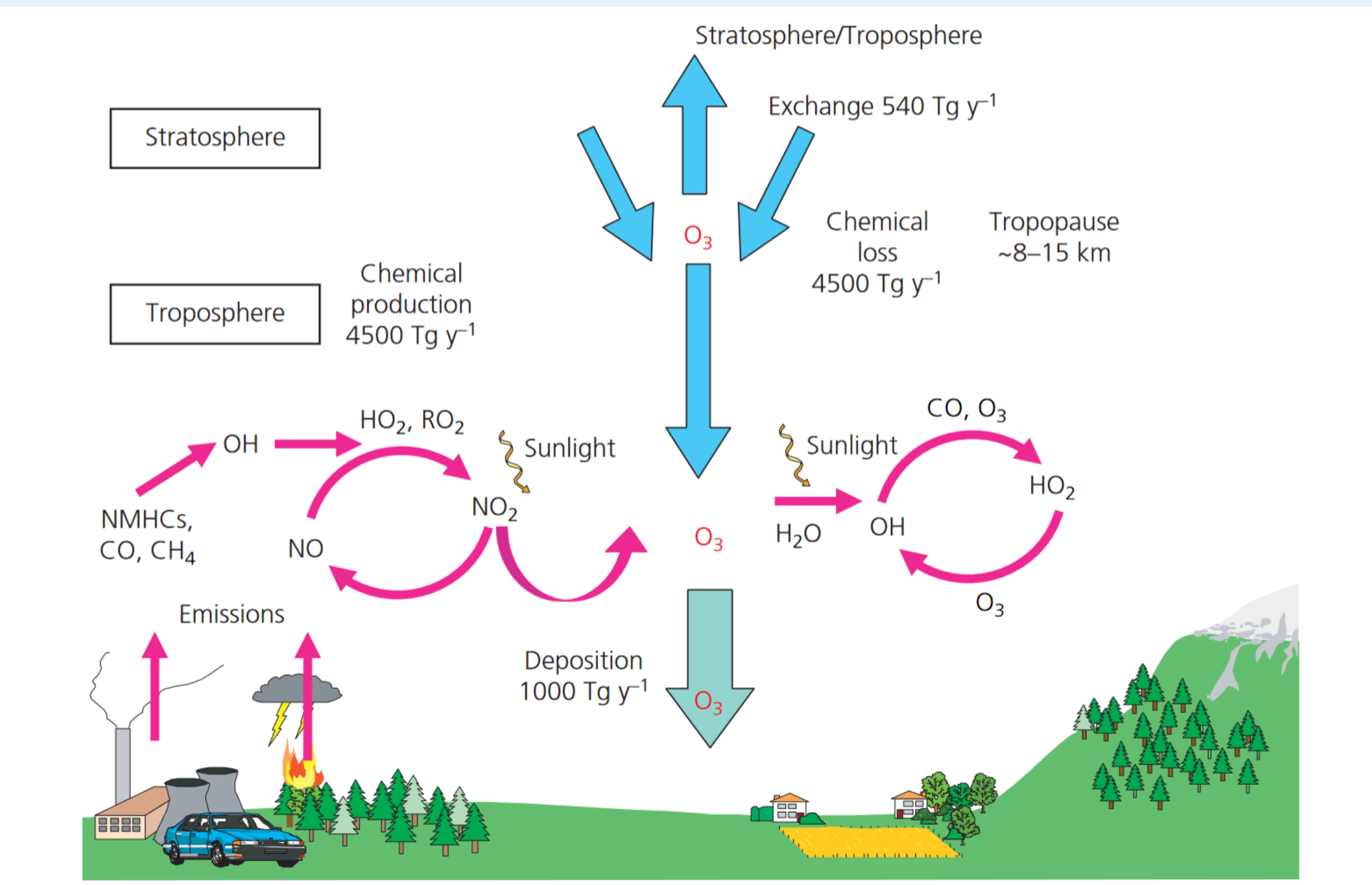


Fig. 1: Schematic of the basic ozone production process (Denman et al. 2007).

Experimental concept

For over one year, a measurement campaign was conducted at a traffic station of the Saxon State Office for the Environment, Agriculture and Geology (LfULG) in Borna, Saxony. The GC5000 with FID detection by AMA Instruments and the GC955 with FID and PID detection by SynSpec are two commercially available online-gas chromatography systems that were tested within this campaign (VDI guideline 2100 sheet 5).

Data availability

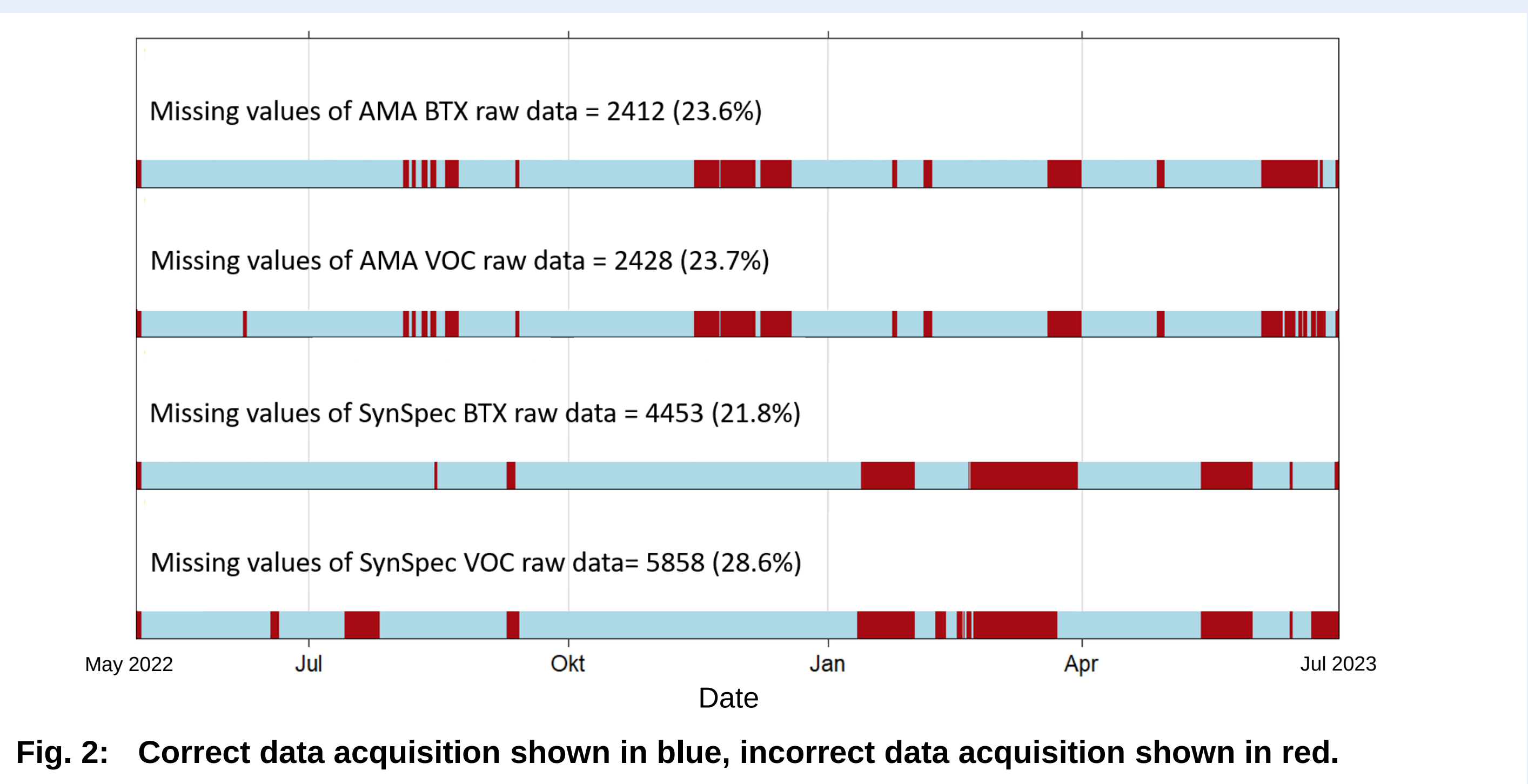


Fig. 2: Correct data acquisition shown in blue, incorrect data acquisition shown in red.

Failures of the gas generators and compressors, failures of the FID and various software and database errors led to multiple off-times of both instruments and loss of measurement data. A rather high level of maintenance is required to achieve low interruption operation of these two online devices.

Comparability of raw and post-processed data

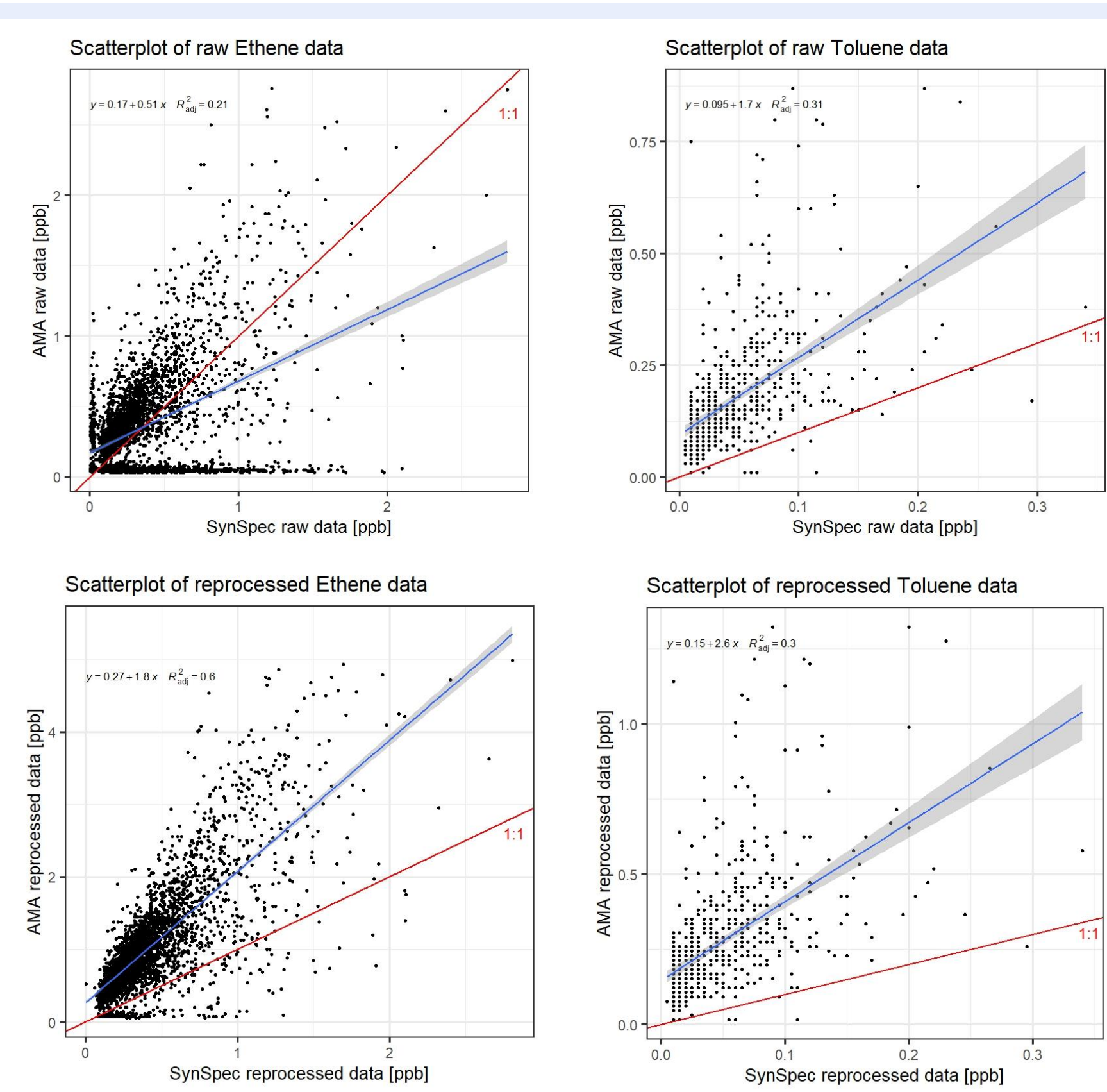


Fig. 3: Correlation of the raw and processed data of the SynSpec GC955 and the AMA Instruments GC5000.

20 of the 56 (US EPA PAMS list) originally calibrated analytes were regularly detected. Due to retention time shifts, peak detection is often inaccurate, resulting in poor comparability. Manual and tedious data post-processing is needed to achieve a significant improvement, especially for the more volatile VOCs. These seem to be particularly dependent on temperature fluctuations in the measuring container and the environment as well as the sample air humidity. An improvement is rarely observed for the BTX analytes.

Time variations of Isoprene

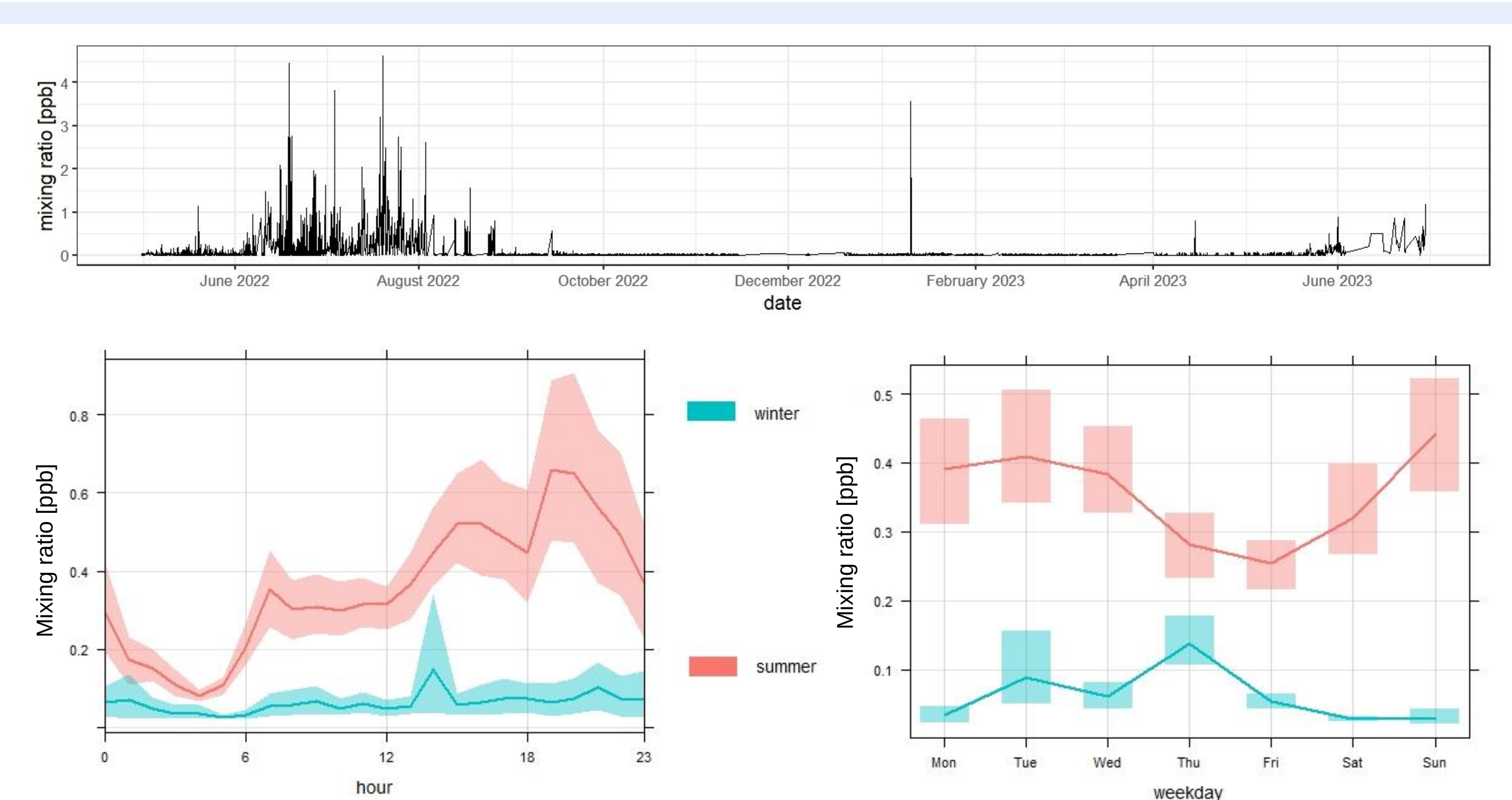


Fig. 4: Diurnal and weekly variation of isoprene in winter (Dec, Jan, Feb; in blue) and summer (Jun, Jul, Aug; in red) for data derived from the AMA GC5000 VOC.

As a biogenic ozone precursor, isoprene is mainly emitted by plants during the vegetation period in spring and summer. In winter there is only very little emission. The diurnal cycle that follows the temperature curve is particularly noticeable. However, the isoprene maximum is shifted far into the evening.

Time variations of Ethane

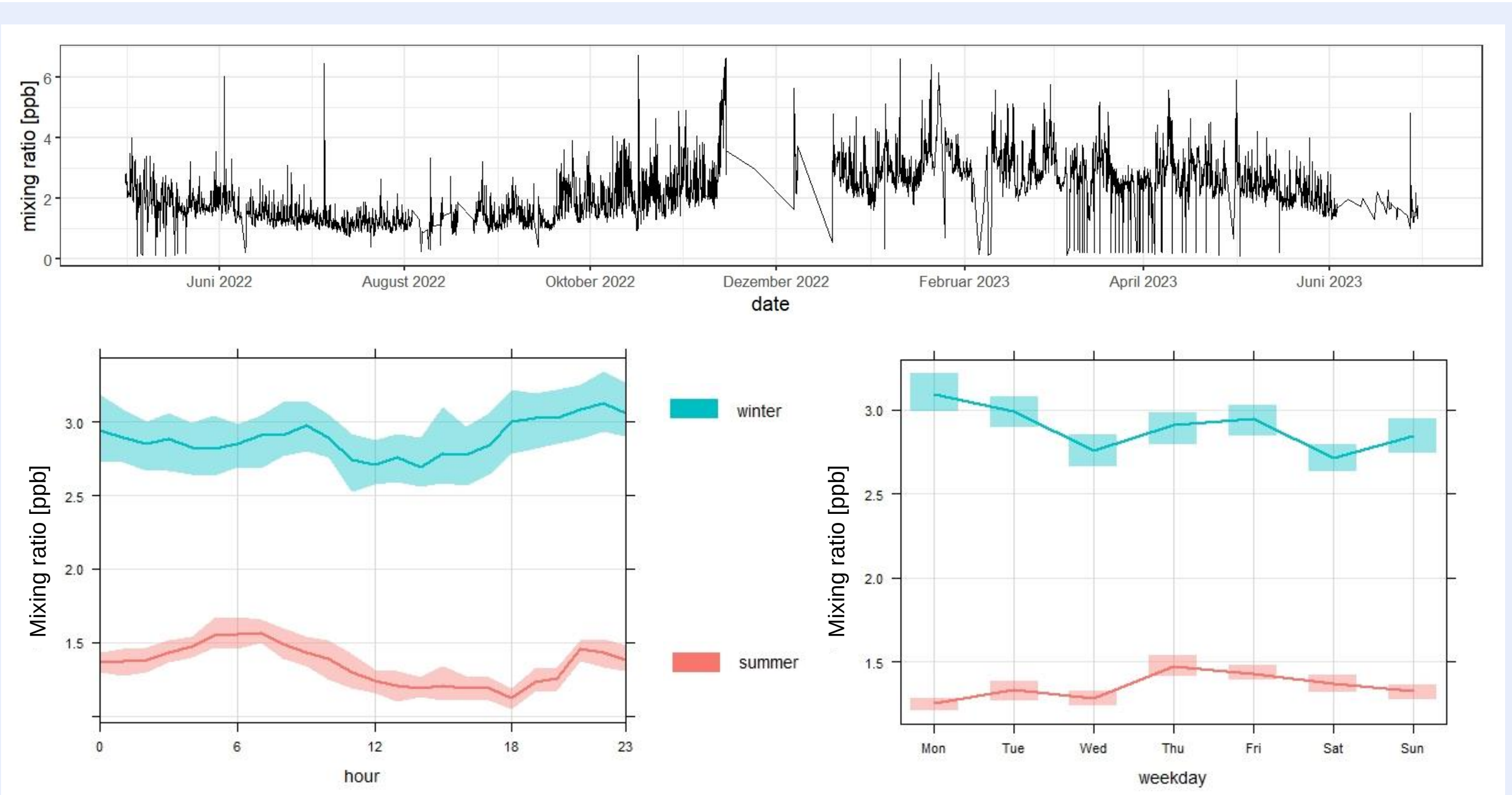


Fig. 5: Diurnal and weekly variation of ethane in winter (Dec, Jan, Feb; in blue) and summer (Jun, Jul, Aug; in red) for data derived from the AMA GC5000 VOC.

The annual variation of anthropogenic emitted ethane shows a clear decrease in summer and increase in winter up to a doubling of the mixing ratios. The average diurnal cycle also shows how the morning maximum shifts by around two hours in winter. Due to the time shift, the later onset of rush hour traffic is likely to play a major role here.

Conclusion

- Poor agreement between raw data sets
- Shifts of the retention time and thus bad peak recognition are major problems with both instruments
- High effort for data post-processing necessary to ensure an acceptable data quality
- Instruments softwares are mainly designed for instrument

- operation, not necessarily for data processing
- Data processing is especially beneficial for highly volatile analytes
- Influences of various emission sources can be derived from daily and weekly patterns

References & acknowledgment

Denman et al., 2007
VDI guideline 2100/5

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