On the development of a new prototype PTR-ToF-MS instrument and its application to the detection of atmospheric amines

Alexander Håland[1,2], Tomáš Mikoviny[1], Elisabeth Emilie Syse[1], and Armin Wisthaler[1,2]

[1]Department of Chemistry, University of Oslo, Oslo, Norway
[2]Centre for Biogeochemistry in the Anthropocene (CBA), University of Oslo, Oslo, Norway

Correspondence to: Armin Wisthaler (armin.wisthaler@kjemi.uio.no)

Abstract. We herein report on the development of a new prototype PTR-ToF-MS instrument that combines a hollow cathode glow discharge (HCGD) ion source with a focusing ion-molecule reactor (FIMR), which consists of a resistive glass drift tube surrounded by quadrupole rods. The new instrument configuration hybridizes the two main current commercial PTR-ToF-MS instrument designs. We provide a detailed technical description of the new analyzer and its optimized operational settings for detecting volatile amines via proton transfer reactions from hydronium (H_3O^+) or ammonium (NH_4^+) ions. We show that the new prototype PTR-ToF-MS instrument is capable of monitoring rapid changes of sticky amines on the timescale of a few seconds and detects atmospheric variations of amines down to single digit pptV levels. Application examples given include the real-time monitoring of i) methylamine emitted from a *Chenopodium vulvaria* L. plant, ii) small alkylamines in ambient air on site of an agricultural research center (Senter for husdyrforsøk, Ås, Norway), and iii) an industrial amine (2-amino-2-methylpropan-1-ol, AMP) on site and downwind of a carbon dioxide (CO_2) capture test center (Technology Centre Mongstad – TCM, Mongstad, Norway).

Deleted:

1

1 Introduction

Proton-Transfer-Reaction Mass Spectrometry (PTR-MS) is widely used in atmospheric sciences for the detection of non-methane organic gases (NMOGs) (de Gouw and Warneke, 2007; Hansel et al., 1995; Yuan et al., 2017). PTR-MS is a direct
25 injection chemical ionization mass spectrometry (CIMS) technique. Direct injection means that the sample is directly introduced into the analyzer without any precollection or pretreatment. The measurements are thus conducted in real time, with a frequency of up to 10 Hz. In its original and still most widely used configuration, PTR-MS uses gas-phase hydronium ions (H_3O^+) as chemical ionization (CI) reagent ions. H_3O^+ ions react with most NMOGs in non-dissociative proton transfer reactions (Hunt and Ryan, 1972; Lindinger et al., 1998). PTR-MS distinguishes itself from other CIMS techniques in the way
30 that the ionization is effected in a small flow tube reactor, at reduced pressure (1-4 mbar) and under the action of an electrostatic field (40-70 V cm^{-1}). The collisional drift of the ions at high velocities prevents them from getting hydrated and limits their residence time in the flow tube. Because of the presence of an electrostatic field, the flow tube reactor is commonly referred to as the drift tube (DT). While the original PTR-MS instrument was equipped with a quadrupole mass spectrometer (QMS), state-of-the-art analyzers include a time-of-flight mass spectrometer (ToF-MS).

35 Currently, atmospheric composition researchers mainly use two types of PTR-ToF-MS instruments, which are manufactured by two different producers. The instrument produced by Ionicon Analytik (Innsbruck, Austria) uses a hollow cathode glow discharge (HCGD) for producing H_3O^+ ions (Hansel et al., 1995; Müller et al., 2020). More details about this ion source are provided in the Methods section. In the conventional and widely used Ionicon instruments, the DT is composed of a stack of stainless steel (SS) rings, which are separated by insulating Teflon spacers. In the instrument produced by Tofwerk (Thun,
40 Switzerland), also known as the VOCUS PTR-TOF or simply as "the VOCUS", H_3O^+ ions are formed in a water plasma burning between two conical electrodes (Krechmer et al., 2018b). In the VOCUS analyzer, the DT consists of a resistive glass tube surrounded by cylindrical quadrupole rods. The latter generate a focusing quadrupole field within the DT, which is thus commonly referred to as focusing ion-molecule reactor (FIMR).

Herein, we report on the development and application of a new prototype PTR-ToF-MS instrument that hybridizes the two
45 commercial PTR-ToF-MS designs, combining an FIMR with an HCGD ion source. In a conventional stacked ring DT, the ion swarm broadens as it drifts through the reactor and only a fraction of the ions is sampled through the exit aperture towards the mass analyzer. This loss in sensitivity can partly be compensated by placing an ion funnel at the end of the DT (Barber et al., 2012). Such an ion funnel is nowadays routinely installed in most Ionicon analyzers (Pugliese et al., 2020). In the FIMR, a focusing quadrupole field acts over the entire drift region, which minimizes ion losses and boosts the instrument sensitivity
50 (10^3-10^4 cps ppbv^{-1}; Krechmer et al., 2018). We thus decided to build an instrument based on the FIMR design proposed by Krechmer et al. (2018). Since the VOCUS ion source was not yet commercially available when we conceived the new instrument, we opted to couple the FIMR with the existing HCGD ion source. When the VOCUS ion source became available, we decided not to retrofit it onto our analyzer. This decision was mostly driven by chemical-analytical concerns that were based on our previous work on water plasma ion sources. The VOCUS ion source has the peculiarity that the entire water
55 plasma effluent is introduced into the FIMR. Electron ionization processes in a water plasma form O^+, H^+, H_2^+, OH^+ and H_2O^+ cations, and H_3O^+ ions are only generated in subsequent reactions between these cations and H_2O molecules. Our first concern was that this conversion to H_3O^+ ions might not be complete when ions enter the FIMR from the VOCUS ion source. NMOGs would thus also be partly ionized via electron transfer reactions, with the presence of non-protonated species complicating the interpretation of mass spectra. Our second and more serious concern was related to the fact that a water plasma effluent
60 typically contains high densities of oxidants such as hydroxyl (OH$^{\bullet}$) radicals. Highly reactive NMOGs would undergo partial oxidation within the FIMR, if exposed to OH$^{\bullet}$ radicals being introduced from the VOCUS ion source. This would result in important positive measurement artifacts for oxidized and highly oxidized compounds, even if only a very small and unnoticeable fraction ($\leq 0.1\%$) of highly reactive NMOGs was oxidized inside the FIMR. It is important to note that we have no experimental evidence that such processes do actually occur in the VOCUS analyzer. On the other hand, there was (and

2

still is) no detailed description or characterization of the VOCUS ion source in the scientific literature, which is why we ultimately decided to install the well-characterized HCGD ion source in our PTR-ToF-MS instrument.

We will describe the new prototype PTR-ToF-MS instrument in the Methods section of this paper. In the Results section, we will describe its performance for the detection of volatile amines and show laboratory and field data. Amines were chosen as target analytes because of the increasing interest of the atmospheric chemistry community in this class of compounds (Ge et al., 2011). This interest is mainly driven by the important role that amines play in new particle formation (*e.g.*, Almeida et al., 2013). Amines are also being emitted to the atmosphere from carbon dioxide (CO_2) capture plants. Since the slip of amines from CO_2 capture plants may result in the atmospheric formation of harmful substances (*e.g.*, nitrosamines and nitramines) (Nielsen et al., 2012), amines are receiving increased interest from the air quality and health community. Atmospheric amines are however particularly challenging to measure. This is on one hand caused by the fact that atmospheric levels are usually extremely low, requiring analyzers to be able to detect single-digit pptV levels. On the other hand, amines are also known to be "sticky", meaning that they easily adsorb onto surfaces in the analyzer and in the inlet lines. Direct injection CIMS is thus the method of choice for measuring pptv levels amines in the atmosphere in real time, and a series of instruments have recently been developed for detecting amines (Hanson et al., 2011; Lee, 2022; Pfeifer et al., 2020; Sellegri et al., 2005; Wang et al., 2020; Yao et al., 2016; You et al., 2014; Yu and Lee, 2012; Zheng et al., 2015). We will herein show that our new PTR-ToF-MS analyzer is also capable of detecting atmospheric amines down to single-digit pptv levels. We will furthermore demonstrate that our new instrument has only minor memory effects and is thus capable of monitoring changes of amines in the air on the timescale of a few seconds.

2 Experimental

2.1 Instrument description

The new prototype PTR-ToF-MS analyzer that combines a conventional HCGD ion source with the more recently developed FIMR is shown in Figure 1.

The HCGD ion source and the processes occurring therein have been described in detail in the original PTR-MS publication (Hansel et al., 1995). Only minor modifications have been implemented since then and the current configuration has been described by Müller et al. (2020). Only the essentials are thus outlined here (Figure 1). A DC water plasma is generated inside a plasma source consisting of a hollow cylinder anode, a hollow cylinder cathode and an anode lens with an exit orifice. The entire effluent from this plasma source, which includes ions, electrons, radicals and mostly neutral H_2O molecules, is introduced into a hollow cylinder electrode, which is commonly referred to as the "source drift region" or "source drift ring" (SDR). The SDR is a key component of the ion source set-up, because it is mostly here where O^+, H^+, H_2^+, OH^+ and H_2O^+ cations react with H_2O molecules to form H_3O^+ ions. It is also here where free electrons recombine with cations and where $OH^•$ and other radical species are destroyed on SS surfaces. Importantly, the water vapor and other neutral plasma effluents are pumped off from the SDR and thus not brought in contact with the sample gas that is introduced into the instrument further downstream. Only ions ($\geq$98% H_3O^+, with O_2^+ and NO^+ making up for the rest) are extracted via the SDR exit lens and injected into the drift region. The entire ion source set-up can be heated. Five parameters can be set in the HCGD ion source: i) the source gas flow (Φ_{source}), ii) the source temperature (T_{source}), iii) the plasma current (I_{plasma}), iv) the voltage between the anode lens and the SDR ($U_{SDR,in}$), v) the voltage between the SDR and the SDR exit lens ($U_{SDR,out}$). The specific settings used for the measurements reported herein will be reported below. The HCGD ion source has also been used for generating other types of CI reagent ions such as O_2^+ or NO^+ (Jordan et al., 2009) and NH_4^+ (Müller et al., 2020; Zhu et al., 2018). We operated the new instrument only in the H_3O^+ mode and in the NH_4^+ mode, since both of these CI reagent ions can be used for detecting amines via non-dissociative proton transfer reactions (Zhu et al., 2018).

Deleted: exemplary

Deleted: ,

Deleted: ,

Deleted: (Lee, 2022).

Deleted: measur

Deleted:

Deleted: ¶

Deleted: instrument

Deleted: single-digit pptV levels of

Deleted: in the atmosphere

Deleted: also

Deleted: for amines

Deleted: rapid

Deleted: level

Deleted: 1

The FIMR has been described in detail by Krechmer et al. (2018). We also use a 10 cm long resistive glass tube, but with a slightly smaller diameter (8 mm OD, 6 mm ID). Four operational parameters can be set in the FIMR: the frequency (f_{FIMR}) and peak-to-peak amplitude voltage ($V_{pp, FIMR}$) of the RF applied on the quadrupole rods, the DC voltage applied across the ends of the glass tube (U_{drift}) and the pressure (p_{drift}) in the vacuum chamber in which the resistive glass tube is placed. The sample gas is introduced into the FIMR via a custom-made passivated (Sulfinert®, Restek, Bellefonte, PA, U.S.A.) gas inlet lens (GIL). The GIL is placed between the SDR exit lens and the FIMR. Two additional voltages can be set relative to the GIL: i) the voltage between the SDR exit lens and the GIL ($U_{GIL,in}$) and ii) the voltage between the GIL and the upper end of the FIMR ($U_{GIL,out}$). The GIL is connected to a 15 cm long 1/16-in. OD Teflon PFA tube, which includes a T-piece to branch off part of the inlet flow into a digital pressure controller (Bronkhorst High-Tech B.V., Ruurlo, The Netherlands). This device keeps the pressure in the Teflon inlet tube (p_{inlet}) (and thereby also p_{drift}) constant. The inlet line and gas inlet lens can be heated (T_{inlet}), which indirectly heats the FIMR. The GIL has a second port that is connected to a capillary leak through which a mass axis calibration gas (1,4-diiodobenzene; Sigma-Aldrich, Oslo, Norway) diffuses into the FIMR. The sample gas is pumped off through a 1 mm gap between the lower end of the FIMR and the skimmer lens at the entrance of the mass spectrometer. The skimmer is grounded and the voltage between the lower end of the FIMR and the skimmer ($U_{FIMR,out}$) can be set. All specific settings used for the measurements reported herein will be reported below.

Our key strategy for reducing the instrumental time response was to maximize the flow through the low-pressure flow reactor. A dry multi-stage Roots pump (ACP40; Pfeiffer Vacuum, Asslar, Germany) pumps up to 0.80 standard liters per minute (slpm; "standard" herein means referenced to a temperature of 273.15 K and a pressure of 101325 Pa) through the FIMR. For the measurements presented herein, we set the flow rate to 0.55 slpm, which is a factor 5 higher than in commercial VOCUS instruments (Krechmer et al., 2018b; Wang et al., 2020). We observed that increasing the reactor flow from 0.05 to 0.50 slpm reduced the $1/e^2$ decay time of a 20 pptv trimethylamine (TMA) signal from ~60 to ~5 seconds.

The mass analyzer used in our instrument is a quadrupole ion guide orthogonal acceleration reflectron ToF-MS (model HTOF; Tofwerk, Thun, Switzerland). The quadrupole ion guide (commonly referred to as the big segmented quadrupole, BSQ) was operated at an RF frequency of 4.4 MHz and an RF amplitude between 300 and 320 V. It is important to note that we operate the BSQ at relatively high RF frequencies to avoid strong mass discrimination effects in the m/z 30 to 60 region, which is typically observed for commercial VOCUS analyzers (Krechmer et al., 2018; Wang et al., 2020).

2.2 Laboratory test

The first application test was carried out in the laboratory. We cultivated a Stinking Goosefoot (*Chenopodium vulvaria* L.) plant, which is a weed covered by minuscule bladder hairs. Upon mechanical stress, these bladder hairs release TMA. The plant was placed in our laboratory next to the analyzer and mechanically stressed. The evolving TMA puff was monitored in real time by our new prototype PTR-ToF-MS instrument.

2.3 Field tests

A first field test was carried out on campus of a research center for animal husbandry (Senter for husdyrforsøk – Livestock Production Research Centre, Norwegian University of Life Sciences, Ås, Norway). The prototype PTR-ToF-MS analyzer was installed in a temperature-controlled enclosed car trailer. The trailer was placed close to large manure tanks where the animal excrements from the entire site are collected. The aim was to monitor atmospheric amines, with a focus on methylamine (MMA), dimethylamine (DMA) and TMA. Air was sampled through a hole in the lateral wall of the trailer, using a 130 cm long, heated (100 °C), Sulfinert®-passivated, 1/4-in. OD SS tube pumped at a flow rate of 25 slpm. The instrument subsampled from this main inlet flow. A flow of 2.5 standard cubic centimeters per minute (sccm) of 1 % ammonia (NH_3) in nitrogen (BOC Ltd., U.K.) was continuously added at the tip of the main inlet for chemically passivating all wetted surfaces in the inlet and in the instrument itself (Roscioli et al., 2015; Zhu et al., 2017). Excess ammonia is known to displace amines adsorbed

4

onto surface sites (Ongwandee et al., 2005). The instrumental background was measured every 12 hours for 25 minutes by overflowing the instrument subsampling flow with ambient air that had passed through a heated (350 °C) Pt/Pd catalyst. We have shown in previous work that MMA, DMA and TMA are efficiently detected in their protonated form if NH_4^+ ions are used as CI reagent ions in PTR-MS instruments (Zhu et al., 2018). In this first field study, we thus operated the HCGD ion source in the NH_4^+ mode with the following settings: Φ_{source} = 6 sccm (1-3% NH_3 in N_2; Nippon Gases Norge AS, Oslo, Norway); I_{source} = 4 mA; T_{source} = 100 °C. Ions with a relative abundance >1% of NH_4^+ were: H_3O^+ (~5%), NO^+ (~3%), O_2^+ (~3%), and $NH_4^+(NH_3)$ (~1%). For quantification, we estimated that NH_4^+ and H_3O^+ have a 50% lower detection efficiency than the other three ion species (due to increased mass discrimination of ions with m/z <20). The operational parameters of the instrument were as follows: T_{inlet} = 100 °C; $U_{SDR,in}$ = 234 V; $U_{SDR,out}$ = 200 V; $U_{GIL,in}$ = 78 V; $U_{GIL,out}$ = 50 V; U_{drift} = 450 V; $U_{FIMR,out}$ = 40 V; p_{drift} = 1.95 mbar, f_{FIMR} = 5.5 MHz, $V_{pp, FIMR}$ = 350 V. The FIMR was operated at relatively high RF frequencies to avoid strong mass discrimination effects in the m/z 30 to 60 region. Calibrations were performed in the field using a liquid calibration unit (LCU) (LCU-a, Ionimed Analytik GmbH, Innsbruck) (Fischer et al., 2013). An aqueous standard solution of MMA, DMA and TMA was prepared by diluting known volumes of commercial solutions of MMA (40±3% wt. in H_2O), DMA (40±2% wt. in H_2O), and TMA (45±3.5% wt. in H_2O) with Type 1 Milli-Q® water. In the LCU, the standard solution was nebulized/evaporated at a known liquid flow rate (2-10 µl min^{-1}) into a known flow (typically 1 slpm) of NMOG-free air. The accuracy of the MMA, DMA and TMA calibration is conservatively estimated to be ±15%.

Two additional field tests were conducted at and near the Technology Centre Mongstad (TCM; Mongstad, Norway). TCM is one of the world's largest test centers for amine-based CO_2 capture (de Koeijer et al., 2011). The measurements were carried out during a test campaign with a solvent containing 2-amino-2-methylpropan-1-ol (AMP) (Languille et al., 2021). The instrument was calibrated with the LCU using an aqueous solution of AMP, which was prepared by diluting a weighted amount of the pure compound (≥99%; Sigma-Aldrich, Oslo, Norway) in Type 1 Milli-Q® water. The accuracy of the AMP calibration is conservatively estimated to be ±15%. The first test was carried out on the premises of TCM to demonstrate that the new instrument is capable of detecting solvent leaks in real time. For this purpose, a gas mixture containing 25 ppmV of AMP was deliberately released into the air at approximately one meter distance from the instrument inlet using a HovaCAL® (model digital 211-MF; IAS GmbH, Oberursel, Germany) gas generator. The second test was to demonstrate that the new and highly sensitive PTR-ToF-MS analyzer is capable of detecting single digit pptV levels of amines in the downwind atmosphere of a CO_2 capture facility. For this purpose, the instrument trailer was placed ~4.4 km north of TCM during a 1-week period with predominantly southerly winds. The measurements took place when ~1 ppmV of AMP of TCM was steadily emitted from TCM. For these measurements, the prototype PTR-ToF-MS analyzer was operated in the conventional H_3O^+ mode. Some operational parameters were thus modified as compared to the first field campaign: Φ_{source} = 6 sccm (H_2O); I_{source} = 4.5 mA; $U_{SDR,in}$ = 377 V; $U_{SDR,out}$ = 202 V; $U_{GIL,in}$ = 89 V; U_{drift} = 400 V. The instrumental background was measured once a day for 20 minutes by overflowing the instrument subsampling flow with ambient air that had passed through a heated (350 °C) Pt/Pd catalyst. The data from the first five minutes of zeroing were discarded because of signal tailing.

3 Results and Discussion

3.1 Laboratory testing: detection of biogenic amines

Figure 2 shows the time evolution of TMA in laboratory air when a *Chenopodium vulvaria* L. plant was mechanically stressed
280 by tipping a leaf with a pen. The stress resulted in a burst of TMA and the new prototype PTR-ToF-MS instrument detected a short-term spike in TMA with a peak width (FWHM) of 16 seconds. This was our first experimental evidence that the new prototype instrument is capable of monitoring rapid changes of amine levels in the air on the timescale of a few seconds. The TMA volume mixing ratio did not drop to pre-spike levels, because the amine was released into and sampled from laboratory air. We did not make any further attempts to quantify TMA emission rates.

285 ### 3.2 Field testing: detection of agricultural amines

After the first successful laboratory tests, the instrument was taken to the field. The goal was to measure small alkylamines in ambient air on campus of an agricultural research center. As mentioned in the Methods section, the prototype PTR-ToF-MS instrument was operated in the NH_4^+ mode.

Figure 3 displays the calibration curves for MMA, DMA and TMA, as obtained from a calibration carried out in the field. The
290 calibration curves show the normalized ion signal response (in *normalized counts per second*, ncps) as a function of amine volume mixing ratios in the 0 to 10 ppbV range. The signals were normalized to the average NH_4^+ signal (measured on the $^{15}NH_4^+$ isotope signal at m/z 19.031) observed over the course of the experiment. The three amines were detected in their protonated form at m/z 32.049, 46.065 and 60.081, respectively. The only additional signals observed were m/z 44.049 (2.5%) and m/z 58.065 (4.0%) for DMA and TMA, respectively. H_2 ejection is a frequently observed minor channel in the CI of
295 amines (Harrison, 1992). No adduct ions were detected due to the high collisional energy of the ions in the FIMR. The protonated amines were detected at a mass resolving power (m/Δm) of 3700, 4100, and 4250, respectively. The instrumental response factors (sensitivities) for MMA, DMA and TMA were 114, 156, and 126 ncps ppbV^{-1}, respectively. The instrumental response did not exhibit any humidity dependence (<3% analyte ion signal change over the range of typical ambient humidities). The relative precision (1σ) at the lowest calibration mixing ratio (~2 ppbV) was 4.3, 2.2 and 4.3 % for MMA,
300 DMA and TMA, respectively. The offset in the calibration curves mainly originated in a constant chemical background in the calibration device (LCU) from previous calibrations. The data shown in Figure 3 were thus not used for deriving instrumental detection limits.

The instrumental response factors of the prototype PTR-ToF-MS analyzer are 1-2 orders of magnitude lower than those reported for commercial VOCUS analyzers (Krechmer et al., 2018b; Wang et al., 2020). This is a result of a combination of
305 various factors. First, we generally observe lower instrumental sensitivities when operating PTR-MS instruments in the NH_4^+ mode (Zhu et al., 2018). Second, we set the upper m/z limit in the TOF-MS to ~500. Reducing the upper m/z limit to 100 would increase the sensitivity by a factor of 2.2 (higher duty cycle). Third and most importantly, our prototype instrument has a relatively large gap between the FIMR and the skimmer (to increase the flow through the reactor and thereby minimize memory effects), which results in increased ion losses at the end of the FIMR. Fourth, we apply a relatively low RF amplitude to the
310 FIMR, because at higher V_{pp}, O_2^+ ions efficiently formed within the FIMR. A high O_2^+ signal on m/z 31.989 severely compromises the detection of MMA at m/z 32.049. Fifth, we also apply a relatively low RF amplitude to the BSQ for avoiding strong mass discrimination effects in the m/z 32 to 60 region. The small spread in the MMA, DMA and TMA sensitivity values confirms that no significant mass discrimination occurred in the m/z range of interest.

Prior to starting the measurements, we carried out another field test. Indole was among the analytes of interest for this field
315 study (even though it was later only sporadically detected at very low levels), and laboratory tests had revealed that this amine is particularly sticky. The headspace from a vial containing indole was thus shortly blown towards the instrument inlet and the

6

protonated indole signal at m/z 118.065 was monitored at 1-second time resolution. Figure 4 shows the time series of indole as observed during this experiment. The initial volume mixing ratio on the order of 100 ppbV decreased by two orders of magnitude within 4 seconds and background levels were reached within ~40 seconds. We are fully aware that this instrument test deviates from the formal experimental procedure for determining an instrumental response time. However, these data do show the performance of the analyzer under field conditions and allow us to conclude that the new prototype instrument is indeed capable of monitoring rapid changes of sticky amines on the timescale of a few seconds.

Figure 5 shows the time series (5-min averages) of DMA and TMA as measured in ambient air on site at the agricultural research center over a period of three days. The instrumental background was stable for both DMA and TMA (see Figure S1), which resulted in a detection limit (3σ, 5-min signal integration) of ~5 pptV for these two amines. It was not possible to detect protonated MMA (m/z 32.049) because of the strong mass spectral interference from the adjacent O_2^+ peak (m/z 31.989). We subtracted the O_2^+ contribution, but the resulting detection limit (3σ, 5-min signal integration) was ~ 170 pptV. It is important to note that direct introduction CIMS methods do not resolve isomeric species. DMA has only one additional isomer (ethylamine, EA), while TMA has three isomers (ethylmethylamine, propylamine, isopropylamine). Previous work (Schade and Crutzen, 1995 and references therein) found trace levels of both EA and DMA in husbandry emissions, which is why we assign the m/z 46.065 ion signal to both of these compounds. The same literature reports that TMA is the dominant C_3-isomer, which is why we assign the m/z 60.081 signal to TMA only. We observed a clear diurnal pattern in the time profile of both species, with maxima occurring during nighttime when the planetary boundary layer is low.

3.3 Field testing: detection of an industrial amine

The field tests at and near the CO_2 capture plant were carried out with the instrument being operated in the conventional H_3O^+ mode. The calibration curve (Figure 6) shows the m/z 90.091 normalized ion signal response (in *ncps*, normalized to the average $H_3O^+ + H_3O^+(H_2O)$ signal observed over the course of the calibration experiment) as a function of the AMP volume mixing ratio. The mass resolving power (m/Δm) for this ion signal was 3700.

The calibration data show that the prototype PTR-ToF-MS instrument generated a signal response $\geq 10^3$ ncps ppbv^{-1}. This is still on the lower end of what has been reported for commercial VOCUS analyzers. As mentioned above, this is mainly due to ion losses in the relatively large gap between the FIMR and the skimmer, which is needed for increasing the FIMR flow. The relative precision (1σ) at the lowest calibration mixing ratio (~2 ppbV) was ±4.2 % for AMP. The offset in the calibration curve was again caused by a constant chemical background in the LCU calibration device and not in the instrument itself. The data shown in Figure 6 were thus not used for deriving the instrumental detection limit for AMP.

The first test carried out at TCM was to demonstrate the new instrument is capable of detecting amine solvent leaks in real time. A gas mixture containing ~25 ppmV AMP was deliberately released into the air at approximately one meter distance from the instrument inlet. The test was carried out during strong and turbulent wind conditions, which are typical for the Norwegian west coast. As seen in Figure 7, single to double digit ppbV levels of AMP were observed in real time (1 Hz). Notably, the instrument response was immediate and the signal quickly returned to baseline levels once the artificial leak was closed.

The second test was to demonstrate that the new PTR-ToF-MS analyzer is capable of detecting ultra-trace levels of industrial amines in the atmosphere. During the measurement period, a steady level of ~1 ppmV AMP was released to the atmosphere from TCM while the PTR-ToF-MS instrument sampled atmospheric air ~4.4 km downwind. Figure 8 shows 5-minute average AMP data collected when the TCM plume crossed the measurement site. The instrumental background was low and stable (0.6 ± 0.2 pptV) throughout the measurement period (see Figure S2), which resulted in a detection limit (3σ, 5-min signal integration) of ~0.5 pptV for AMP. As seen in Figure 8, at 5-minute signal integration variations <1 pptV can be observed.

7

4 Conclusion

The PTR-MS technique was developed in the mid-1990ies at the University of Innsbruck. Initial method improvements focused on using different mass analyzers (*e.g.*, Blake et al., 2004; Prazeller et al., 2003). The ion source and drift tube only
455 underwent minor geometrical changes over a period of two decades. The past five years have, however, seen major developments in the drift tube and ion source design (*e.g.*, Breitenlechner et al., 2017; Krechmer et al., 2018). We have herein presented one additional instrument variation, in which the well-characterized and "clean" HCGD ion source originally described by Hansel et al. (1995) is combined with the recently developed and highly sensitive FIMR design by Krechmer et al. (2018). We have shown data that demonstrate the capabilities of this new instrument in monitoring atmospheric amines at
460 single digit pptV levels. We have also shown that the new instrument has only minor memory effects for sticky amines, making it capable of monitoring rapid changes of amine levels in the air on the timescale of a few seconds. Further work is, however, required for achieving a time response of 1 second or less. This could be achieved by further optimizing the gas inlet or by heating the FIMR to ≥100 °C. We have also made an argument that maximizing the instrument sensitivity should not be the only focus of PTR-MS instrument development and optimization. Minimizing potential neutral and ionic side reactions in the
465 DT, reducing sample memory effects and eliminating mass discrimination effects over the *m/z*-range of interest are important for generating easily interpretable and quantifiable mass spectra. This is particularly important for the non-expert user. The PTR-MS method is being rapidly developed in various directions, and different types of PTR-MS instruments and operation modes are nowadays being used for different types of applications. The PTR-ToF-MS presented herein has been optimized for the detection of atmospheric amines, which are currently in the research focus of our group. In future work, we will show how
470 we have used the new prototype PTR-ToF-MS instrument for quantifying amine emission rates from animal husbandry and for investigating the atmospheric impact of amine emissions from CO_2 capture.

8

Deleted: Exemplary data have been

Deleted: provided to

Deleted: ,

Deleted: ,

Deleted: analyzable,

Deleted:

Deleted:

500

References

Almeida, J., Schobesberger, S., Kürten, A., Ortega, I. K., Kupiainen-Määttä, O., Praplan, A. P., Adamov, A., Amorim, A., Bianchi, F., Breitenlechner, M., David, A., Dommen, J., Donahue, N. M., Downard, A., Dunne, E., Duplissy, J., Ehrhart, S., Flagan, R. C., Franchin, A., Guida, R., Hakala, J., Hansel, A., Heinritzi, M., Henschel, H., Jokinen, T., Junninen, H., Kajos, M., Kangasluoma, J., Keskinen, H., Kupc, A., Kurtén, T., Kvashin, A. N., Laaksonen, A., Lehtipalo, K., Leiminger, M., Leppä, J., Loukonen, V., Makhmutov, V., Mathot, S., Mcgrath, M. J., Nieminen, T., Olenius, T., Onnela, A., Petäjä, T., Riccobono, F., Riipinen, I., Rissanen, M., Rondo, L., Ruuskanen, T., Santos, F. D., Sarnela, N., Schallhart, S., Schnitzhofer, R., Seinfeld, J. H., Simon, M., Sipilä, M., Stozhkov, Y., Stratmann, F., Tomé, A., Tröstl, J., Tsagkogeorgas, G., Vaattovaara, P., Viisanen, Y., Virtanen, A., Vrtala, A., Wagner, P. E., Weingartner, E., Wex, H., Williamson, C., Wimmer, D., Ye, P., Yli-Juuti, T., Carslaw, K. S., Kulmala, M., Curtius, J., Baltensperger, U., Worsnop, D. R., Vehkamäki, H. and Kirkby, J.: Molecular understanding of sulphuric acid–amine particle nucleation in the atmosphere, Nature, 502, doi:10.1038/nature12663, 2013.

Barber, S., Blake, R. S., White, I. R., Monks, P. S., Reich, F., Mullock, S. and Ellis, A. M.: Increased Sensitivity in Proton Transfer Reaction Mass Spectrometry by Incorporation of a Radio Frequency Ion Funnel, , doi:10.1021/ac300894t, 2012.

Blake, R. S., Whyte, C., Hughes, C. O., Ellis, A. M. and Monks, P. S.: Demonstration of Proton-Transfer Reaction Time-of-Flight Mass Spectrometry for Real-Time Analysis of Trace Volatile Organic Compounds, Anal. Chem., 76(13), 3841–3845, doi:10.1021/ac0498260, 2004.

Breitenlechner, M., Fischer, L., Hainer, M., Heinritzi, M., Curtius, J. and Hansel, A.: PTR3: An Instrument for Studying the Lifecycle of Reactive Organic Carbon in the Atmosphere, Anal. Chem., 89, 5824–5831, doi:10.1021/acs.analchem.6b05110, 2017.

Fischer, L., Klinger, A., Herbig, J., Winkler, K., Gutmann, R. and Hansel, A.: The LCU: Versatile Trace Gas Calibration, in 6th International Conference on Proton Transfer Reaction Mass Spectrometry and its Applications, edited by A. Hansel and J. Dunkl, pp. 192–195, Innsbruck University Press, Innsbruck. [online] Available from: https://openpub.fmach.it/retrieve/handle/10449/23075/9394/ptrms_2013.pdf#page=193, 2013.

Ge, X., Wexler, A. S. and Clegg, S. L.: Atmospheric amines - Part I. A review, Atmos. Environ., 45, 524–546, doi:10.1016/j.atmosenv.2010.10.012, 2011.

de Gouw, J. and Warneke, C.: Measurements of volatile organic compounds in the earth's atmosphere using proton-transfer-reaction mass spectrometry, Mass Spectrom. Rev., 26(2), 223–257, doi:10.1002/mas.20119, 2007.

Hansel, A., Jordan, A., Holzinger, R., Prazeller, P., Vogel, W. and Lindinger, W.: Proton transfer reaction mass spectrometry: on-line trace gas analysis at the ppb level, Int. J. Mass Spectrom. Ion Process., 149–150, 609–619, doi:10.1016/0168-1176(95)04294-U, 1995.

Hanson, D. R., Mcmurry, P. H., Jiang, J., Tanner, D. and Huey, L. G.: Ambient Pressure Proton Transfer Mass Spectrometry: Detection of Amines and Ammonia, Environ. Sci. Technol, 45, 8881–8888, doi:10.1021/es201819a, 2011.

Harrison, A. G.: Chemical Ionization Mass Spectrometry, 2nd ed., Routledge, New York., 1992.

Hunt, D. F. and Ryan, J. F.: Argon-water mixtures as reagents for chemical ionization mass spectrometry, Anal. Chem., 44(7), 1306–1309, doi:10.1021/ac60315a024, 1972.

Jordan, A., Haidacher, S., Hanel, G., Hartungen, E., Herbig, J., Märk, L., Schottkowsky, R., Seehauser, H., Sulzer, P. and Märk, T. D.: An online ultra-high sensitivity Proton-transfer-reaction mass-spectrometer combined with switchable reagent ion capability (PTR + SRI − MS), Int. J. Mass Spectrom., 286(1), 32–38, doi:10.1016/J.IJMS.2009.06.006, 2009.

de Koeijer, G., Enge, Y., Sanden, K., Graff, O. F., Falk-Pedersen, O., Amundsen, T. and Overå, S.: CO2 Technology Centre Mongstad–Design, functionality and emissions of the amine plant, Energy Procedia, 4, 1207–

9

1213, doi:10.1016/j.egypro.2011.01.175, 2011.

Krechmer, J., Lopez-Hilfiker, F. D., Koss, A. R., Hutterli, M. A., Stoermer, C., Deming, B. L., Kimmel, J. R., Warneke, C., Holzinger, R., Jayne, J. T., Worsnop, D. R., Fuhrer, K., Gonin, M. and De Gouw, J.: Evaluation of a New Reagent-Ion Source and Focusing Ion-Molecule Reactor for Use in Proton-Transfer-Reaction Mass Spectrometry, Anal. Chem., 90(20), 12011–12018, doi:10.1021/acs.analchem.8b02641, 2018a.

Krechmer, J., Lopez-Hilfiker, F. D., Koss, A. R., Hutterli, M. A., Stoermer, C., Deming, B. L., Kimmel, J. R., Warneke, C., Holzinger, R., Jayne, J. T., Worsnop, D. R., Fuhrer, K., Gonin, M. and De Gouw, J.: Evaluation of a New Vocus Reagent-Ion Source and Focusing Ion-Molecule Reactor for use in Proton-Transfer-Reaction Mass Spectrometry, , doi:10.26434/chemrxiv.6502652.v1, 2018b.

Languille, B., Drageset, A., Mikoviny, T., Zardin, E., Benquet, C., Ullestad, Ø., Aronson, M., Kleppe, E. R. and Wisthaler, A.: Best practices for the measurement of 2-amino-2-methyl-1-propanol, piperazine and their degradation products in amine plant emissions, SSRN Electron. J., doi:10.2139/ssrn.3812339, 2021.

Lee, S.-H.: Perspective on the Recent Measurements of Reduced Nitrogen Compounds in the Atmosphere, Front. Environ. Sci., 10, doi:10.3389/fenvs.2022.868534, 2022.

Lindinger, W., Hansel, A. and Jordan, A.: Mass Spectrometry On-line monitoring of volatile organic compounds at pptv levels by means of Proton-Transfer-Reaction Mass Spectrometry (PTR-MS) Medical applications, food control and environmental research, Int. J. Mass Spectrom. Ion Process., 173(191) [online] Available from: https://ac.els-cdn.com/S0168117697002814/1-s2.0-S0168117697002814-main.pdf?_tid=6947df56-c693-4be9-b40e-ab04872de81e&acdnat=1521625411_035eff2bdb9bba93d0690998674cbc36 (Accessed 21 March 2018), 1998.

Müller, M., Piel, F., Gutmann, R., Sulzer, P., Hartungen, E. and Wisthaler, A.: A novel method for producing NH4+ reagent ions in the hollow cathode glow discharge ion source of PTR-MS instruments, Int. J. Mass Spectrom., 447, 116254, doi:10.1016/j.ijms.2019.116254, 2020.

Nielsen, C. J., Herrmann, H. and Weller, C.: Atmospheric chemistry and environmental impact of the use of amines in carbon capture and storage (CCS), Chem. Soc. Rev. Chem. Soc. Rev, 41(41), 6684–6704, doi:10.1039/c2cs35059a, 2012.

Ongwandee, M., Bettinger, S. S. and Morrison, G. C.: The influence of ammonia and carbon dioxide on the sorption of a basic organic pollutant to a mineral surface, Indoor Air, 15(6), 408–419, doi:10.1111/j.1600-0668.2005.00380.x, 2005.

Pfeifer, J., Simon, M., Heinritzi, M., Piel, F., Weitz, L., Wang, D., Granzin, M., Müller, T., Bräkling, S., Kirkby, J., Curtius, J. and Kürten, A.: Measurement of ammonia, amines and iodine compounds using protonated water cluster chemical ionization mass spectrometry, Atmos. Meas. Tech., 13(5), 2501–2522, doi:10.5194/amt-13-2501-2020, 2020.

Prazeller, P., Palmer, P. T., Boscaini, E., Jobson, T. and Alexander, M.: Proton transfer reaction ion trap mass spectrometer, Rapid Commun. Mass Spectrom., 17(14), 1593–1599, doi:10.1002/rcm.1088, 2003.

Pugliese, G., Piel, F., Trefz, P., Sulzer, P., Schubert, J. K. and Miekisch, W.: Effects of modular ion-funnel technology onto analysis of breath VOCs by means of real-time mass spectrometry, Anal. Bioanal. Chem., 412(26), 7131–7140, doi:10.1007/s00216-020-02846-8, 2020.

Roscioli, J. R., Zahniser, M. S., Nelson, D. D., Herndon, S. C. and Kolb, C. E.: New Approaches to Measuring Sticky Molecules: Improvement of Instrumental Response Times Using Active Passivation, , doi:10.1021/acs.jpca.5b04395, 2015.

Schade, G. W. and Crutzen, P. J.: Emission of aliphatic amines from animal husbandry and their reactions: Potential source of N2O and HCN, J. Atmos. Chem., 22(3), 319–346, doi:10.1007/BF00696641, 1995.

Sellegri, K., Umann, B., Hanke, M. and Arnold, F.: Deployment of a ground-based CIMS apparatus for the detection of organic gases in the boreal forest during the QUEST campaign, Atmos. Chem. Phys., 5(2), 357–372,

10

doi:10.5194/acp-5-357-2005, 2005.

Wang, Y., Yang, G., Lu, Y., Liu, Y., Chen, J. and Wang, L.: Detection of gaseous dimethylamine using vocus proton-transfer-reaction time-of-flight mass spectrometry, Atmos. Environ., 243(August), 117875, doi:10.1016/j.atmosenv.2020.117875, 2020.

Yao, L., Wang, M. Y., Wang, X. K., Liu, Y. J., Chen, H. F., Zheng, J., Nie, W., Ding, A. J., Geng, F. H., Wang, D. F., Chen, J. M., Worsnop, D. R. and Wang, L.: Detection of atmospheric gaseous amines and amides by a high-resolution time-of-flight chemical ionization mass spectrometer with protonated ethanol reagent ions, Atmos. Chem. Phys., 16(22), doi:10.5194/acp-16-14527-2016, 2016.

You, Y., Kanawade, V. P., De Gouw, J. A., Guenther, A. B., Madronich, S., Sierra-Hernández, M. R., Lawler, M., Smith, J. N., Takahama, S., Ruggeri, G., Koss, A., Olson, K., Baumann, K., Weber, R. J., Nenes, A., Guo, H., Edgerton, E. S., Porcelli, L., Brune, W. H., Goldstein, A. H. and Lee, S.-H.: Atmospheric amines and ammonia measured with a chemical ionization mass spectrometer (CIMS), Atmos. Chem. Phys, 14, 12181–12194, doi:10.5194/acp-14-12181-2014, 2014.

Yu, H. and Lee, S.-H.: Chemical ionisation mass spectrometry for the measurement of atmospheric amines, Environ. Chem., 9(3), 190, doi:10.1071/EN12020, 2012.

Yuan, B., Koss, A. R., Warneke, C., Coggon, M., Sekimoto, K. and De Gouw, J. A.: Proton-Transfer-Reaction Mass Spectrometry: Applications in Atmospheric Sciences, Chem. Rev., acs.chemrev.7b00325, doi:10.1021/acs.chemrev.7b00325, 2017.

Zheng, J., Ma, Y., Chen, M., Zhang, Q., Wang, L., Khalizov, A. F., Yao, L., Wang, Z., Wang, X. and Chen, L.: Measurement of atmospheric amines and ammonia using the high resolution time-of-flight chemical ionization mass spectrometry, Atmos. Environ., 102, 249–259, doi:10.1016/j.atmosenv.2014.12.002, 2015.

Zhu, L., Mikoviny, T., Wisthaler, A. and Nielsen, C. J.: A Sampling Line Artifact in Stack Emission Measurement of Alkanolamine-enabled Carbon Capture Facility: Surface Reaction of Amines with Formaldehyde, Energy Procedia, 114(November 2016), 1022–1025, doi:10.1016/j.egypro.2017.03.1247, 2017.

Zhu, L., Mikoviny, T., Kolstad Morken, A., Tan, W. and Wisthaler, A.: A compact and easy-to-use mass spectrometer for online monitoring of amines in the flue gas of a post-combustion carbon capture plant, Int. J. Greenh. Gas Control, 78, 349–353, doi:10.1016/j.ijggc.2018.09.003, 2018.
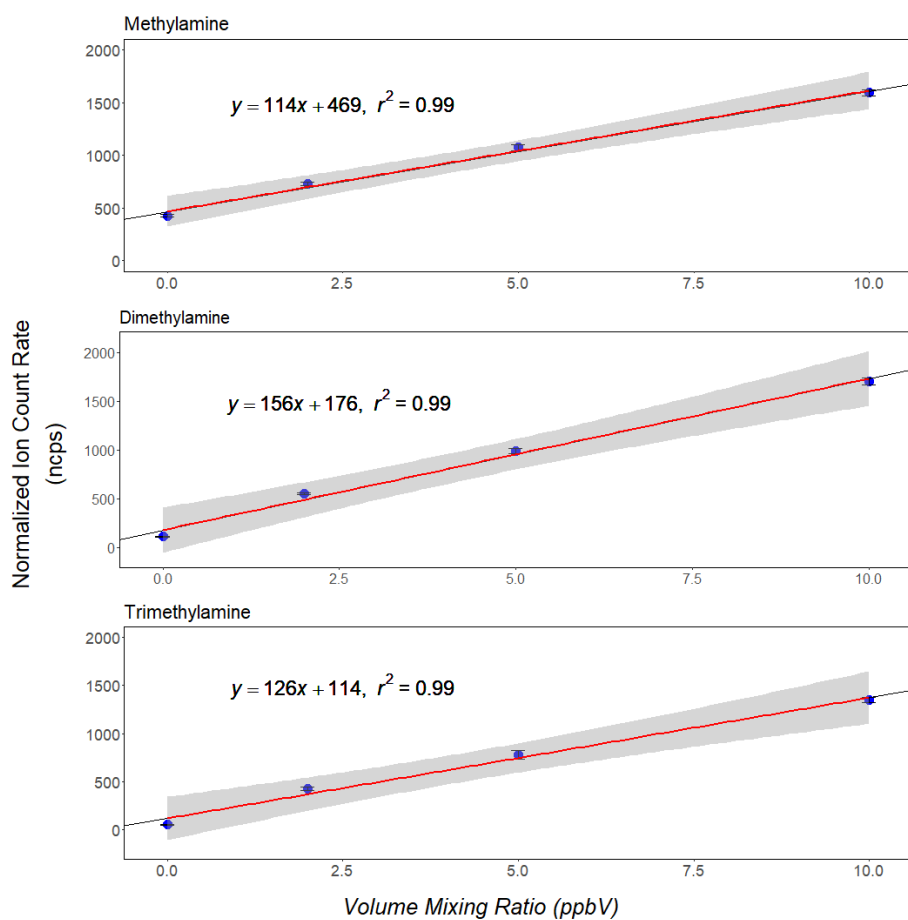
620
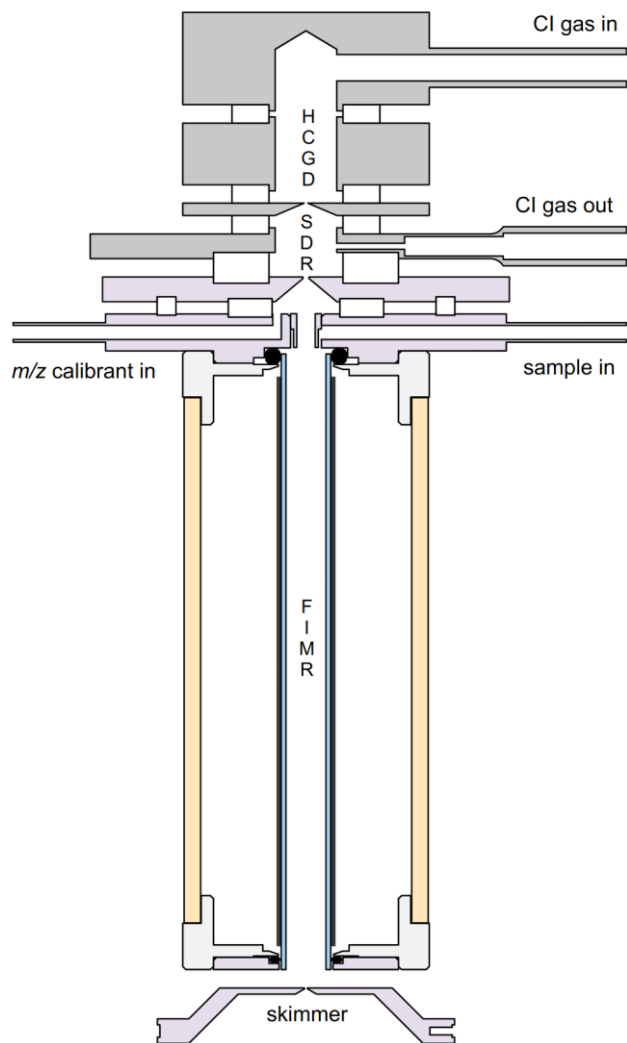
Figure 1. Schematic drawing of the new prototype PTR-ToF-MS analyzer. The instrument consists of a hollow cathode glow discharge (HCGD) ion source, a source drift region (SDR) and a focusing ion-molecule reactor (FIMR), which is a resistive glass drift tube surrounded by cylindrical quadrupole rods.

625
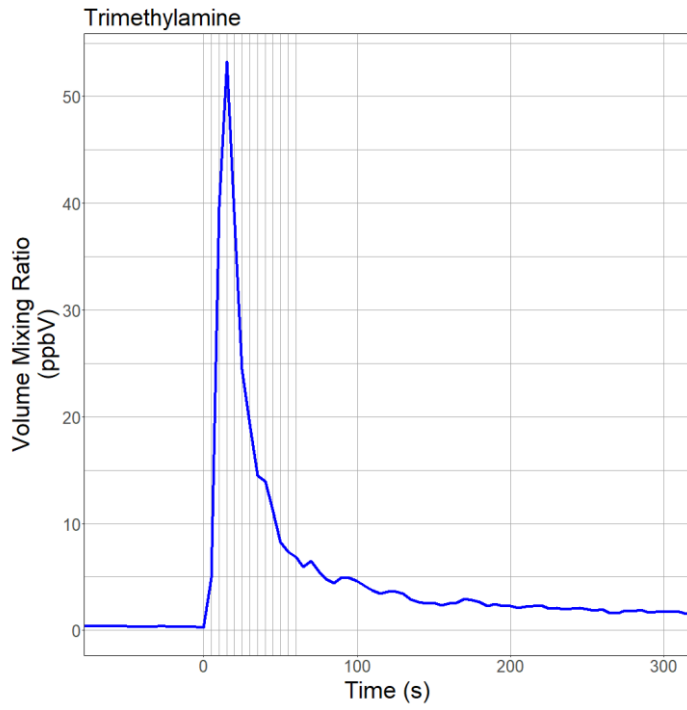
Figure 2. Time series of trimethylamine as measured in laboratory air when a *Chenopodium vulvaria* L. plant was mechanically stressed by tipping a leaf with a pen.
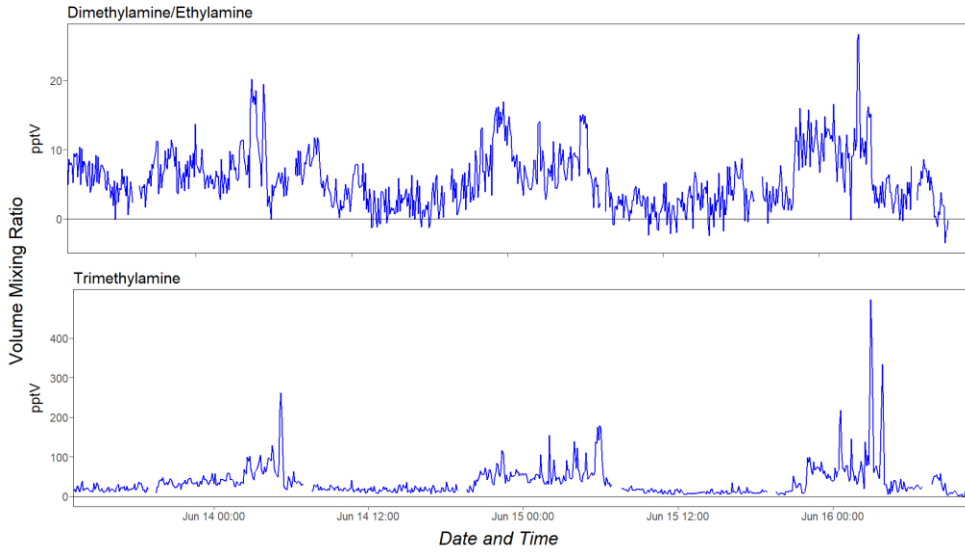
Methylamine

$y = 114x + 469$, $r^2 = 0.99$

Dimethylamine

$y = 156x + 176$, $r^2 = 0.99$

Trimethylamine

$y = 126x + 114$, $r^2 = 0.99$

Normalized Ion Count Rate (ncps)

Volume Mixing Ratio (ppbV)

Figure 3. Calibration curves for methylamine (upper panel), dimethylamine (middle panel), and trimethylamine (lower panel). The PTR-ToF-MS instrument was operated in the NH_4^+ mode (see text).

Deleted: -PT

14
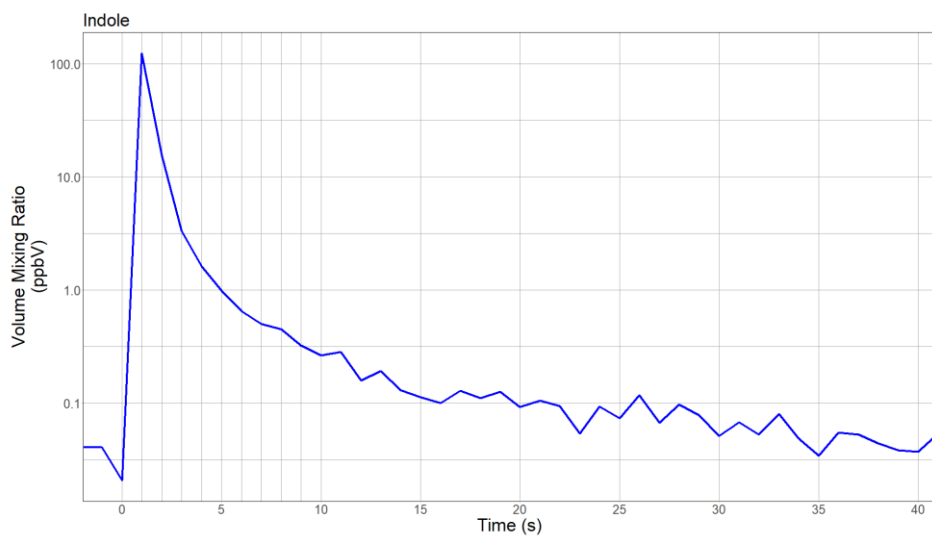
640

Figure 4. Time evolution of the observed indole VMR when the headspace from a vial containing indole was shortly blown towards the PTR-ToF-MS instrument in its field configuration.

645

Figure 5. Time series (5-min averages) of dimethylamine/ethylamine (upper panel) and trimethylamine (lower panel) as observed in ambient air on site of an agricultural research center.
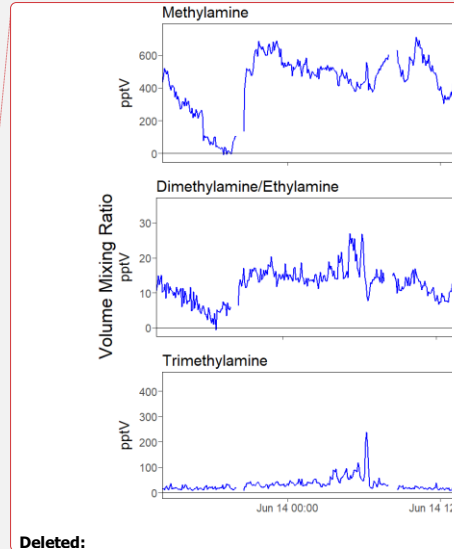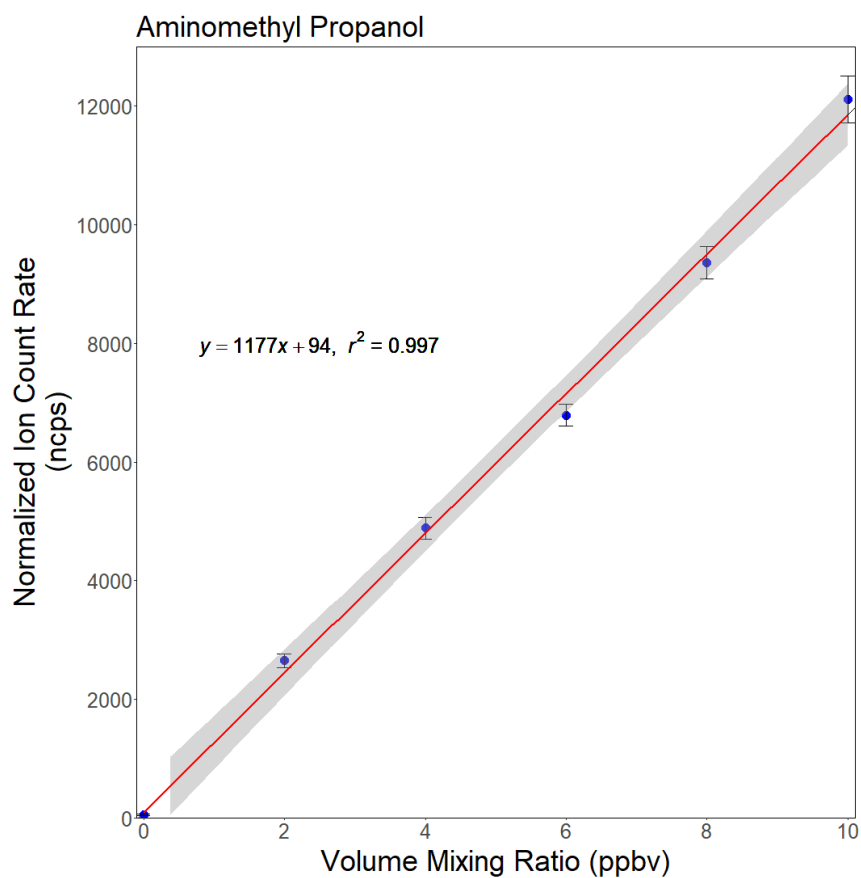
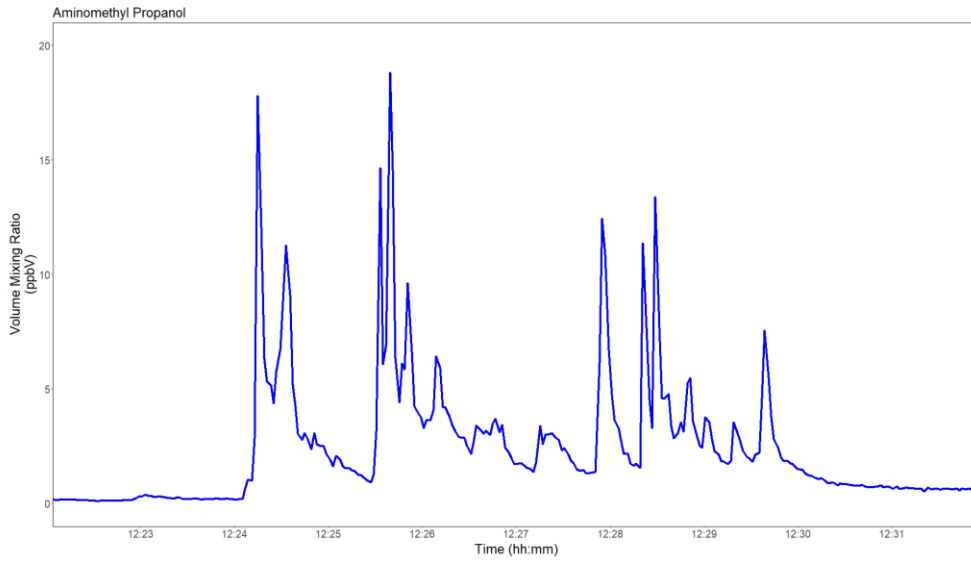**Figure 6: Calibration curve for 2-amino-2-methylpropan-1-ol (AMP). The PTR-ToF-MS instrument was operated in the H₃O⁺ mode (see text).**
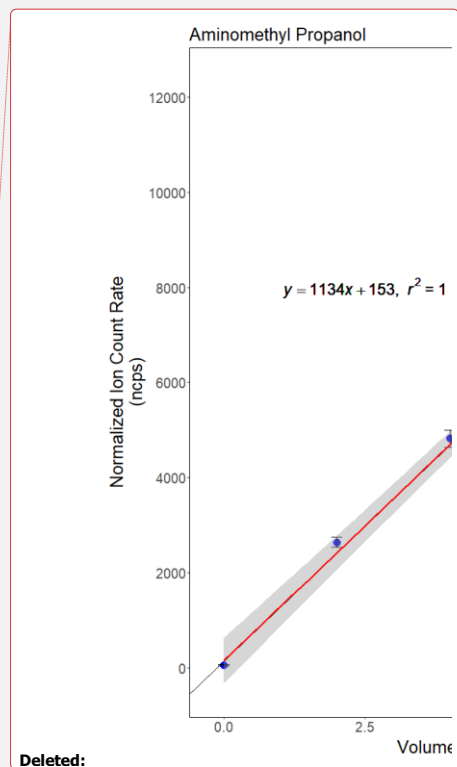
Figure 7: Time series (1 Hz) of 2-amino-2-methylpropan-1-ol (AMP) as measured when ~25 ppmV of this industrial amine were deliberately released into the air at approximately one meter distance from the instrument inlet.
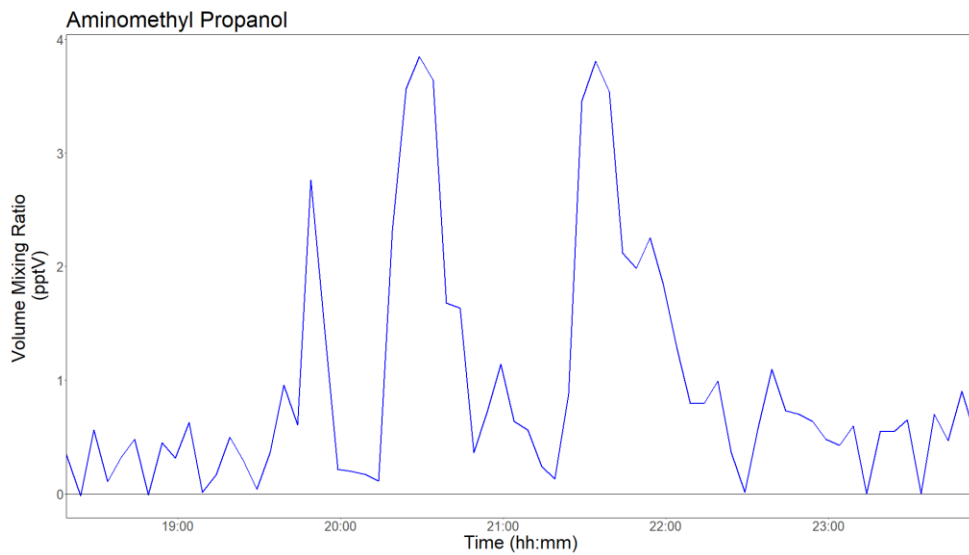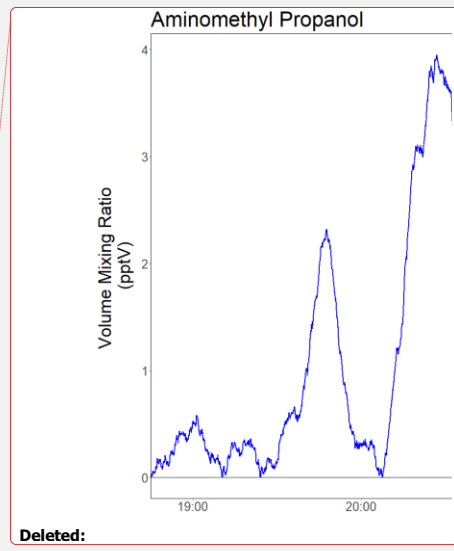
665

Figure 8: Time series (5-min averages) of 2-amino-2-methylpropan-1-ol (AMP) as measured at Sande, 4.4 km downwind from the TCM CO₂ capture plant. A steady level of ~1 ppmV of AMP was released from the stack during the measurement period, which resulted in single-digit pptV enhancements of AMP at the downwind site.

670

Deleted:

Deleted: 10-min running means