Monitoring of Volatile Organic and Inorganic Compounds in Wintertime Air: A Demonstration of Iodide Chemical Ionization with a Vocus CI-TOF Mass Spectrometer

Felipe Lopez-Hilfiker, Carla Frege,
Veronika Pospisilova, Abigail Koss
TOFWERK, Switzerland & USA

Iodide Chemical Ionization

The Vocus CI-TOF is a chemical ionization mass spectrometer (CI-MS) that measures trace volatile compounds in air in real time. Chemical ionization is a highly sensitive ionization method that ionizes analyte ions with little or no fragmentation by way of chemical reactions with reagent ions that are abundantly present in the instrument's ion-molecule reactor. Different reagent ions can be used, each of which is selective for specific classes of compounds. Iodide reagent ions (I^-) form adduct ions with a wide variety of both volatile organic and inorganic compounds (VOCs and VICs), making iodide CI mass spectrometry attractive for many applications. Here we describe observations of inorganic gases, organic acids, nitroaromatics, and highly oxidized VOCs during a two-week measurement of ambient air in the Swiss Alps using iodide chemical ionization with a Vocus CI-TOF.

Methods

Iodide chemical ionization mass spectrometry [1] has been used to great effect in atmospheric chemistry field studies [2][3]. Most previous research using iodide reagent ions used polonium-based sources for reagent ion generation. Radioactive material is strictly controlled, complicating the deployment of such instruments. TOFWERK's Vocus Aim reactor, used in this work, uses a vacuum ultraviolet (VUV) source to produce reagent ions, achieving approximately the same sensitivity as traditional polonium sources in a safer, more easily deployable package. An additional advantage of the Aim reactor over other designs for iodide CI-MS is its humidity independent response for VOC measurements.

A Vocus 2R CI-TOF equipped with an Aim reactor and I- reagent ions (Vocus Aim I^-) was used for ambient sampling in Thun- Switzerland, for 15 days during wintertime. The instrument was deployed side-by-side with a Vocus 2R CI-TOF equipped with a PTR reactor, which used proton-transfer-reaction chemical ionization to measure volatile organic compounds (Vocus PTR). The measurements took place between December 22, 2020 and January 5, 2021 at TOFWERK headquarters in Thun, Switzerland. During this time of the year in this Swiss Alpine region, it is expected to see some biomass burning emissions from local wood burning and some chlorine emissions from road salt during and after snow, in addition to some urban and natural emission from the area.

Volatile Inorganic Compounds

The measurement of volatile inorganic compounds (VICs) is of great interest in different fields, from atmospheric research to industrial scenarios. Many VICs were observed in ambient air during the measurement period, including SO_2, SO_3, N_2O_5, HNO_3, and various halogenated molecules including $BrNO_2$ and chlorine-containing species. Figure 1 shows continuous ambient measurement of Cl_2, N_2O_5, HNO_3 and $ClNO_2$. Figure 2 shows an expanded view of the time period from December 24-30 , showing chlorine activation via N_2O_5 present in the particle or liquid phase [4]. The instrument can also measure HCl [5], but none was observed at this location during this time period.

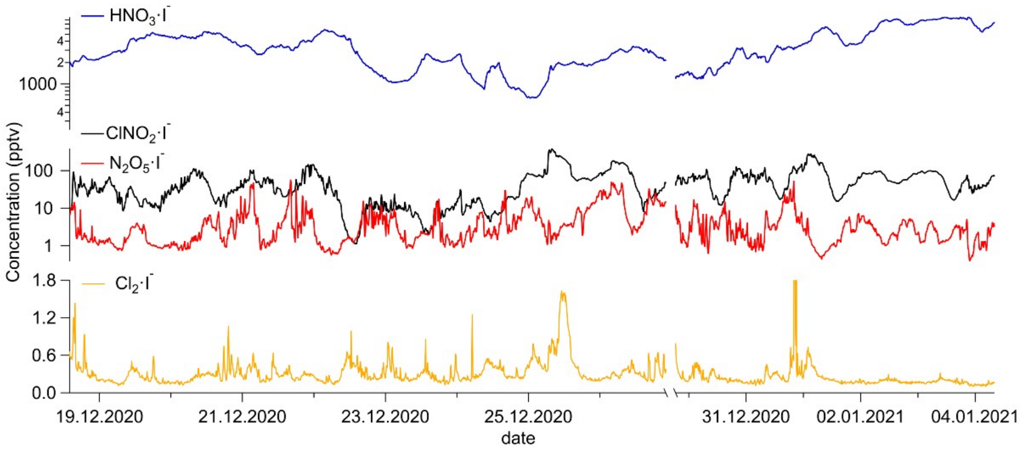

Figure 1. Vocus Aim I- measurement of select volatile inorganic compounds over a 15-day wintertime period in Thun, Switzerland.

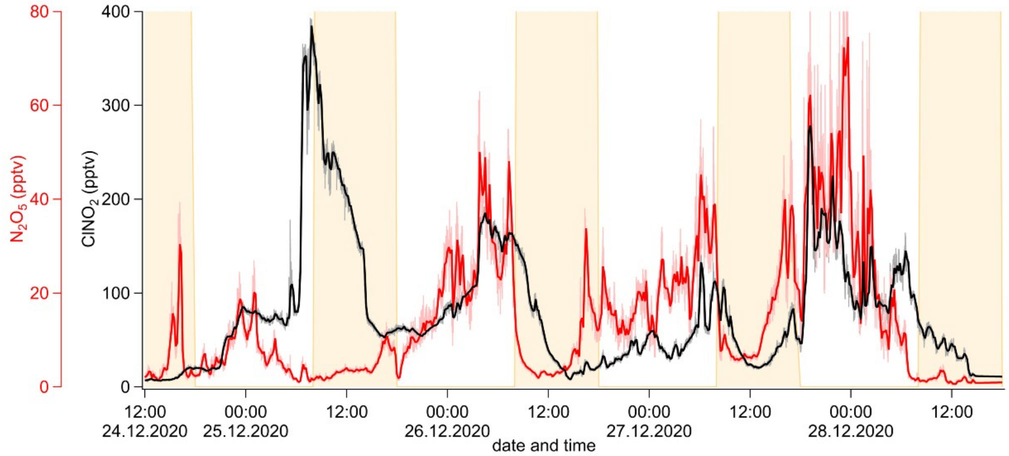

Figure 2. Chlorine activation event from midday on the December 25 through December 28: a peak in $ClNO_2$ follows a peak in N_2O_5 on several days. The light lines show the 1-second Vocus Aim I- measurements; the darker bold lines show the 10 min average signal. The shaded area shows the time of solar radiation at this time of the year.

Organic Acids

Iodide CI-MS is an especially sensitive detector for organic acids. Many of these acids were evident in ambient air during the measurement period. Figure 3 shows a diurnal average time series over 15 days of measurement of vanillin, malonic acid, glyceric acid and succinic acid. The diurnal patterns typically display a slight increase during the morning (09:00-13:00) and a stronger increase in the afternoon, peaking earlier for malonic acid than for other compounds.

Nitroaromatic compounds can be emitted from combustion and industrial activities, as well as photochemical processes [6]. Many nitroaromatic compounds are toxic and mutagenic [7 and references therein]. Their role in atmospheric chemistry is increasingly recognized as an important source of nitrous acid. Precise and sensitive measurement of these compounds is necessary to understand their sources and impact on human health.

The Vocus Aim I- is a sensitive detector of nitroaromatics in the atmosphere. Figure 4 shows the average diurnal pattern of four nitroaromatic compounds during the 15 days of sampling. The diurnal patterns are consistent with previous observations of nitrophenols in polluted environments [6].

Highly Oxidized Species and Biomass Burning Indicators

Iodide CI-MS is also proven to be a particularly good method to measure highly oxidized species [8]. Figure 5 shows the Vocus Aim I- time series of two highly oxidized species, one of

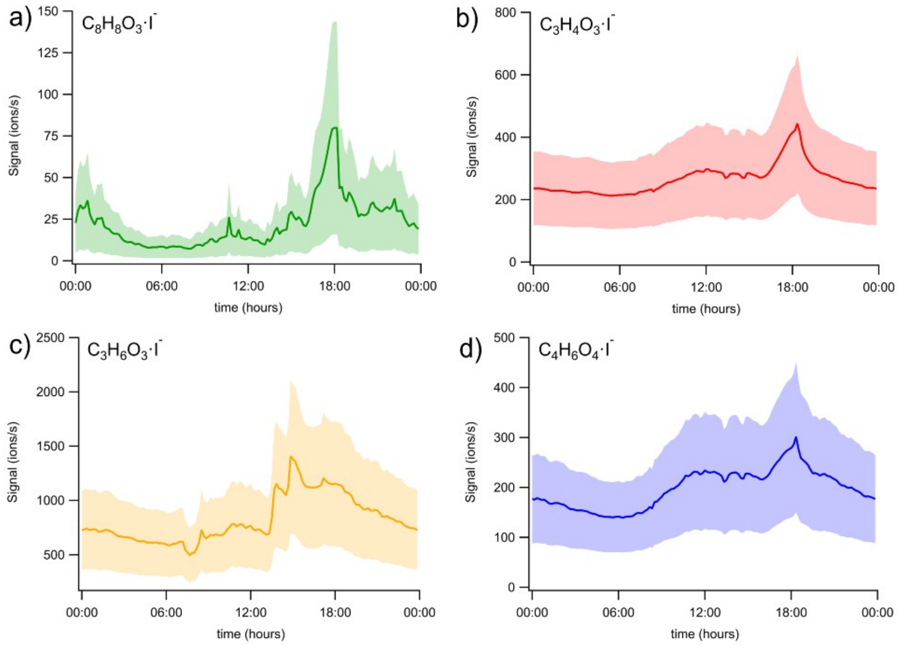

Figure 3. Average diurnal pattern of commonly measured VOCs over 15 days of measurement: a) vanillin ($C_8H_8O_3$), b) malonic acid ($C_3H_4O_3$), c) glyceric acid ($C_3H_6O_3$) and succinic acid ($C_4H_6O_4$). The shaded area shows the error deviation from the average.

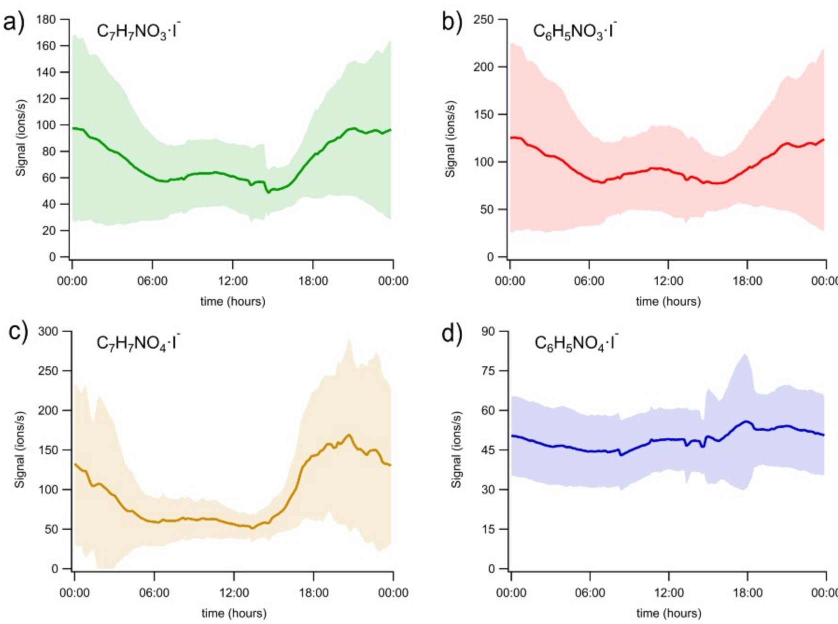

Figure 4. Diurnal pattern of four nitroaromatics: a) 4-methyl-2-nitrophenol, b) 4-nitrophenol, c) Methyl-nitrocatechol and d) 4-nitrocatechol. The lines show the mean value at that time of day, averaged over 15 days. The shaded area shows the standard deviation

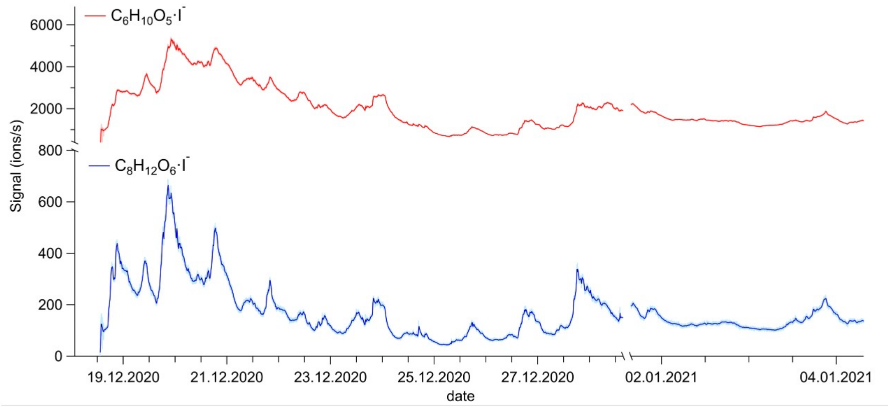

Figure 2. Time series of two highly oxidized molecules: levoglucosan ($C_6H_{10}O_5$) (red line, top) and $C_8H_{12}O_6$ (blue, bottom).

them levoglucosan ($C_6H_{10}O_5$), which is a biomass burning indicator. Other biomass burning indicators were also observed, including the nitroaromatic compounds discussed previously, vanillin, vanillic acid, phenol, and guaiacol.

Performance Compared to Vocus PTR

The stability and performance of the Vocus CI-TOF using the Aim reactor are demonstrated by comparison with the system using the PTR reactor across these several weeks of unattended operation. The sum of isomers with the formula $C_2H_4O_2$ shows nearly identical time series on both instruments (Figure 6). The Vocus PTR (red line) measured the sum of acetic acid and glycolaldehyde, while the Vocus Aim I- (blue line) is more specific and measures acetic acid only [9]. The responses of both instruments are humidity independent, therefore no correction to the data was needed.

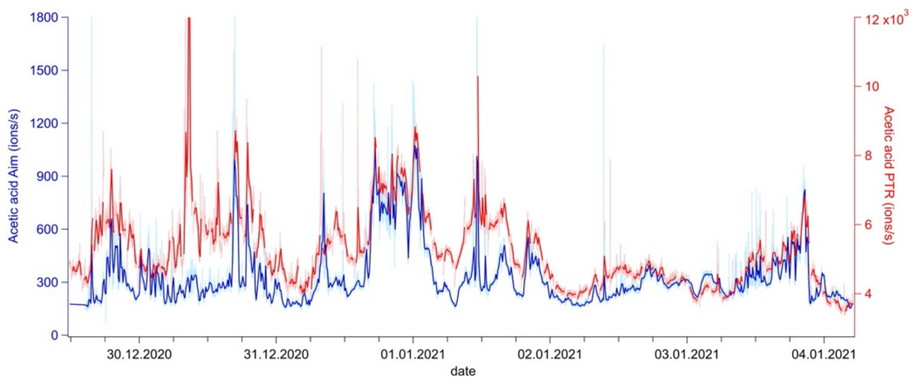

Figure 3. Acetic acid measured by AIM (blue, left axis) compared to the PTR measurement of acetic acid plus glycolaldehyde (red, right axis).

References

[1] Lopez-Hilfiker et al. "Constraining the sensitivity of iodide adduct chemical ionization mass spectrometry to multifunctional organic molecules using the collision limit and thermodynamic stability of iodide ion adducts." Atmos. Meas. Tech., 9, 1505-1512, 2016.

[2] Lee et al. "An Iodide-Adduct High-Resolution Time-of-Flight Chemical-Ionization Mass Spectrometer: Application to Atmospheric Inorganic and Organic Compounds." Atmos. Meas. Tech., 9, 1505–1512, 2016.

[3] Gaston et al. "Online molecular characterization of fine particulate matter in Port Angeles, WA: Evidence for a major impact from residential wood smoke." Atmospheric Environment 138, 2016.

[4] Kercher et al. "Chlorine activation by N2O5: simultaneous, in situ detection of ClNO2 and N2O5 by chemical ionization mass spectrometry." Atmos. Meas. Tech., 2, 193–204, 2009.

[5] Lee et al. "Flight Deployment of a High-Resolution Time-of-Flight Chemical Ionization Mass Spectrometer: Observations of Reactive Halogen and Nitrogen Oxide Species". Journal of Geophysical Research: Atmospheres, 123, 7670–7686, 2018.

[6] Yuan et al. "Secondary formation of nitrated phenols: insights from observations during the Uintah Basin Winter Ozone Study (UBWOS)." Atmos. Chem. Phys., 16, 2139–2153, 2016.

[7] Ju and Parales. "Nitroaromatic Compounds, from Synthesis to Biodegradation." Microbiology and Molecular Biology Reviews, 250–272, 2010.

[8] Riva et al. "Evaluating the performance of five different chemical ionization techniques for detecting gaseous oxygenated organic species." Atmos. Meas. Tech., 12, 2403–2421, 2019.

[9] Koss et al. "Non-methane organic gas emissions from biomass burning: identification, quantification, and emission factors from PTR-TOF during the FIREX 2016 laboratory experiment." Atmos. Chem. Phys., 18, 3299-3319, 2018.

Contact
vocus.info@tofwerk.com