

On behalf of the co-authors, I would like to thank the reviewer for the valuable comments and input which helped to improve the quality of the paper. Our responses to the comments are written in green font.

RC1:

Summary:

The authors measured negative atmospheric ions above the SMEAR II boreal forest site from a novel aircraft platform. Level flight legs were performed in the stable boundary layer, residual layer, mixed layer, and free troposphere at various times of day across several weeks. The measurements illustrate the evolution of negative ions in the atmosphere as the boundary layer rises. Ion composition is variable between different layers on each day, and variable within each layer across different days due to changes in airmass history. I found this paper to be very clearly written and depicted, and it is a useful contribution to the knowledge of atmospheric ions and their impacts on new particle formation. I have just a few minor comments below, and recommend publication in ACP.

Comments:

Line 176: Can you provide more details here for readers who may be unfamiliar with sampling with an APi-TOF, e.g., are ion transmission rates of ~1% normal? How do your transmissions rates compare with previous field measurements of ions, or with the ground measurements at the SMEAR II site?

AC: The measured transmission of the APi-TOF with 1% is a common characteristic of this instrument. It has also been shown in publications, e.g., Heinritzi et al. (2016) and Junninen et al. (2010). The characterisation of the transmission of the APi-TOF is usually done in the laboratory due to the rather bulky setup. So, therefore we have done the calibration in the lab before the campaign (as mentioned in the text). The inter-comparison of the flying APi-TOF and the stationary APi-TOF showed that the transmission of both of these instruments are around 1%.

In order to give more insight to the reader regarding the transmission, we added the following sentence to the manuscript (*italic*):

A transmission characterisation of the full setup (including the sliding inlet-system for the APi-TOF) was performed in the laboratory before the campaign. The transmission of ions between 100 Th and 400 Th was in the range 1–2%, and for ions >500 Th the transmission was below 0.5% (Fig. S3). *Those transmission values match with the characterization of other APi-TOFs, e.g., Heinritzi et al. (2016) and Junninen et al. (2010).*

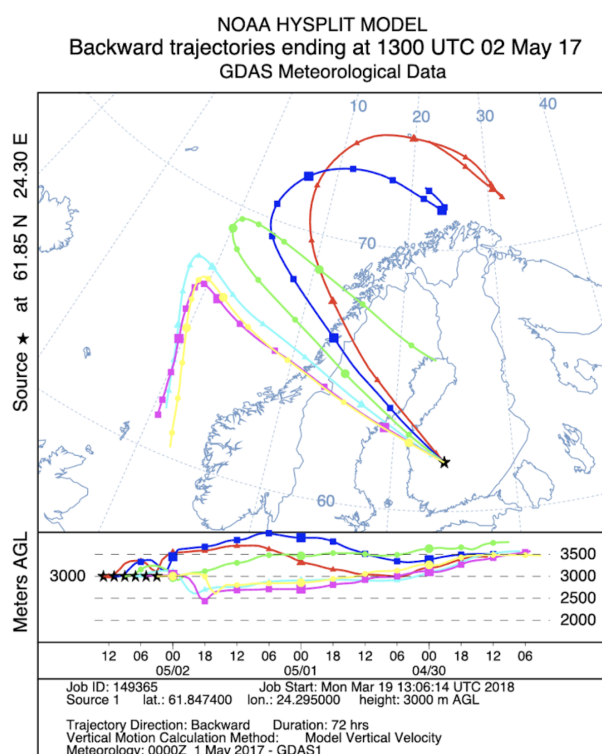
Line 220: When the flight setup was operated in the tower, did it include the same sliding inlet system to see if the inlet contributed to any differences between instruments?

AC: Yes, we kept the inlet system from the Cessna setup attached to the APi-TOF, and also operated it with the same vacuum pump, flow rates and instrument settings, including the regular cycle of x-ray in the inlet, in order to have the same measurement circumstances as during the flight.

Line 374: You are saying the FT air had marine origin in both morning and afternoon flights on 2 May 2017. You justify this as the reason for measuring halogenated compounds in the morning and MSA in the afternoon. Do you have any thoughts on why the halogenated compounds were not present in the afternoon and MSA was not present in the morning? Is this a result of charge transfer, as you discuss later on (e.g. line 438), or something else?

AC: The charge transfer to the sulfur containing compounds is certainly one of the main reasons why we primarily observe sulfuric acid and MSA rather than halogens in the afternoon.

The origin of gas-phase MSA is the oxidation of DMS via OH, so MSA is formed during daytime. The lifetime of DMS is 1-2 days (Boucher et al., 2003; Chen et al., 2018), and according to the 72 h back trajectories in the supplementary Figure S15 (c) (see below), the air mass was above the sea > 12 hours before arriving above SMEAR II station at 13 UTC (i.e. 15 EET). The back trajectories also show that the source changes from the West coast of Norway (Norwegian Sea) in the early morning to the North coast (Barents Sea) in the afternoon. Thus, it is more likely that we see MSA only in the afternoon due to the air mass change. According to Lana et al. (2010), the DMS production in May is higher in the Barents Sea than in the Norwegian Sea, and it is likely that the MSA concentration within that air mass was higher than in the air mass of the morning hours.



Line 478: I wonder if you find any correlation between ground level monoterpene concentrations and/or ozone concentrations with HOM in the SBL. Maybe there is a way to explain some of the slight variations in HOM across different days. Were there monoterpene measurements at SMEAR II during these times?

AC: Indeed, the ozone and / or monoterpene concentration were relatively high during the days with high amounts of HOM in the SBL. Below we show a figure with the time series of monoterpenes (MT), O₃, NO_x and the temperature (at the 4.2-m height). Unfortunately, there is a data gap in the MT concentration on 5 May 2017 during the morning hours, however the concentration in the previous evening reached 0.8 ppb at 19:29 local time before the data gap appeared. Possibly, the concentration was still rather high on 5 May morning.

The table below shows the average values of O₃ and MT during the measurements. The maximum of O₃ concentration was reached on 5 May and the maximum of MT concentration on 16 May 2017, when a high amount of especially HOM dimer were observed. The abundance of O₃ and MT could explain the high amount of detected HOM (dimers).

Table 1: Median of Ozone and monoterpene (MT) concentration at 4.2 m height during early morning hours when the measurements were taken in the SBL. On 5 May 2017, no MT data was available, therefore the last measured value from the day before is shown in the table.

	O ₃ (ppb)	MT (ppb)
2 May (04:00 - 04:30)	39	0.08
3 May (04:00 - 04:30)	34	0.16
4 May (04:00 - 04:30)	39	0.09
5 May (04:00 - 04:30)	40	(4 May 19:29: MT = 0.8 ppb)
12 May (03:30 - 04:00)	28	0.18
16 May (03:30 - 04:00)	32	0.3

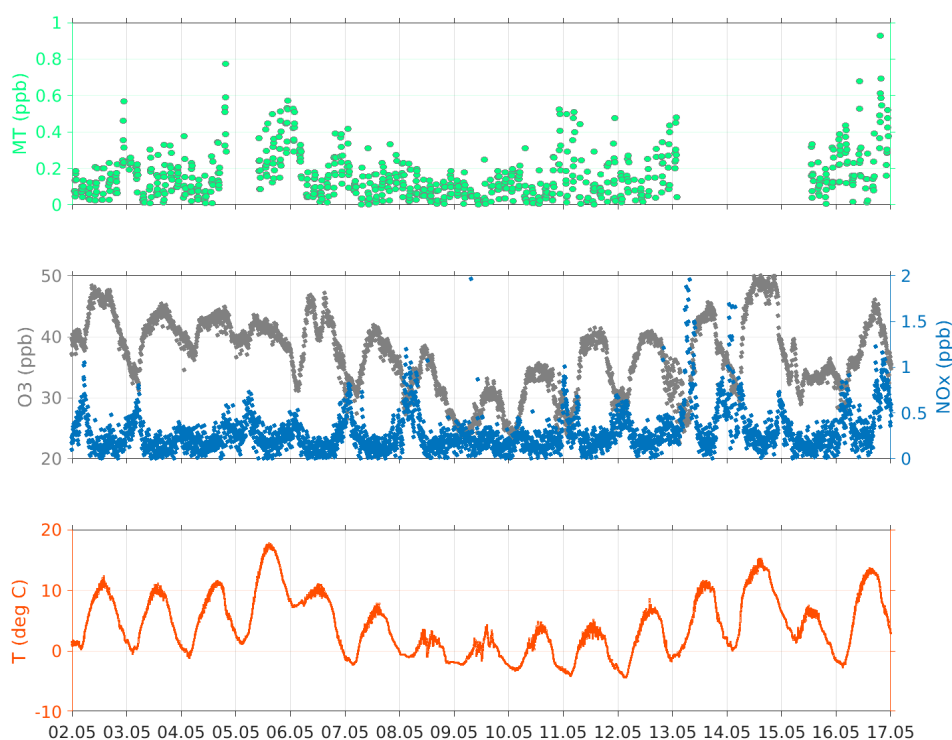


Figure 1: Monoterpene (MT) (green), Ozone (grey) and NO_x concentration (blue) given in ppb, as well as temperature in °C (red) at SMEAR II station from 2 May to 16 May 2017 at 4.2 m height above ground level.

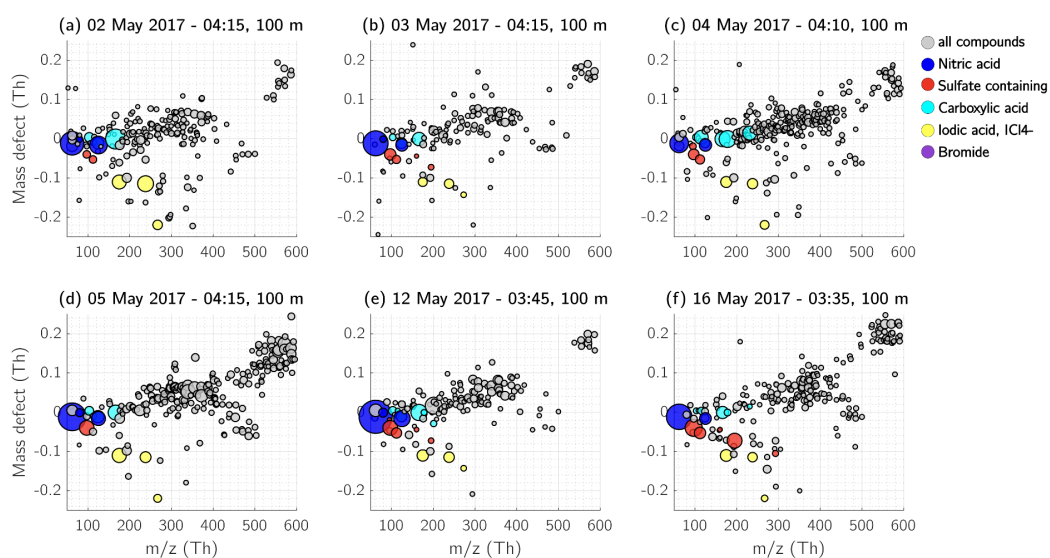


Figure 12 from the manuscript: Mass defect of the detected ions in the SBL at 100 m height. Each measurement day is shown separately. Nitric acid containing ions are coloured dark blue, and ions and clusters with sulfuric acid, MSA, or both and the the SO_5^- ion are indicated in red. The compounds containing carboxyl functional groups are shown in cyan, and iodic acid and iodine-containing compounds are shown in yellow. The size of the dots corresponds to the measured signal (ions s^{-1}).

Fig S2: Can you colour by altitude? That would help make the plot clearer I think.

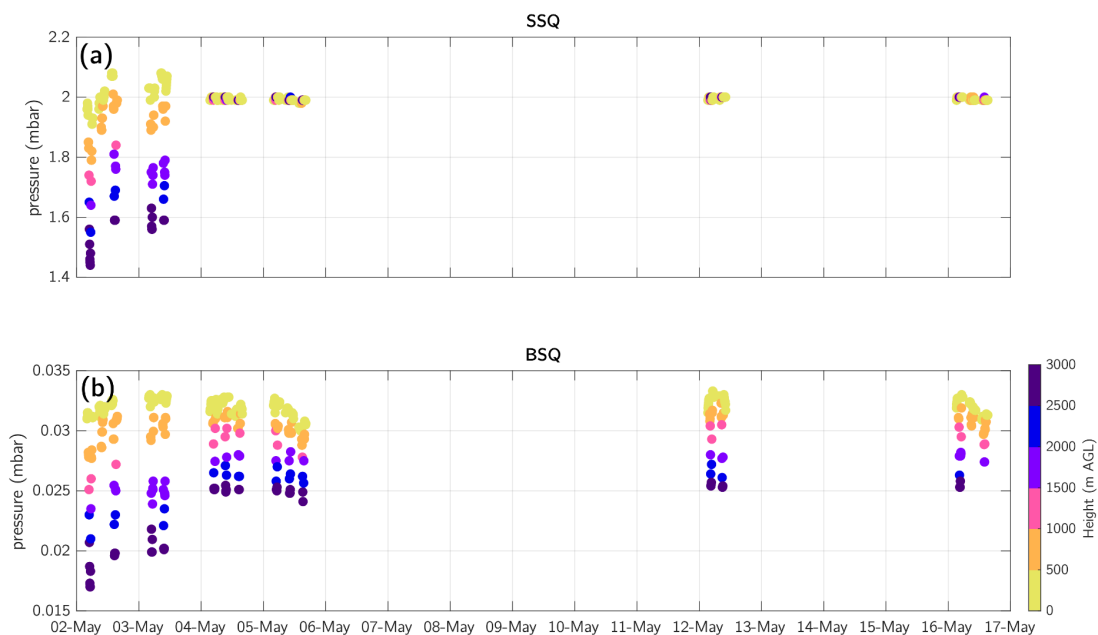


Figure S2 Time series of pressures inside the API-TOF during the measurement campaign. (a) Pressure of the Small Segmented Quadrupole (SSQ) chamber inside the API-TOF as well as (b) the Big Segmented Quadrupole (BSQ) during all measurement flights. The pressure of the SSQ was kept stable at 2 mbar on 4 out of 6 measurement days (4, 5, 12 and 16 May 2017). The BSQ pressure dropped with the ambient pressure on each flight, but did not reach values below 0.025 mbar during flights when the SSQ was at 2 mbar. The depicted pressures are coloured by height in m AGL.

AC: Thank you for the suggestion. We added the color for the height and also removed some data between the actual flight measurements to clean up the figure. Note that the pressure of the SSQ chamber was kept constant at 2 mbar in the last 4 out of 6 measurement days, the colors overlap and the values above 500 m are barely visible.

General comment: This paper focuses mainly on presenting the data, and it would be even more useful if you could expand upon what these results mean for atmospheric processes that depend on ions. For instance, what does the variable distribution of negative ions mean for the likelihood of NPF in each different layer of the atmosphere? Is NPF favored by the ions found in the boundary layer and mixed layer, or disfavored by the lack of HOM in the free troposphere? Please expand somewhere, perhaps in the conclusions section, even if it is to clarify that not enough is known yet about what role each subclass of ions ultimately plays in NPF.

AC: Considering that we only show observations of about 40 hours of measurement (i.e. 16 flights performed in 5 days) during springtime, we were rather careful with drawing too big conclusions, but we added the following paragraph to the conclusion section (green font).

From the conclusion:

A new tailored flying API-TOF mass spectrometer was deployed in a Cessna 172 aircraft to measure the vertical profiles of atmospheric ions above the boreal forest at the SMEAR II station, covering the stable boundary layer (SBL), residual layer (RL), mixed layer (ML) and free troposphere (FT). The measurements showed that the ion composition within the BL and FT is distinctly different, and that the ion chemistry of ML, SBL, RL, and FT is highly dependent on the time of day and air mass origin.

We detected HOM, originating from the forest VOC emissions, within the whole BL during daytime. The measured spectra in the ML were identical to a co-located reference measurement, which was performed on top of a 35-meter tower. Due to ongoing photo-oxidation during the daytime, most of the detected negative ions were the bisulfate ion and its clusters with sulfuric acid, forming sulfuric acid dimer and trimer, and bisulfate-HOM and nitric acid-HOM clusters within the whole ML. The nocturnal RL was clearly distinguishable from the other layers by its differing ion composition and revealed its own ion chemistry with the highest day-to-day variability compared to the other layers. Depending on the air mass origin and possible decoupling of the SBL, the measured air in the RL could contain halogen compounds, MSA and carboxylic acids, and HOM. The FT showed a distinctly different ion composition than the ML, SBL or RL. In the FT, a high abundance of carboxylic acids and some unknown compounds with masses in the range 200–400 Th were observed, probably clustered with carboxylic acids. Furthermore, we detected some very specific ion patterns on two days of measurements within the FT, which likely contained halogens (most likely chlorine), due to their apparent isotopic pattern. The daytime measurements in the FT mainly showed sulfuric acid, MSA, nitric acid and malonic acid, however we did not detect HOM.

As we summarised in the introduction, ion-induced nucleation is the main NPF pathway in several environments, especially under conditions when abundances of nucleating precursor gases are relatively low. At high enough precursor concentrations, ion-induced nucleation becomes less relevant for initiating atmospheric NPF. The compounds we observed in the various layers favour NPF, and even though our measurements focused on ions rather than neutral vapours, the ion chemistry sheds light on the available precursor gases. From our observations we could conclude that in the FT above the boreal forest, NPF could be initiated via ion-induced nucleation of inorganic compounds, such as sulfuric acid and iodic acid, also under the aspect that lower temperatures favour the nucleation (e.g. He et al., 2021; Duplissy et al., 2016). Within the boundary layer, however, it is more likely that a mixture of various compounds initiates the nucleation, especially as HOM have been observed within the whole ML. Furthermore, NPF has been observed at Jungfraujoch (Bianchi et al., 2016) and the Himalayan mountains (Bianchi et al., 2021) when organic compounds were transported upwards and mixed into the free troposphere. Also Rose et al. (2015) observed NPF at Puy de Dôme, at the interface between the boundary layer and FT, albeit nucleation there was driven by neutral compounds rather than via ion-induced pathways. Still, this could

indicate that a possible mixing of the organics in the mixing layer with the inorganics in the FT would provide good conditions for nucleation, e.g. during roll vortex events (Lampilahti et al., 2020). Thus, it could be speculated that the multi-component nucleation as proposed by Lehtipalo et al. (2018) is driving the nucleation. Moreover, above we discussed the nucleation mechanisms and nucleating precursor vapours, while it should not be forgotten that for NPF as a whole, also vapours that further grow small clusters into larger sizes are highly relevant.

Our observations represent only a snapshot of the ion composition in the BL and FT during springtime above the boreal forest. More observations, especially in the RL and FT, during other times of the year would be necessary for getting a better understanding of the chemistry and behaviour of ions in those layers and, ultimately to quantify the role of ions in NPF in different parts of the global troposphere.

References:

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