LABORATORY OF ATMOSPHERIC CHEMISTRY

PAUL SCHERRER INSTITUT PSI

Mobile measurements of ammonia:

Spatial variations in Wallis and Zurich

M. Elser, I. el Haddad, E. Bruns, S. Pieber, R. Wolf, N. Kumar,

A.S.H. Prévôt, U. Baltensperger

December 16, 2013

1 Heated inlet for the Picarro NH_3 Analyzer

The Picarro NH_3 Analyzer is a real time, trace gas monitor that measures ammonia (NH_3) levels in the range 0-10ppm. The measurement time resolution is ~3 seconds, but the response and recovery times depend on the range of operation. The analyzer is based on Wavelength-Scanned Cavity Ring Down Spectroscopy and uses a near-infrared laser to measure the spectral signatures of specific molecules (Nhu-Thuc et al., 2013). Since ammonia is a very sticky compound, the use of an inlet line increases the response and recovery times, which may hinder real time mobile measurements. To minimize this effect, we have tested a heated inlet line (PTFE, d_{out}: 6mm, L: 1m, T: 110°C) with an auxiliary flow (~ 5 l/min). The use of the heated line helps reducing the absorption of the NH_3 on the walls of the line, by increasing the adsorption and desorption rates, whereas the auxiliary flow decreases the residence time of the gas in the line.

Fig. 1 illustrates laboratory calibrations of the system response time using the same inlet setup as during the mobile measurements. It can be clearly seen that the response is concentration dependent, slower at lower concentrations. For example, increasing from 0 to 15ppb, the system needs ~45 min. to get 99% of the final value; starting from 20ppb and increasing to 25ppb, the system just needs 7 min. to reach 99% of the final value. This calibration curves will be ultimately used to correct the ambient measurements in a later stage of the data analysis.

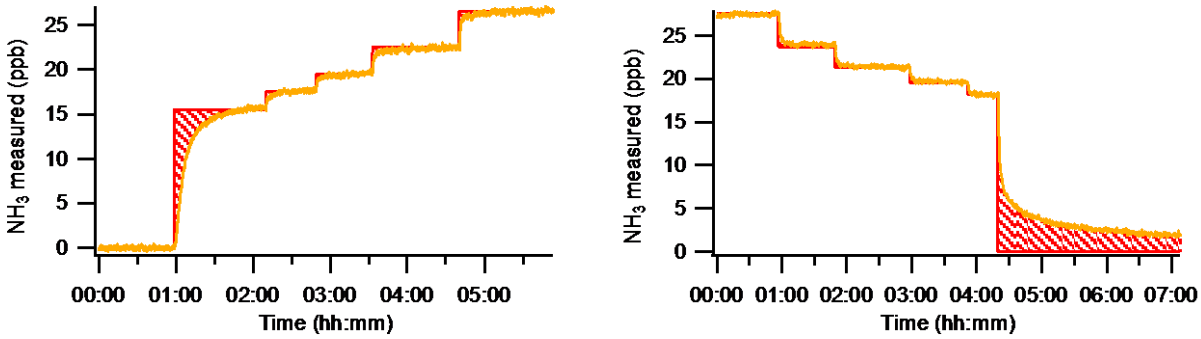

Figure 1: Response time of the NH_3 signal (orange line) when injecting different amounts of NH_3 (red line) in the system. The dashed area represents the delay of the measurement, mostly due to absorption (left) or desorption (right) of NH_3 on the inlet line.

At 110°C ammonium salts present in the atmosphere (mainly ammonium nitrate (NH_4NO_3) and ammonium sulfate ($(NH_4)_2SO_4$)), can volatilize in the inlet line creating a positive artifact in the NH_3 measurement (Ellis et Al., 2010).Tests realized in the laboratory showed that with our setup NH_4NO_3 quantitatively evaporates in the heated line (see Fig. 2), whereas all the $(NH_4)_2SO_4$ stays in the particle phase. Under these conditions, the measured ammonia concentrations represent the aggregate of gas phase ammonia and ammonium nitrate.

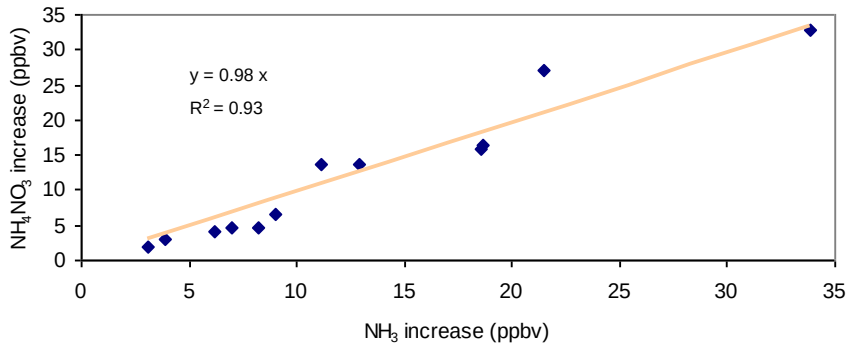

Figure 2: Linear relation between NH_4NO_3 and NH_3 increase

Using the Aerosol Mass Spectrometer (AMS) ammonium nitrate measurements, the ammonia measurements were corrected for the evaporation of NH_4NO_3. Fig. 3 shows the result of this correction on the NH_3 time series for the seven days of drives performed in Zurich. As during this measurement period the ammonium nitrate concentrations were significantly lower than the ones of ammonia, the impact of this correction is almost negligible.

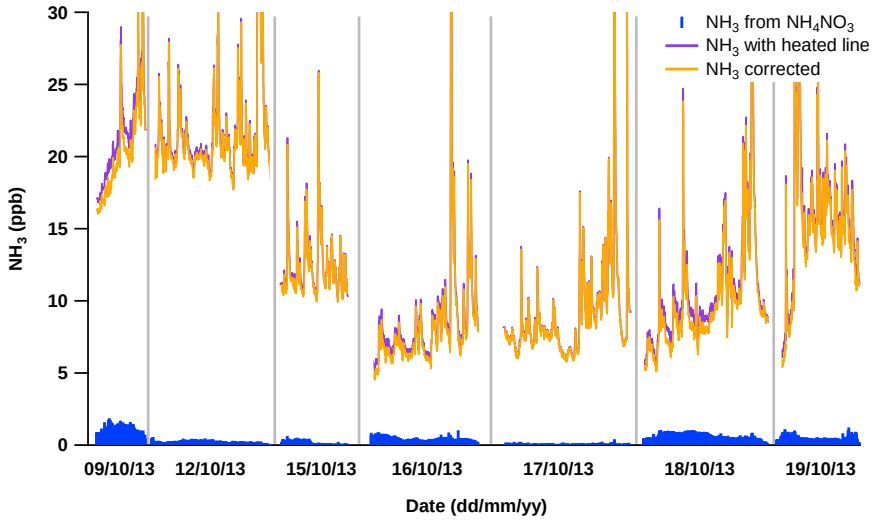

Figure 3: Time series of ammonium nitrate (blue), ammonia measured with the heated line (purple) and corrected ammonia values (orange).

2 Time series of Ammonia and other measured pollutants

In order to study the spatial distribution of ammonia and to identify and characterize its sources, mobile measurements were conducted during 2013. Specifically two days of measurements were conducted in the Wallis region (24th and 25th of January) and 7 days in Zurich (between the 9th and 19th of October). In the Wallis, besides the NH_3, also BC and CO_2 were measured. For the measurements in Zurich a more complete setup was used, including also HR-ToF-AMS (for the determination of organic and inorganic aerosols) and NO measurements.

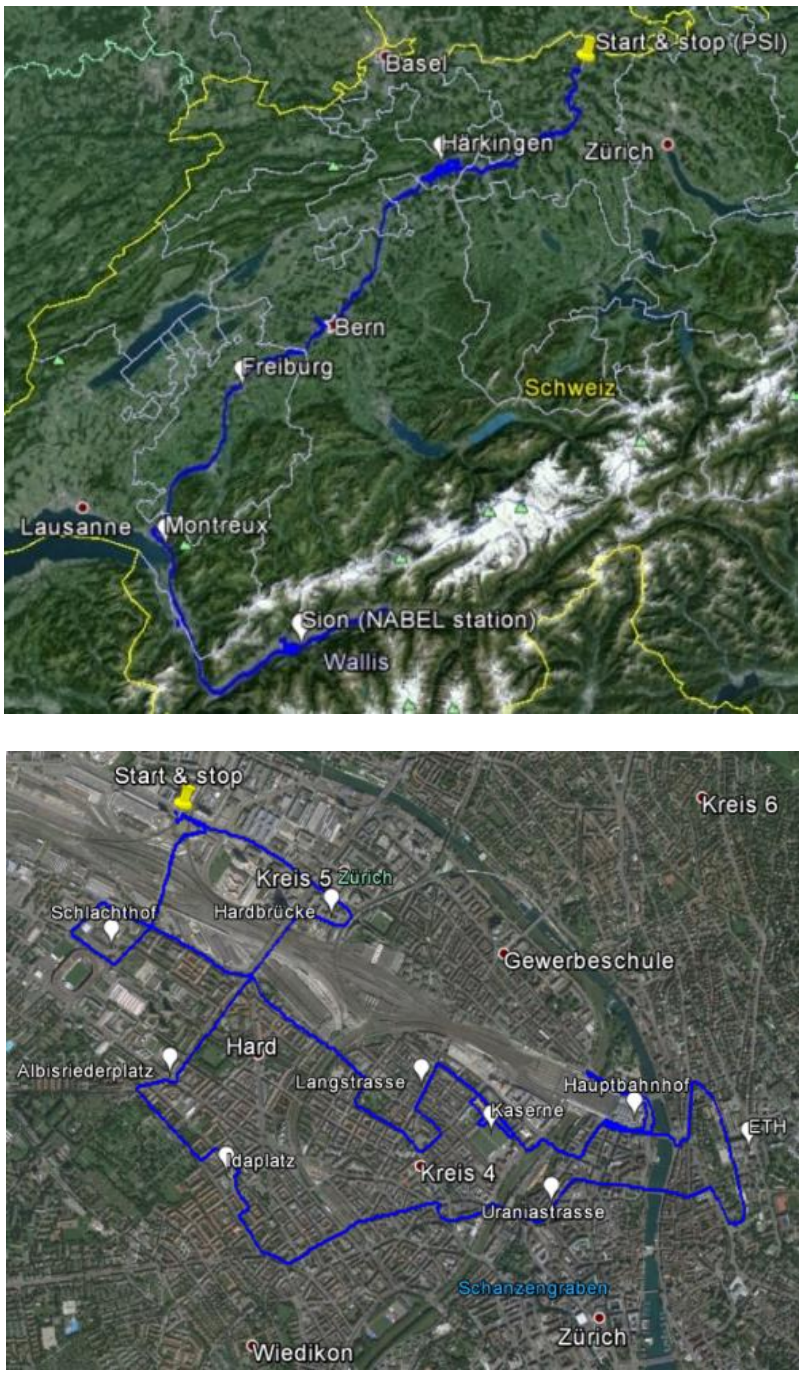

Figure 4: Representation of the GPS data for the drives to the Wallis region (top) and in Zurich (bottom)

Figure 5 shows the time series of the different measured pollutants for the two days of measurements in the Wallis region. A clear correlation between the traffic markers (BC and CO_2) and the NH_3 peaks can be noticed. This is especially evident for the on road measurements, whereas for the "stationary" night measurements another source appears to have an influence on the NH_3 concentrations. As shown in more details in Section 4 of this report, this source is most probably related to wood burning emissions.

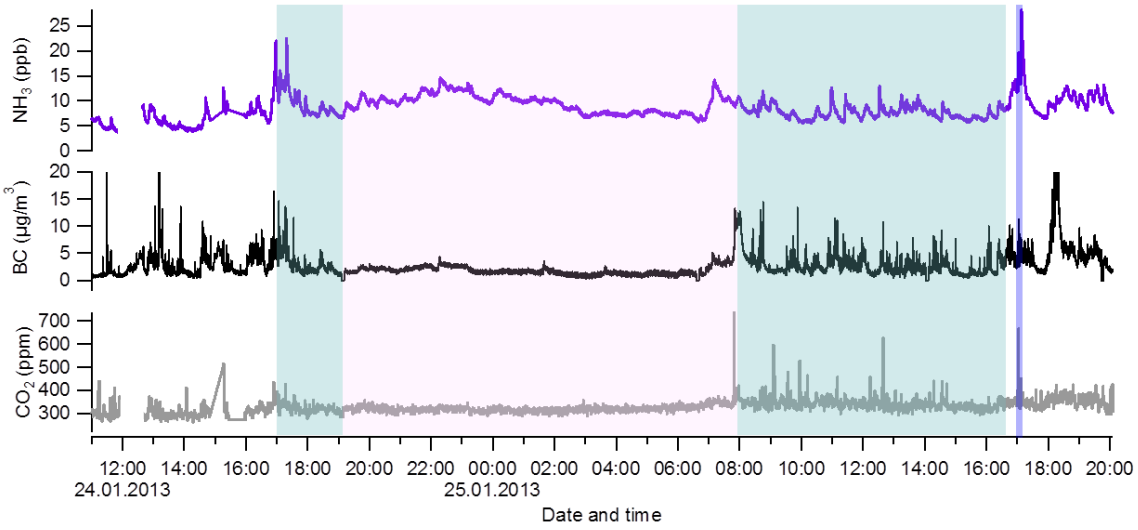

Figure 5: NH_3, BC and CO_2 time series for the drives in the Wallis region. Blue and pink backgrounds represent respectively on road and stationary measurements in the Wallis region; white background represents mostly highway measurements between our institute (start&stop point in Fig. 4 left) and the starting of the Wallis region (close to Montreux); violet indicates an event reported in Section 4.

For the measurements in Zurich the NH_3 time series can be also compared with other traffic tracers, including NO, and a number of AMS fragments characteristic of traffic emissions,$C_4H_9^+$ and m/z57. Secondary species are also shown including inorganic ions NO_3^-, SO_4^{2-} and NH_4^+, and oxygenated organic fragments (e.g. m/z44).

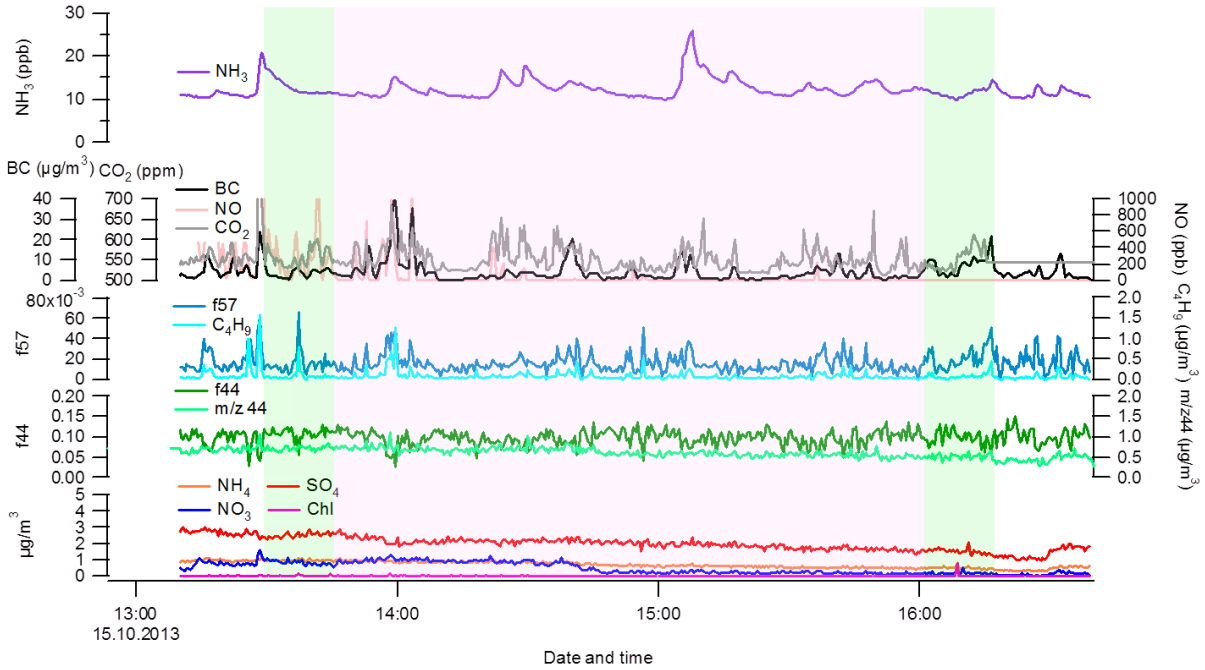

Figure 6: NH_3, traffic tracers (BC, CO_2, NO, f57 and $C_4H_9^+$), secondary organic aerosol tracers (org(44) and f44) and inorganic ions (NO_3^-, SO_4^{2-}, Cl^- and NH_4^+) time series for one day of measurements in Zurich. White background represents road measurements between our institute and the highway; green background stays for highway measurements; pink background represents measurements inside the city of Zurich (route shown in Fig.4). f57 and f44 correspond to the relative fraction of the concentrations at m/z57 and m/z44 divided by the total organic concentration.

As an example, figure 6 shows the time series of all these compounds/fractions for one day of measurements in Zurich (see also S1 to S7). It can be seen that, also in this case, the majority of NH_3 peaks coincide with the peaks of traffic tracers. A more detailed analysis of the time series of the different pollutants indicated also an influence of other emission sources on the NH_3 levels, including wood burning and cooking (Section 4).

3 Ammonia spatial distribution in Zurich

As already observed from the time series above (Fig 6), during the drives in Zurich most of the NH_3 peaks observed are related with traffic emissions. Unfortunately there are several factors that complicate the statistical analysis of the data: the traffic volume and distribution is highly variable among the day, the NH_3 data needs to be corrected (to take into account the delay due to the instrumental response and recovery times) and an appropriate averaging approach needs to be used in order to get general results.

3.1 Regional background of ammonia

It can be observed in Fig. 3, that the background of ammonia varied considerably during the measurement days in Zurich. A closer inspection of the data reveals that the NH_3 backgrounds are spatially coherent, with similar values in the city and the surroundings (Fig 6 and Fig S1-6 in the supplementary). The variability of these backgrounds is consistent with that of regional pollutants such as OA and CO_2, suggesting that unlike BC which is mainly locally emitted a large fraction of NH_3 is regional.

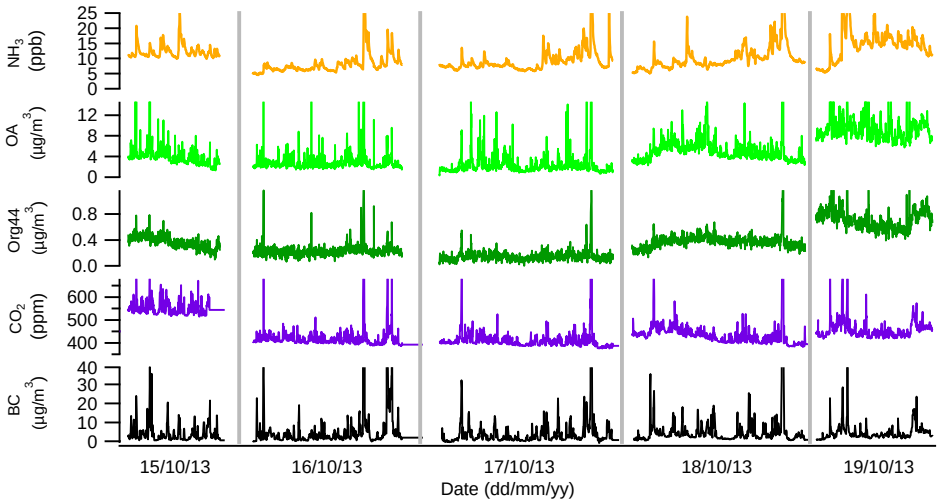

Figure 7: NH_3, OA, Org44, CO_2 and BC time series for the 5 consecutive days of measurements in Zurich. Note: very high peaks (normally related to drives into tunnels) have been cut out from the graph in order to also show the background variations.

3.2 Daily variability of ammonia levels

Table 1 summarizes the daily background, average and maximum levels of NH_3 in Zurich. Also the fraction between the maximum and the background is reported. In the calculations of these values just the data acquired inside Zurich was used. The values relative to the first two days (with gray background) should be taken into consideration more carefully as problems occurred with the NH_3 acquisition yielding a high and variable background values.

	NH_3 background (ppb)	NH_3 average (ppb)	NH_3 maximum (ppb)	Maximum / Background
09.10.2013	19.3	21.6	29.0	1.5
12.10.2013	17.8	21.1	31.3	1.8
15.10.2013	10.0	12.9	26.0	2.6
16.10.2013	5.7	7.6	11.4	2.0
17.10.2013	5.8	8.8	19.9	3.4
18.10.2013	6.6	10.6	24.7	3.7
19.10.2013	7.5	16.3	28.5	3.8

Table 1: Daily averages of the NH_3 characteristic levels for the 7 days of measurements in Zurich.

In general NH_3 background levels varied between 5 and 10 ppb whereas the average levels were between 7 and 17ppb. Moreover, as shown from the ratio between the maximum and background values, the higher peaks of NH_3 (always related to traffic emissions) can be between two and four times higher than the background.

3.3 Ammonia spatial distribution

Reported in Fig 8 are the spatial distributions of NH_3 and BC for one single loop in Zurich. The two compounds exhibit very similar distributions, indicating again that the NH_3 maxima in Zurich are principally due to traffic. In this specific case, the highest levels of both BC and NH_3 were observed in the city center (Uraniastrasse, after the crossing of Bahnhofstrasse) whereas the lowest values were in the Zurich Kaserne station.

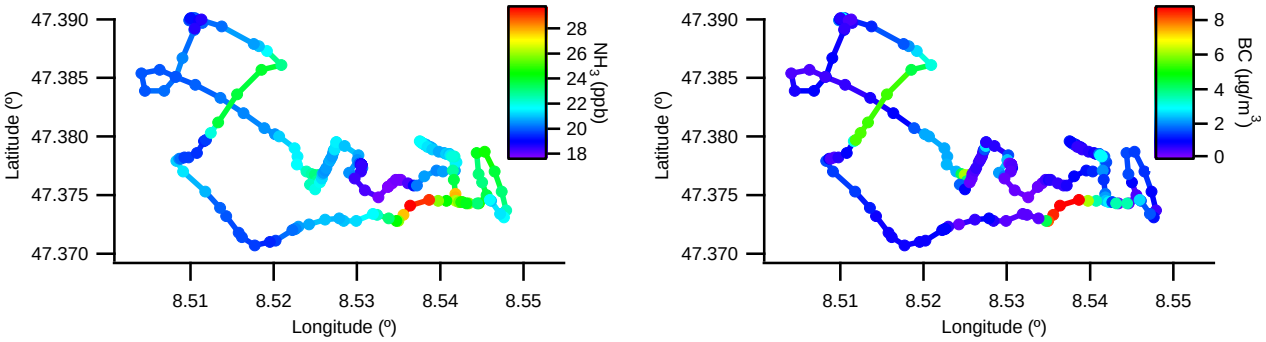

Figure 8: Spatial distribution of NH_3 (left) and BC (right) during one of the drives in Zurich. NH_3 levels are reported in ppb, whereas the BC levels are in $\mu g/m^3$.

With some exceptions (see section 4) the analysis of single loops (20 in total) shows that NH_3 closely follows the BC distribution. Moreover, whereas the minima of these two compounds are almost always in the non-traffic influenced zone of Zurich Kaserne, the maxima have a high spatial variability (normally due to the variability of the traffic source). Figure 9 includes the NH_3 distribution of 8 overlapping loops (corresponding to different times and days of measurements). In order to show the general spatial variability, the values of NH_3 were normalized to the maximum concentration of each loop.

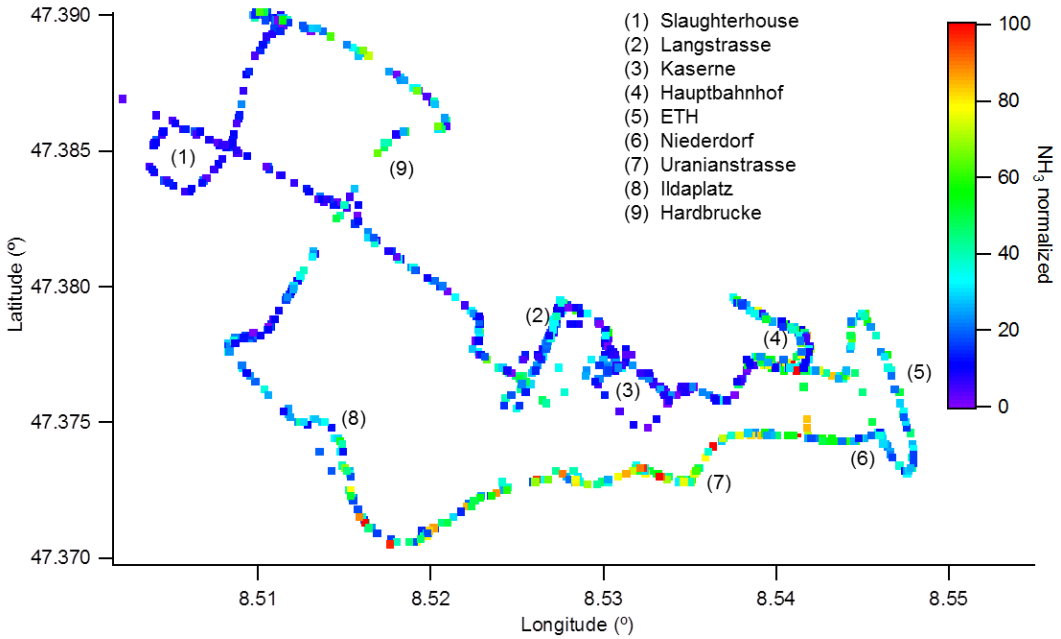

Figure 9: NH_3 spatial distribution for 8 overlapping loops. Values of NH_3 have been normalized to the maximum concentration of each loop in percent.

As anticipated, the generalization of the results to obtain the spatial distribution of NH_3 in Zurich needs a thorough analysis. Nonetheless, several zones can already be distinguished:

(1) Zones with city background levels: like Kaserne and all the zone close to the slaughterhouse

(2) Zones with medium influence: zone around the ETH, Hardbrucke and Ildaplatz.

(3) Zones with high traffic impact and high NH_3 levels: Langstrasse, Hauptbahnhof, and the streets between Niederdorf and Uraniastrasse.

3.4 Preliminary estimated contribution of traffic on ammonia concentrations

As shown in the previous sections, most of the NH_3 peaks during the drives in Zurich are related to traffic emissions. One approach to estimate the contribution of traffic to the measured NH_3 levels is to use the traffic emission profiles. NH_3 emission factors (EF) can be calculated from the data acquired while driving inside tunnels (Emmenegger et al, 2004), with the reliable assumption that all the pollutants present inside the tunnels (after the background subtraction) are due to traffic emissions.

Very high peaks of BC, CO_2, OA and NH_3 appear when driving through the tunnel (NH_3 up to 120 ppb). Integrating the area below this peaks leads to the calculation of the emission factors. While the signals for BC, CO_2 and OA reach background values shortly after the exit of the tunnel, NH_3 peaks show the usual delay due to the system recovery time, which have to be taken into account in the calculation of the EF. The equation used for this calculation, for example for the BC, is:

$$EF\left(\frac{mg\ BC}{Kg\ fuel}\right) = \frac{\int (BC - BC_0)(\frac{mg}{m^3})}{\int (CO_2 - CO_{2,0})(\frac{kg}{m^3})} x \frac{44}{12} x\ 0.85$$

where the factors 44/12 and 0.85 are respectively the conversion factors from $[CO_2]^{-1}_{mass}$ to $[C]^{-1}_{mass}$ and from $[C]^{-1}_{mass}$ to $[fuel]^{-1}_{mass}$.

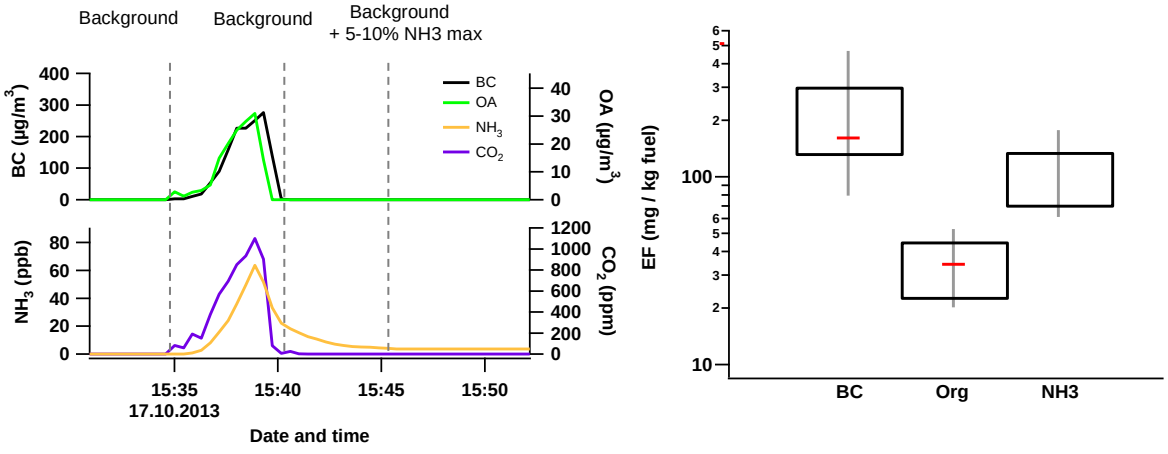

Figure 10: Left: characteristical signals (background subtracted) of BC, OA, NH_3 and CO_2 when driving through a tunnel; Right: calculated traffic emissions factors for BC, Org and NH_3. Red line indicates the mean value, boxes the Q75-Q25 percentiles and grey line are the Q90-Q10 percentiles.

The BC, CO_2 and OA signals are integrated until the signal falling edge reaches the background levels corresponding to the tunnel exit. For the NH3, however, due to the signal times, the integration was performed over the time when the signal reaches the backround values + 5% of the maximum value observed in the tunnel. Using the data of 10 tunnel drives the traffic EF for BC, Org and NH_3 showed in the right panel of Fig 10 were calculated. Most of this measurements were done in a highway tunnel (Gubristtunnel, average speed between 80 and 120km/h) unless two that were performed in urban tunnels

(Mitchbucktunnel in Zurich and Badstrasse in Ennetbaden, average speed of 30 to 50 km/h), but no influence of the velocity can be seen from these results.

Under the hypothesis that all the background corrected levels of BC and CO_2 measured in Zurich are related to traffic emissions and making use of the estimated EF, the results in table 2 are obtained. Also in this case the values corresponding to the first two days of measurements are not taken into account in the average, as their background values are not reliable. This table shows that the estimated contribution of traffic emissions on the NH_3 daily average levels in Zurich varied between 10-40% depending on the background levels, with an average of around 20-30%.

DAILY AVERAGES	NH_3 measured (ppb)	NH_3 estimated from BC* (ppb)	Estimated from BC / Measured (%)	NH_3 estimated from CO_2* (ppb)	Estimated from CO_2 / Measured (%)
09.10.2013	21.6	2.7	12.4	1.7	7.9
12.10.2013	21.1	1.2	5.8	2.0	9.6
15.10.2013	12.9	3.4	25.9	2.3	18.0
16.10.2013	7.6	2.4	30.6	1.9	25.2
17.10.2013	8.8	2.7	29.7	2.2	24.5
18.10.2013	10.6	3.8	37.8	3.5	33.3
19.10.2013	16.3	2.8	17.0	1.4	8.4
* Considering that all BC or CO_2 come from the traffic		**Average ± σ**	**28.2 ± 7.6**	**Average ± σ**	**21.9 ± 9.3**

Table 2: Daily averages of the NH_3 levels, NH_3 levels estimated from BC and CO_2 and fraction of NH3 estimated to come from traffic emissions in both cases.

The use of the BC for the estimation of the NH_3 emissions from traffic has some uncertainties related to the different traffic sources of these two compounds: whereas BC is known to be emitted from diesel cars, NH_3 is probably emitted mostly from gasoline cars. On the other hand, the use of the CO_2 for this estimation has also uncertainties, related to the fact that CO_2 can also be emitted from non-traffic combustion emissions. Assuming that the traffic in Zurich is well mixed (almost same amount of gasoline and diesel cars) and that the contributions of other sources to CO_2 are low, the estimated values should be quite indicative. In fact, although the fraction estimated using the CO_2 is always smaller than when using the BC, the two estimations quite consistent and on average they even overlap when considering the errors of these calculations.

4 Other sources of ammonia

Despite that during these measurements only traffic was identified as significantly contributing to NH_3, there are other potential sources that may affect NH_3 levels and contribute to its background.

4.1 Biomass burning emissions

One of the sources that can become important in the winter season is the wood burning emissions for residential heating.

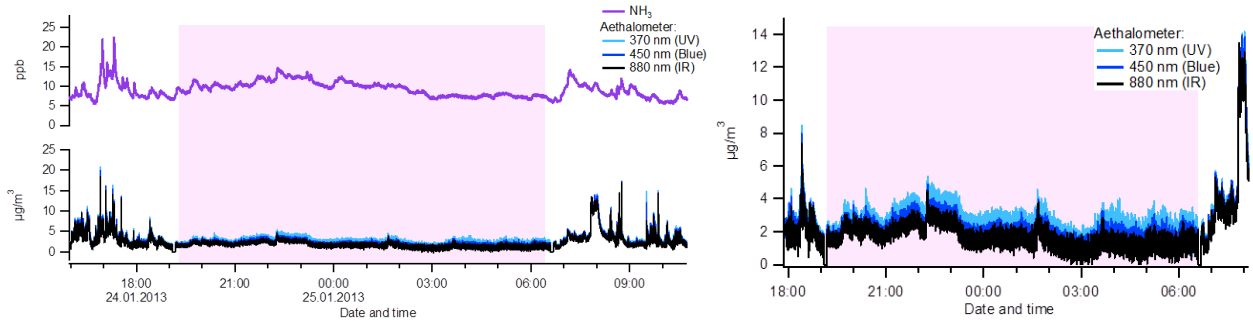

Figure 11: Left: Traces of NH_3 and of 3 wavelengths of the aethalometer for one part of the measurements in the Wallis region; Pink background represents stationary measurements in the NABEL station in Sion. Right: Zoom into the night hours of the aethalometer traces.

Represented in Fig. 11 are the time series of NH_3 and the aethalometer data for three different wavelengths, 370, 450 and 880 nm (signal at 880 nm the one taken as BC) for one part of the drive in the Wallis region. During the daytime, all three traces of the aethalometer are superimposed and the NH_3 shows the same trends as the BC. In the evening, the blue and especially the UV traces show first an enhancement (until around 11pm) and then a slow decrease until the end of the stationary measurements (~6:30am). The enhancement of the blue and UV traces is due to the presence of short-wavelength-absorbing organic compounds, which are associated with wood smoke. As the same trend is also followed by the NH_3 trace, wood burning emissions seem to also influence NH_3 levels to some extent.

During the measurements in Zurich it was not expected to find significant contribution of wood burning emissions, as the average temperature during the drives was above 10ºC. But in one of the drives along Langstrasse (zone with many restaurants) coinciding with the lunch time, there was an increase in the NH_3 levels not explained by traffic tracers (see fig 12, left panel). This increase coincided in this case with a small increase in the organic aerosol. The analysis of the high resolution mass spectrum of the organics showed that this peak was related to a mixture of cooking and biomass burning emissions, possibly coming from a restaurant wood oven.

4.2 Cooking emissions

As just explained, it seems that also cooking emissions can influence NH_3 levels. During other drives along Langstrasse the NH_3 showed an increase not present in the traffic tracers but in the organic aerosols. The right panel of figure 12 represents one of these cases, in which the high resolution mass spectrum of the organics can relate this event to cooking emissions.

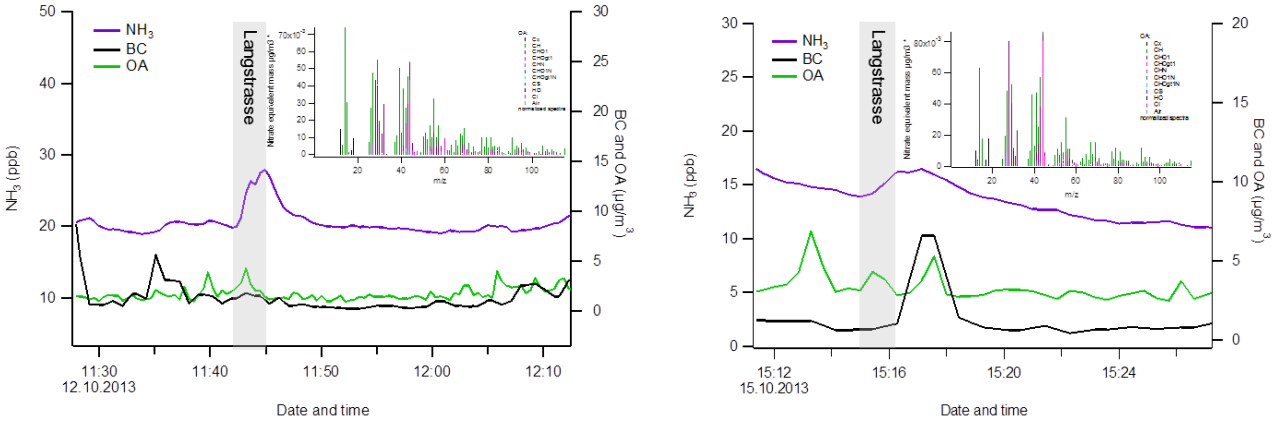

Figure 12: Left: traces of NH_3, BC and OA during an event with biomass burning and cooking emissions. Right: traces of NH_3, BC and OA for a cooking emissions event.

4.3 High engine load emissions

Ammonia emissions from traffic depend on vehicles velocity and acceleration: higher load implies higher ammonia emissions (Heeb et al, 2006). This effect has been clearly observed many times in these mobile measurements, when NH_3 peaks higher than the ones expected based on the BC levels were detected while following vehicles driving uphill. Figure 13 shows two examples of these events: gray area in the plot on the left is relative to measurements while following a truck going uphill, while the one in the right plot corresponds to measurements going uphill inside Zurich (from Hardbrucke to Wipkingen; not included in the GPS trace map).

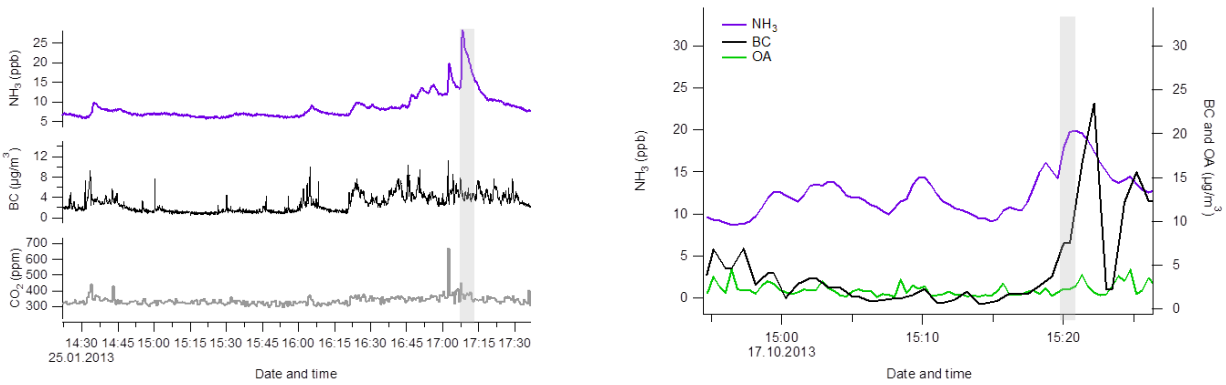

Figure 13: Left: NH_3, BC and CO_2 time series during two hours of measurements in the Wallis region; Gray background shows very high NH_3 increase but not high increase in traffic tracers while following a truck going uphill. Right: NH_3, BC and OA time series in Zurich (between Hardbrucke and Wipkingen); Gray background shows NH_3 increase while following cars going uphill, with BC level lower than 10 µg/m^3.

4.4 Sources contributing to the regional background

From the measurements relative to the drives between our institute and Zurich, other sources contributing to the regional backgrounds were observed.

It is well known that the agricultural activity has a big contribution to the total emissions of NH_3, but it is still interesting to assess the magnitude of these sources. In the left plot of Fig 14, the NH_3, BC and OA traces are represented while driving close to a field covered with natural fertilizer. In this case there is a very high peak in NH_3 levels (up to 60 ppb), that is not present neither in the BC nor in the OA traces. It is interesting to see that this peak is almost as high as the one during a tunnel drive (in the left of the plot).

Another potential source of ammonia identified is the industrial scale composting areas (see Fig 14, right), while parking for 2 minutes at ~20m from a building where they produce biogas from compost, an increase of ~ 5 ppb of NH3 was observed (and the increase was not followed by BC and OA).

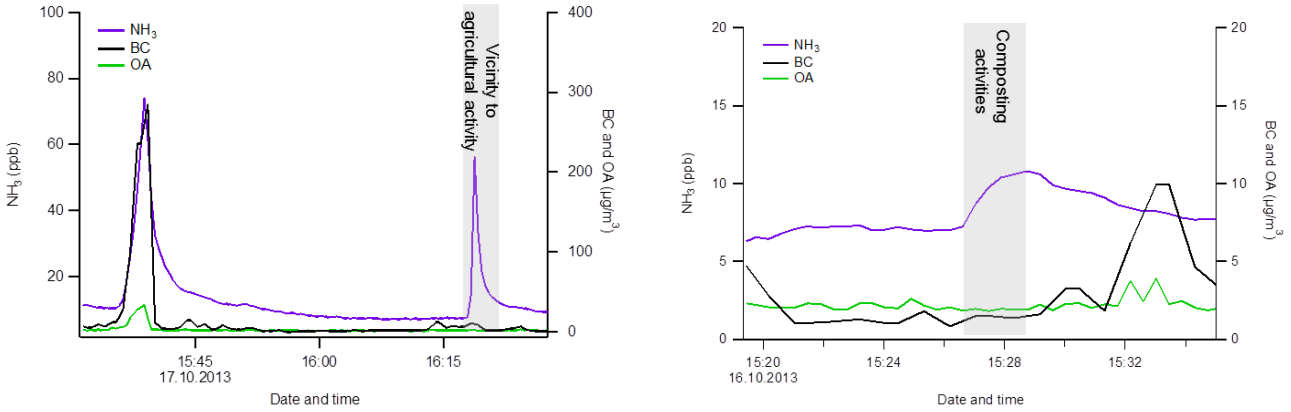

Figure 14: Left: traces of NH_3, BC and OA during an event of agricultural activity emissions. Right: traces of NH_3, BC and OA during an event with emissions from compost.

5 Conclusion/Outlook

Mobile measurements of ammonia and other pollutants were conducted in the Wallis region and in Zurich in order to study the spatial distribution of ammonia and identify its major emission sources in these regions. A new heated inlet setup has been used in order to improve the performance of the ammonia measurements.

It was observed that the background values of ammonia have a regional origin, as other pollutants affected by regional changes show similar background trends. These values of the background varied between 5 to 10 ppb.

The major local source of ammonia observed during these measurements was traffic, producing increases on the NH_3 levels up to 4 times the background values. On a daily average the traffic was estimated to contribute between 20 -30% of the ammonia levels measured in Zurich based on emission ratios during tunnel measurements. Other sources of ammonia that can also contribute significantly to the levels of ammonia have also been observed. These sources include wood burning, cooking, agricultural activity and compost.

In the future analysis, the ammonia traces will be corrected to take into account the delay in the measurements due to the instrumental response and recovery times and an appropriate averaging approach will be used. Instead of using the emission ratios in the tunnel, we may use then the smaller peaks measured in the city of Zurich.

References

Ellis R. A., Murphy J. G., Pattey E., van Haarlem R., O'Brien J. M., Herndon S. C., 2010. *Characterizing a Quantum Cascade Tunable Infrared Laser Differential Absorption Spectrometer (QC-TILDAS) for measurements of atmospheric ammonia*. Atmospheric Measurement Techniques 3. Pp. 397–406

Emmenegger L., Mohn J., Sigrist M.W., Marinov D., Steinemann U., Zumsteg F., Meier M., 2004. *Measurement of ammonia emissions using various techniques in a comparative tunnel study*. International Journal of Environment and Pollution 22, pp. 326–341

Heeb N.V, Zimmerli Y., Czerwinski J., Schmid P., Zennegg M., Haag R., Seiler C., Wichser A., Ulrich A., Honegger P., Zeyer K., 2006. *Three-way catalyst-induced formation of ammonia; velocity and acceleration-dependent emission factors*. Atmospheric Environment 40, pp. 5986-5997

Nhu-Thuc P,, Ki-Hyun K., Zang-HO S., Eui-Chan J., Kweon J., Nam-Jin K., 2013. *Analysis of ammonia variation in the urban atmosphere*. Atmospheric Environment 65, pp. 177-185

Supplementary

Figures S1-S7 show the time series of the 7 days of measurements in Zurich. These plots show the NH_3, traffic tracers (BC, CO_2, NO, f57 and C_4H_9), secondary organic aerosol tracers (org(44) and f44) and inorganic ions (NO3-, SO42-, Cl- and NH4+) time series for each day of measurements. White background represents road measurements between our institute and the highway; green background stays for highway measurements; pink background represents measurements inside the city of Zurich (route shown in bottom of Fig.4).

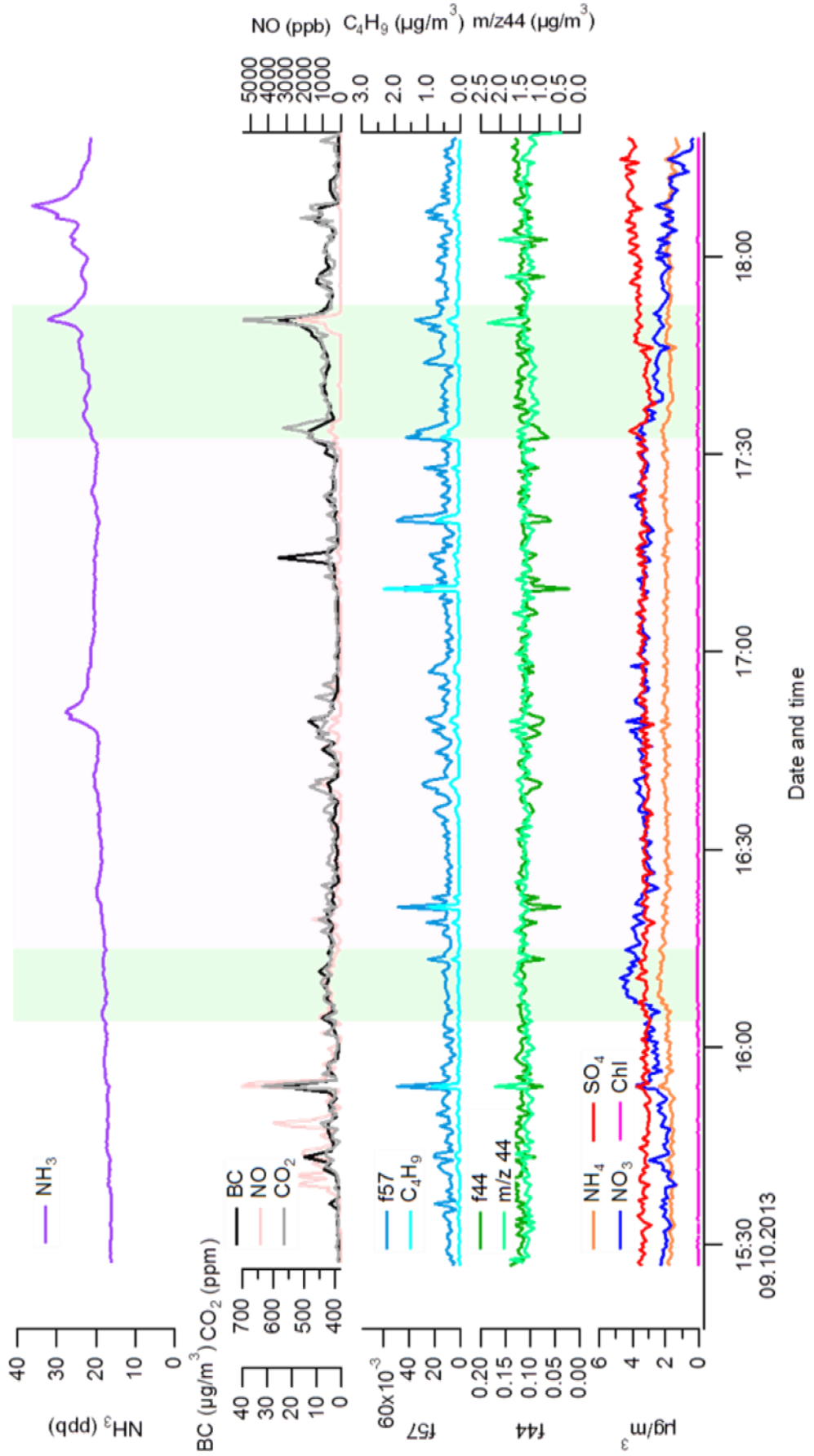

Figure S1: Time series at 09.10.2013

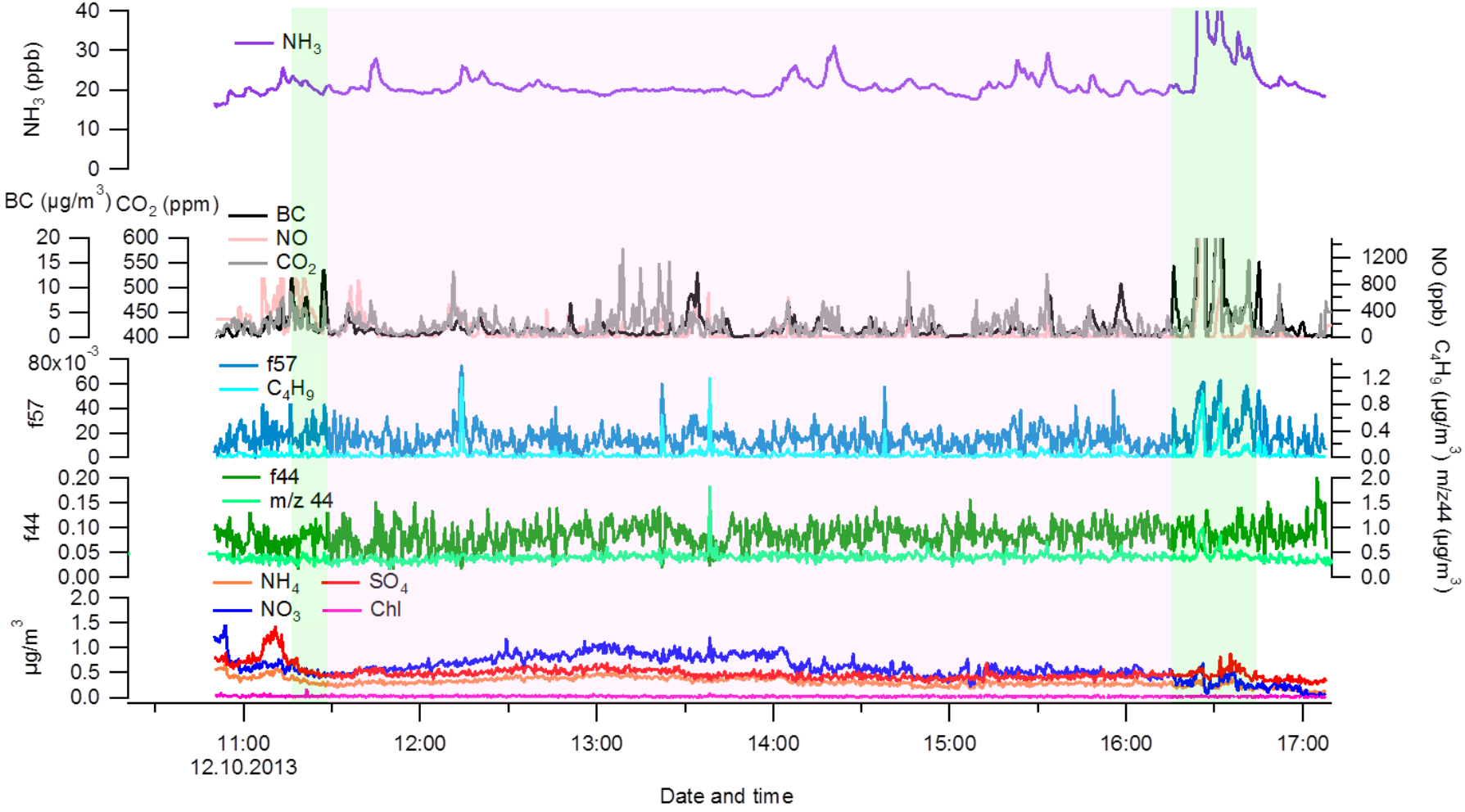

Figure S2: Time series at 12.10.2013

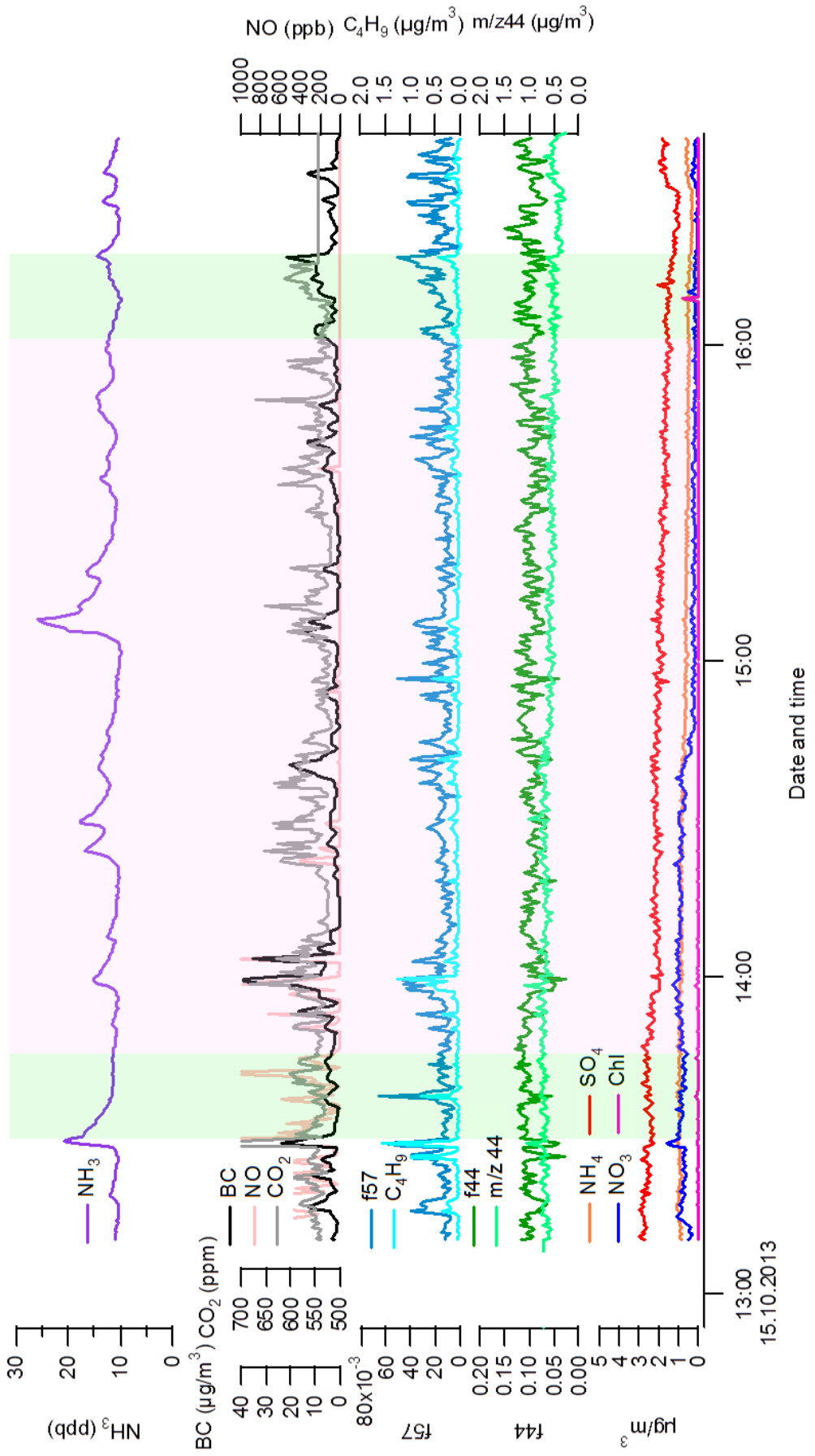

Figure S3: Time series at 15.10.2013

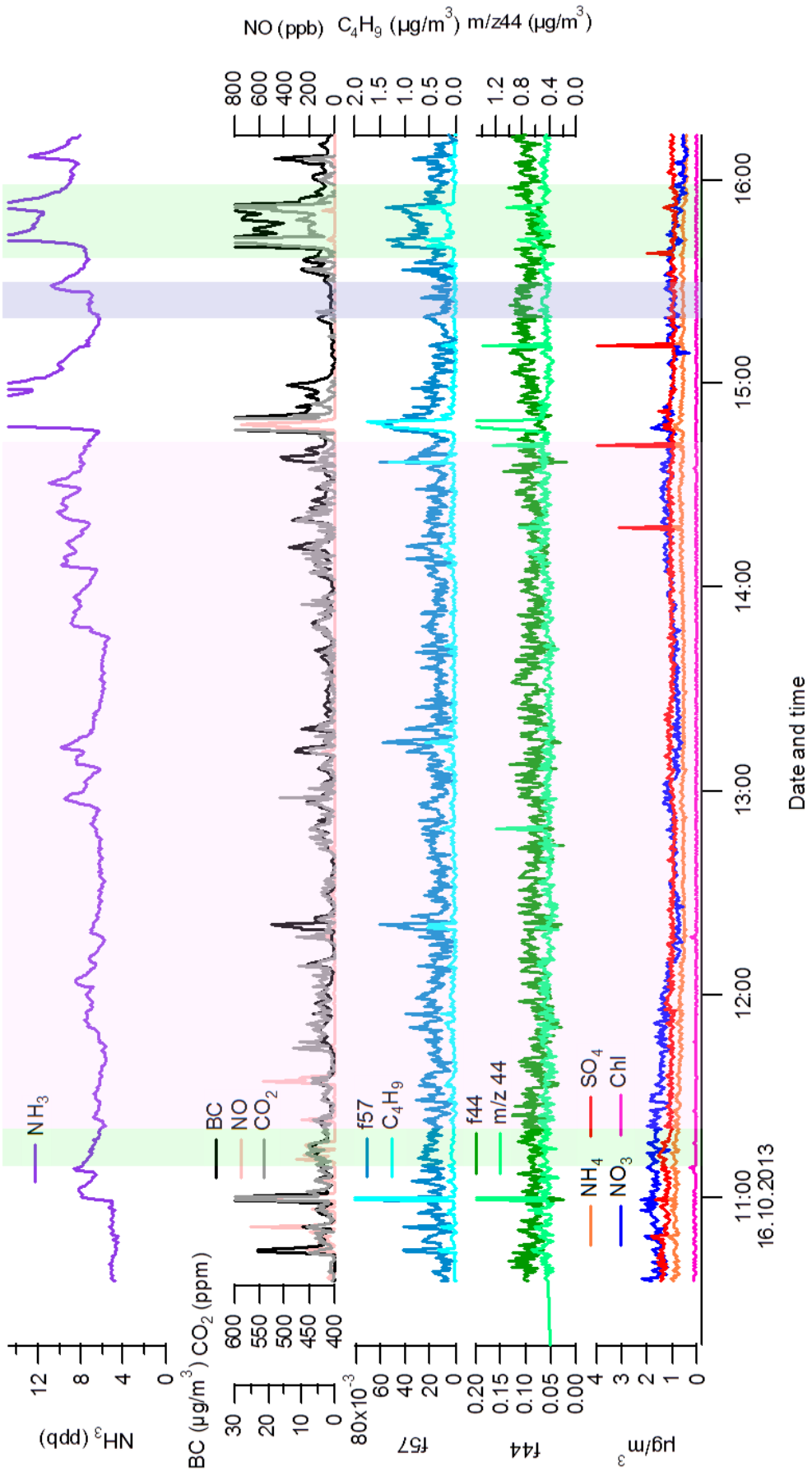

Figure S4: Time series at 16.10.2013

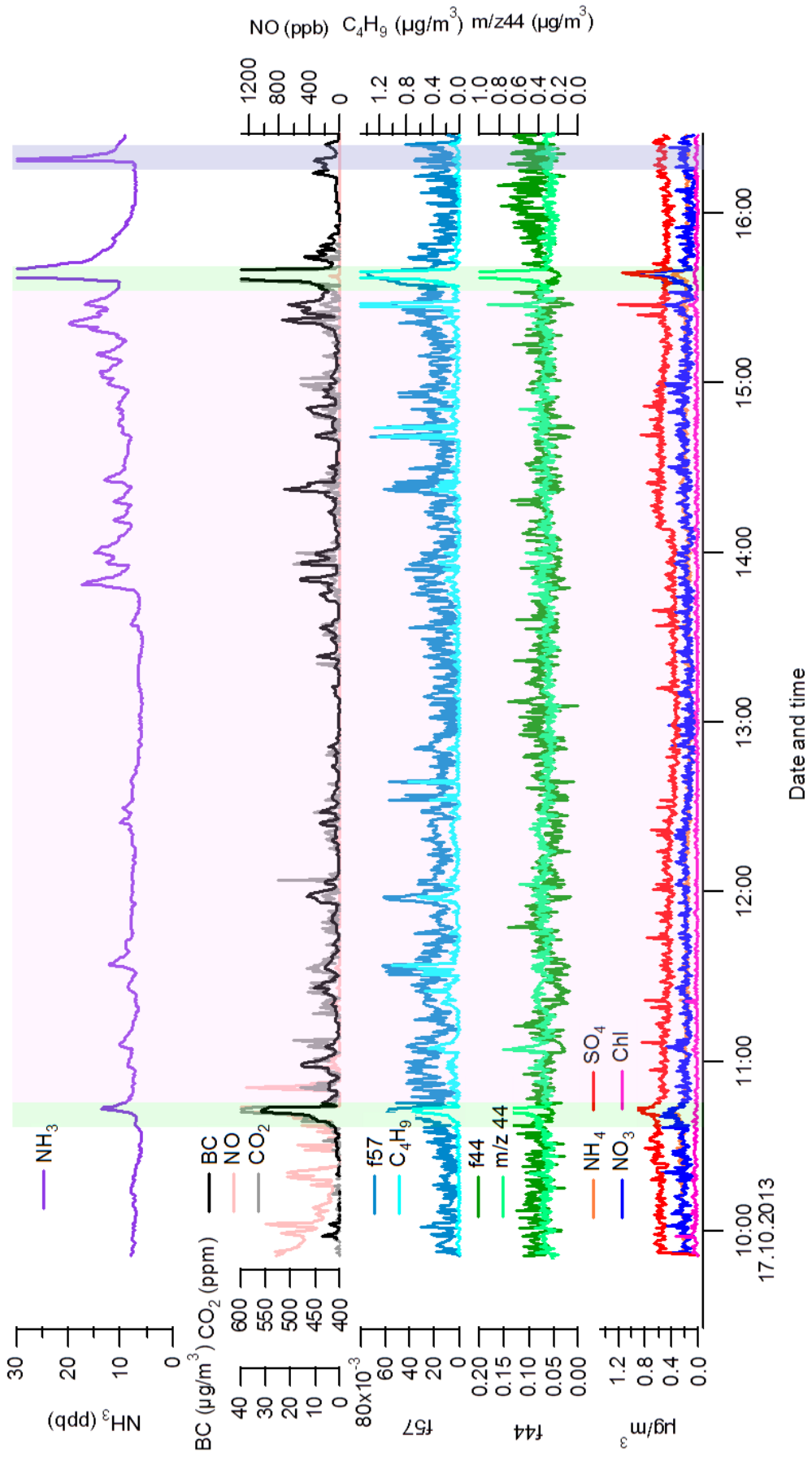

Figure S5: Time series at 17.10.2013

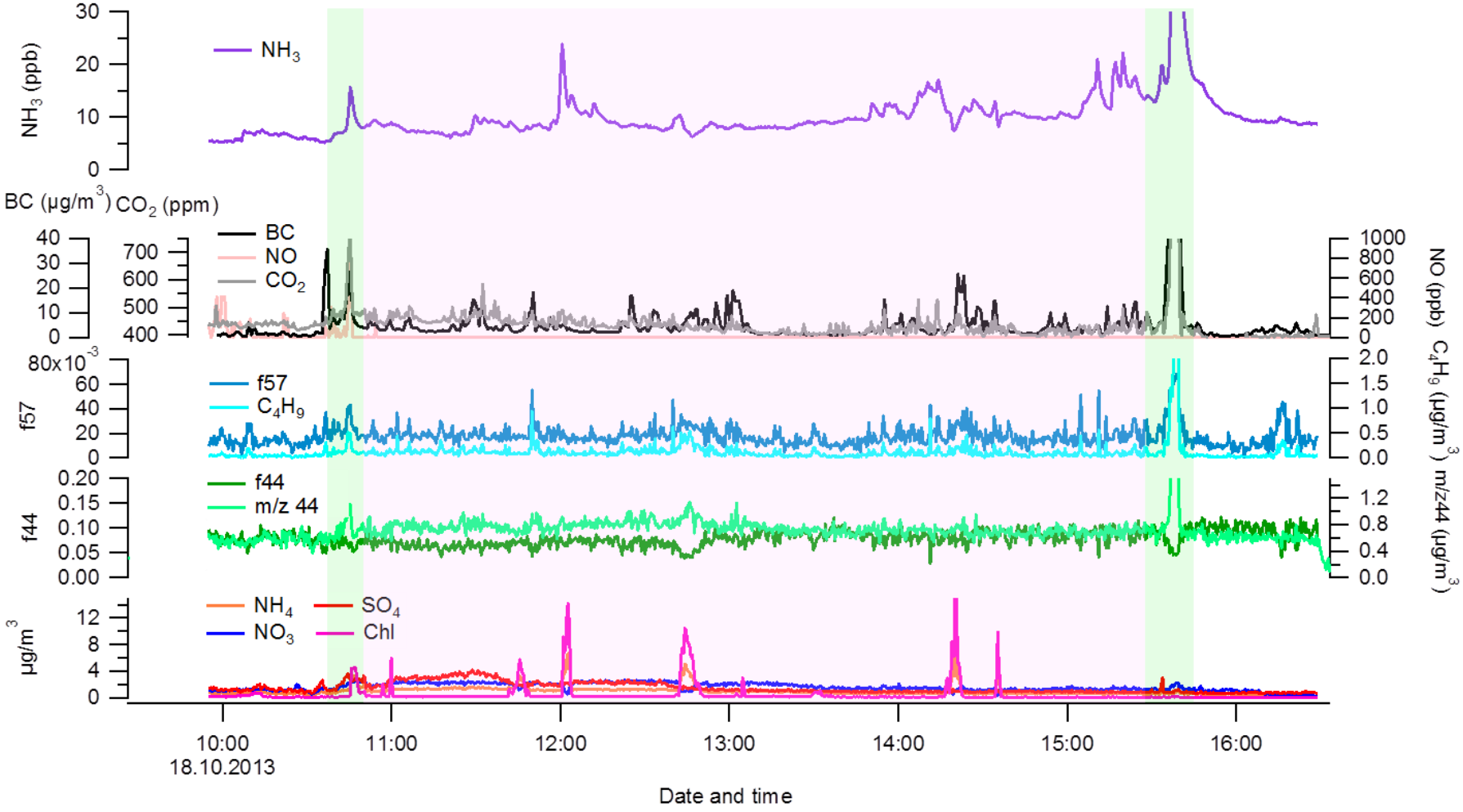

Figure S6: Time series at 18.10.2013

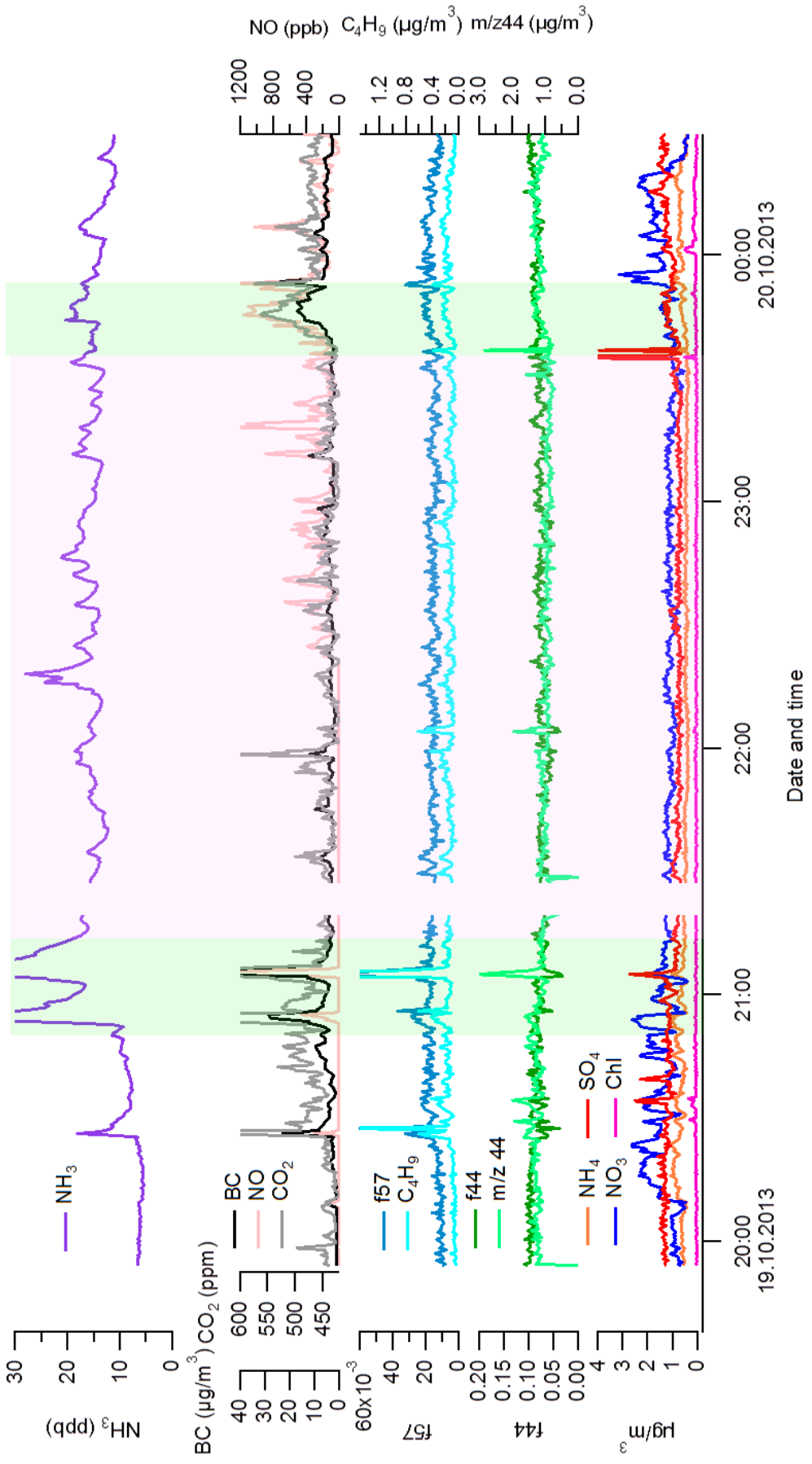

Figure S7: Time series at 19.10.2013