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Insights into atmospheric oxidation processes by performing factor analyses on subranges of mass spectra

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Figures

Figure S1 Mathematical parameters for PMF results of Ranges 1, 2, 3 and Range Combined. Left panels (a-d) shows Q/Qexp values as a function of the number of factors, and right panels (e-h) show mean scaled residuals. From top to bottom, the results for Range 1 (a, e), Range 2 (b, f), Range 3 (c, g) and Range Combined (d, h) are shown.

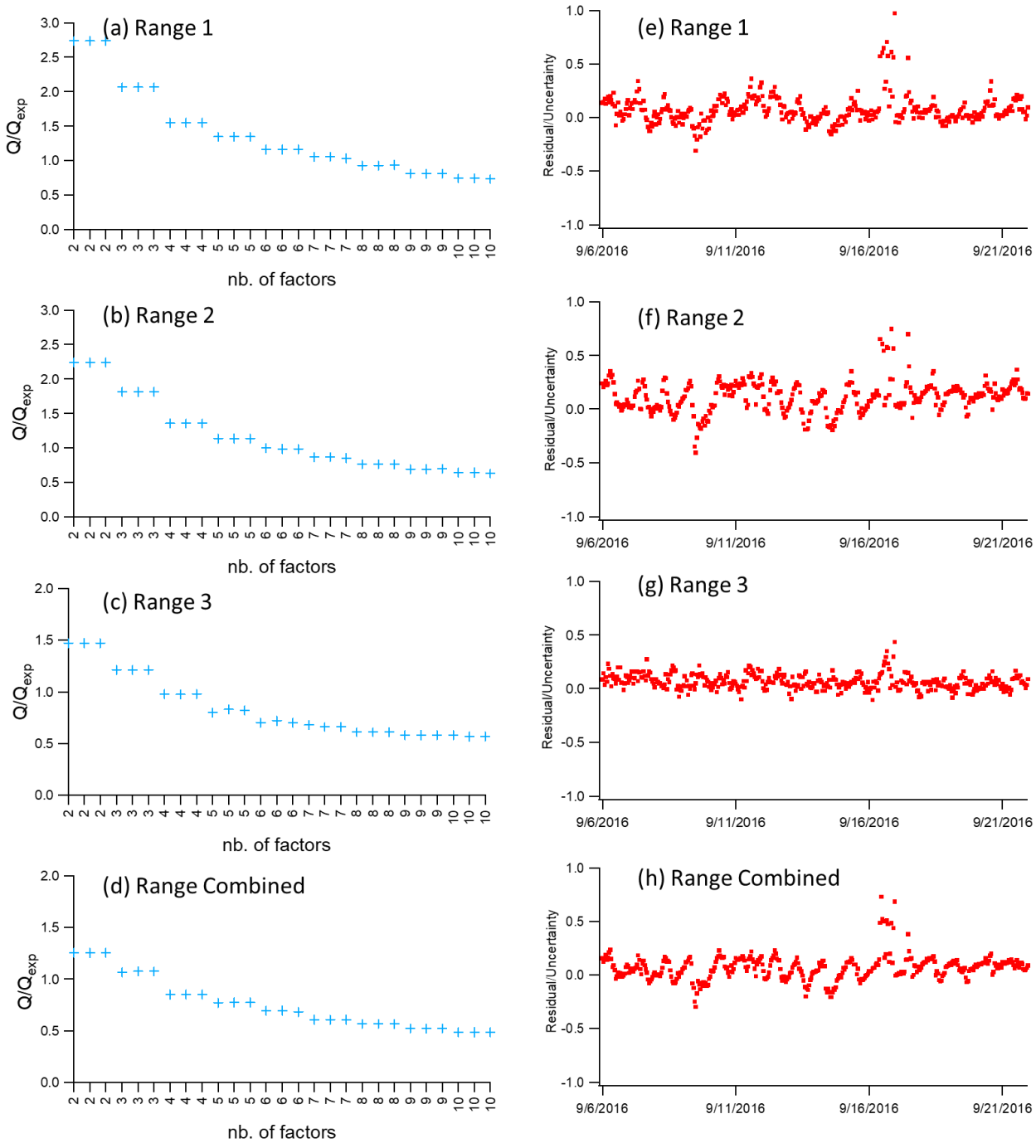
Figure S2 The contamination factor resolved from 6-factor result in Range 2, with the main masses 324 Th and 339 Th showing apparent negative mass defect

Figure S3 Time series of three contamination compounds in 1-min time resolution

Figure S4 Normalized signals for three fluorinated compounds during a 3-h cycle (180 minutes), with $(CF_2)_3CO_2HF{\cdot}NO_3^-$ (275.9748 Th) in red, $(CF_2)_5C_2O_4H^-$ (338.9721 Th) in blue, and $(CF_2)_6CO_2HF{\cdot}NO_3^-$ (425.9653 Th) in black. We selected 25 cycles and normalized all the cycles by their individual maximum. The yellow window shows the zeroing time, for around 10 minutes, which has been removed from the data analysis. Light colors display the individual cycles, and the bold solid colors stand for the average for each compounds.

Figure S5 Time series correlation between three contamination compounds, in 1-min time resolution (upper panels: a, b), and1-h time resolution (lower panels: c, d), with zero data (left: a, c) and without zero data (right: b, d).

Figure S6 Comparison of profiles for contamination factors for Range Combined and Range 3



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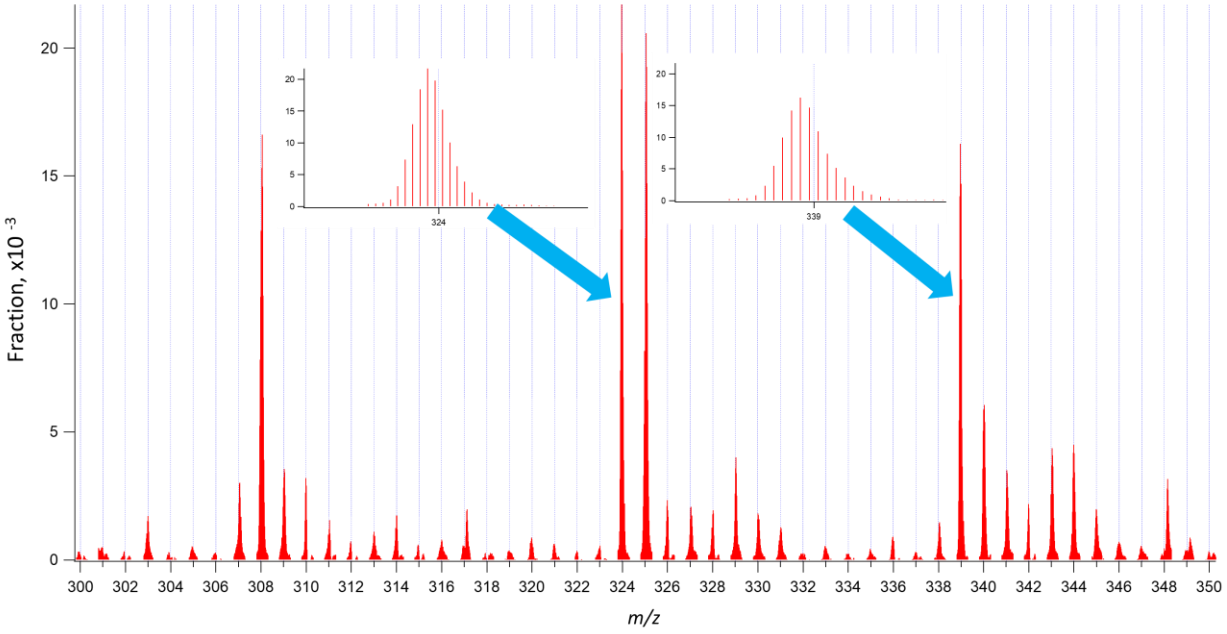

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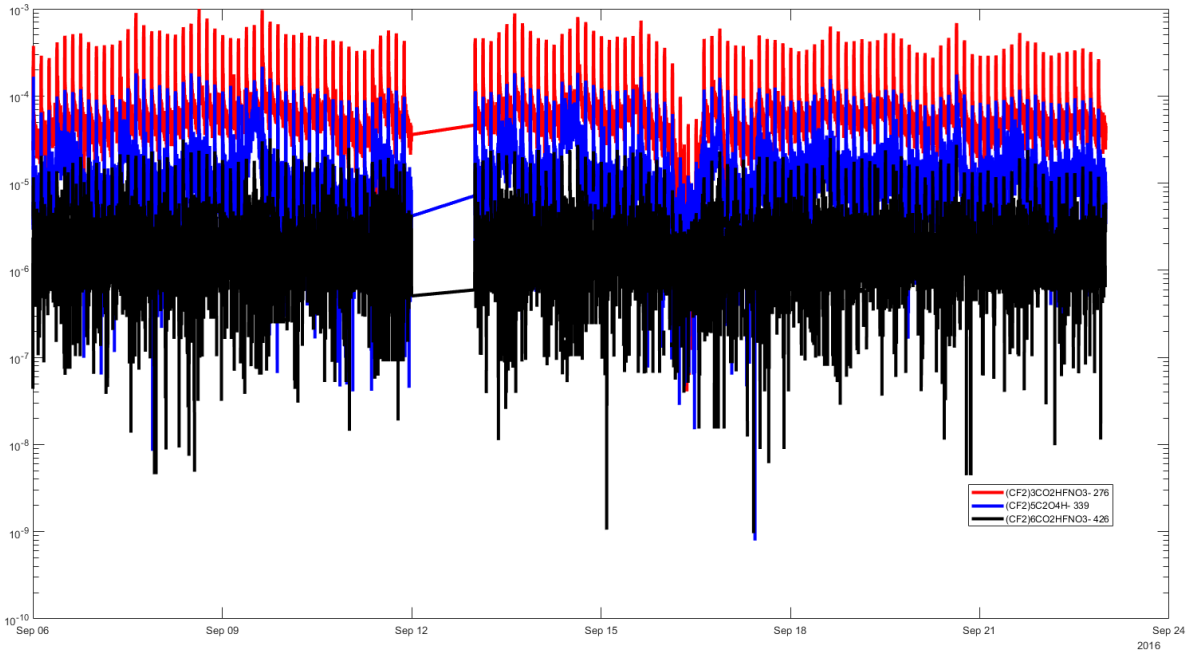


Figure S3 Time series of three contamination compounds in 1-min time resolution

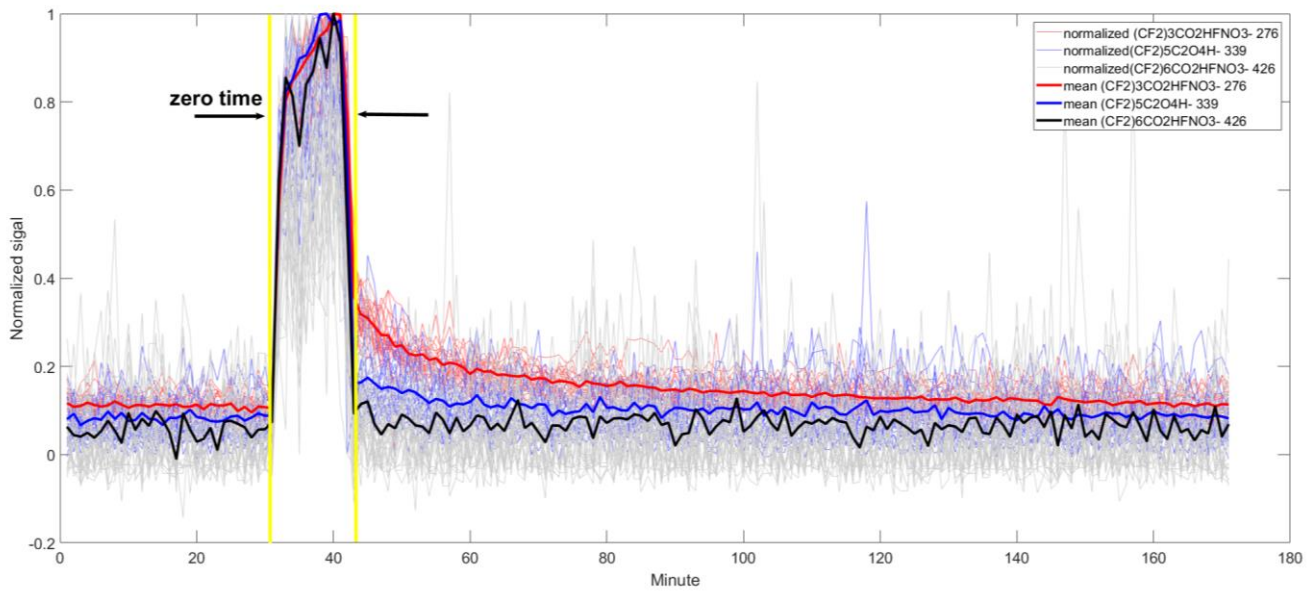
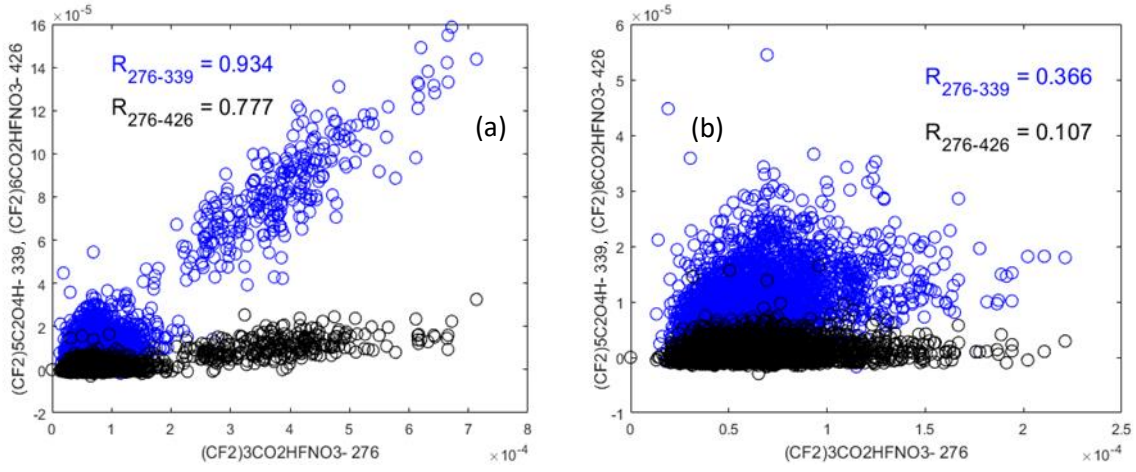
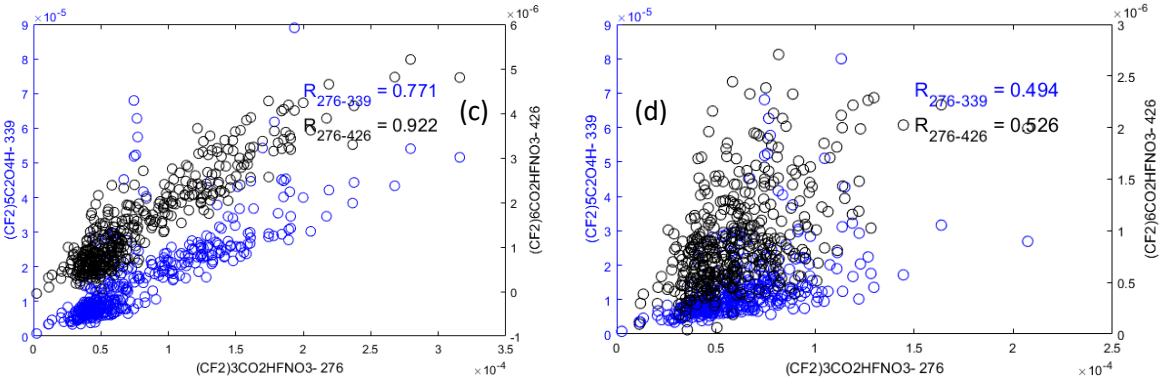


Figure S4 Normalized signals for three fluorinated compounds during a 3-h cycle (180 minutes), with $(CF_2)_3CO_2HF{\cdot}NO_3^-$ (275.9748 Th) in red, $(CF_2)_5C_2O_4H^-$ (338.9721 Th) in blue, and $(CF_2)_6CO_2HF{\cdot}NO_3^-$ (425.9653 Th) in black. We selected 25 cycles and normalized all the cycles by their individual maximum. The yellow window shows the zeroing time, for around 10 minutes, which has been removed from the data analysis. Light colors display the individual cycles, and the bold solid colors stand for the average for each compounds.





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63 Figure S5 Time series correlation between three contamination compounds, in 1-min time resolution (upper
64 panels: a, b), and1-h time resolution (lower panels: c, d), with zero data (left: a, c) and without zero data (right:
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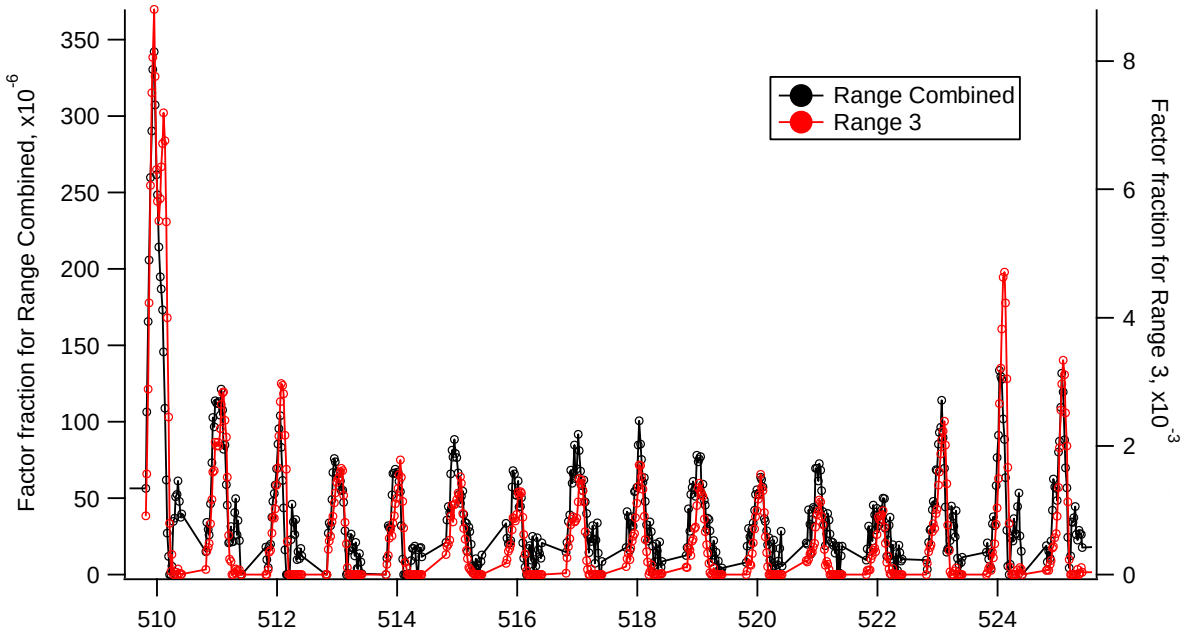

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69 Figure S6 Comparison of profiles for contamination factors for Range Combined and Range 3

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Text

Fluorinated compounds / Contamination factor

During the campaign, an automated instrument zeroing every three hours was conducted, by switching a valve to pass the air through a HEPA filter. Each zeroing process lasted for 10 min. While the zeroing successfully removed the low-volatile HOM and H_2SO_4, the zeroing process introduced contaminants into the inlet lines. The contaminants were primarily different types of perfluorinated organic acids, often off-gassing from e.g. Teflon tubing. For IVOC contaminants, these would be flushed through the inlet, while (E)LVOC would condense onto the inlet walls and not come off. However, SVOC contaminants may stick to the inlet tubing and slowly evaporate back into the sampled air. We removed all the 10-min zeroing periods, and averaged the data to 1-h time resolution, but contaminants were still identified in all ranges by binPMF.

Contamination contributed 10%, 3%, 19% and 4% to Range 1, 2, 3, and Combined, respectively, in the binPMF solutions where the contamination factor was first separated. This also explains why the contamination factor was separated much earlier in Ranges 1 and 3 than in Range 2. However, despite contributing slightly more to Range Combined than to Range 2, the contamination factor was separated when the factor number was increased by one in Range Combined. Here, the difference in volatility of the contaminants in the different sub-ranges may play a role, such that the contaminants in different sub-ranges behave differently. Thus, the behavior of the contamination factor across the combined range is not consistent. Therefore, we examined the zeroing effect with finer time resolution, i.e. 1 min, with three of the largest fluorinated compounds in each range of our mass spectrum, $(CF_2)_3CO_2HF{\cdot}NO_3^-$ (275.9748 Th), $(CF_2)_5C_2O_4H^-$ (338.9721 Th), and $(CF_2)_6CO_2HF{\cdot}NO_3^-$ (425.9653 Th). Since the overall signal levels were very low for these compounds, the time series became very noisy with such high time resolution. This made it impossible to perform HR fitting for the data, and instead we summed up the signal from the mass ranges where we expected unperturbed signal from these ions.

The time series with sawtooth pattern of the three fluorinated compounds is shown in Figure S3 in Supplement. From the time series, we selected a period of around three days of the 3-h cycles (25 in total), and in Figure S4 the cycles were aligned and superimposed on top of one another, normalized by the maximum during the zeroing. The normalized signals of the three compounds are shown in light colors, and the mean values shown in bold sold lines. This data includes also the zeroing periods to highlight the effect, but these periods were removed from the data used for our PMF analyses.

The signals of the three fluorinated compounds increased by 10 to 20 times during the zeros, due to off-gassing either in the filter or in the tubing in the zeroing setup. Immediately after the zeroing was stopped, signals of all three compounds dropped by about 60-90%, followed by a gradual decay. The decay period coincided with our ambient sampling, and therefore these signals are part of our dataset. It is evident that the three fluorinated compounds were from the same source (zeroing process), but due to their different volatilities, they were lost at different rates. This, in turn, means that the spectral signature of this source will change as a function of

time, at odds with one of the basic assumptions of PMF. Panels a and b in Figure S5 displays the temporal correlation with and without zeroing period with 1 min time resolution. The correlation coefficients dropped greatly when the zero period was removed, from 0.9 to 0.3 for R^2 between 276 Th and 339 Th, and 0.8 to 0.1 between 276 Th and 426 Th. Similar effect is also found with the 1 h averaged data (Fig. S5c, d).

This detailed analysis of fluorinated contamination in our system was here merely used as an example to show that volatility can impact source profiles over time. In this case, the contamination factor was still identified both from the separate sub-ranges and from the combined data set using binPMF. However, the contamination profile in the combined range is now averaged, compared to that from separate ranges: the fractional contributions of contamination compounds to this profile, vary during the process of each zeroing due to different volatility properties. In Figure S6, contamination factor profiles from Range 3 and Range Combined were compared. It can be clearly seen that the profile of Range Combined is more noisy than that of Range 3, probably due to the varied fractional contributions of contamination compounds to the profile. In ambient data, products from different sources can have undergone atmospheric processing, altering the product distribution. Our aim with this analysis was to highlight the importance of differences in the sink terms due to different volatilities of the products. This may be an important issue for gas phase mass spectrometry analysis, potentially underestimated by many PMF users, as it is likely only a minor issue for aerosol data, for which PMF has been applied much more routinely. If failing to achieve physically meaningful factors using PMF on gas phase mass spectra, our recommendation is to try applying PMF to sub-ranges of the spectrum, where IVOC, SVOC and (E)LVOC could be analyzed separately.