Reply to anonymous referee #2:

We thank reviewer #2 for insightful comments and suggestions. Our detailed answers are below. Reviewer comments are duplicated in blue to provide the context.

In terms of peak integration it is not clear, if the peak/integration borders are adjusted for each spectrum or if constant settings based on the sum spectrum are used. For highly variable compounds the signal intensity can vary substantially and the broadness of the peak changes. Signals of high concentrations could exceed the set borders of the sum spectrum. How does the peak integration deal with background/zero air measurements?

The integration boundaries are NOT adjusted per spectrum. Constant boundaries are used for all spectra in any particular raw-data file. This is a consequence of the strategy to calculate the mass scale calibration parameters and the resolution per raw-data file (from the SumSpectrum). This information will be added to the revised version.

Peak broadness (i.e. the resolution) and peak shape do not change with peak intensity as long as saturation effects of the counting electronics can be neglected. Therefore the peak integration routine does not differentiate between high or low signal measurements including zero air and instrumental background.

Line 20, page 1634: Why is a threshold of 8 used for the peak detection? Using the LOD (3) or LOQ (10) seems to be a more obvious choice.

This threshold has been developed empirically with the goal of minimizing both, false peak detections, and overlooked real peaks. The application of commonly used standards would reduce the performance of the routine.

Line 15-17, page 1635: The signals of H3O+ (19.018 Da) and H2O.H3O+ (37.028 Da) often show effects of saturation so that the signal is cut off and the highest data point does not necessarily correspond to the peak maximum. Therefore different (not massively) time bins would be associated with the H3O+ and H2O.H3O+ mass, respectively. Is this effect taken into account or can be neglected, since the range is small enough?

These lines describe the first step of the mass scale calibration, which is (for the reasons mentioned by the reviewer) very crude. However, the first crude calibration is good enough to identify the peaks caused by $H_3{}^{18}O^+$ (21.022 Da) and $C_3H_6OH^+$ (59.049 Da), which are subsequently used for a much better mass scale calibration. So, there is no need to apply any corrections.

Line 2, page 1637: Are the parameters yielding to the best match transferred automatically for the further analysis?

Yes

Line 7, page 1640: What is the origin of the thresholds for DpB_sm of 0.55 and 5% of the maximum value?

These are empirical thresholds that limit the number entries to the 'unified mass list'. In principle, only peaks are included that are detected in 5% of the files and at least in 3 files. If the set to be evaluated consists of a relatively low number of files, the absolute threshold of 0.55 is more restrictive. In the most extreme case (only 3 files in the set to be evaluated) a peak needs to be detected in all files (100%) to be added to the unified mass list.

Line 10, page 1642: Usually a default value of 2x10^(- 9) cm^3 mol^(-1) is chosen (e.g. (Holzinger et al., 2010). Can the default value for the reaction rate be changed and set individually?

We concluded in Holzinger at al. (2010) that a value of 2x10^(- 9) cm^3 mol^(-1) is too low for organics desorbed from aerosols (our primary field of application of the Utrecht PTR-TOF-MS). However, the default reaction rate constant can be easily changed (see Appendix C).

Figure 2: The orange and the red line do not differ much and the different red markers are hard to distinguish. It would help the reader to pick up the details of this plot (upper panel) more easily, if more different or contrasting colours would be used.

Done.

Figure 3: As the highest two peaks exceed the others in intensity by far, they are hardly visible. A break in the y-axis or an enlargement of the lower range could help here. The y-axis labelling for the lower three panels is too small.

Improved.

Figure 8, lower panel: Low contrast in colours (blue, black, green). Especially in a print out it is hard to differentiate between the black and blue markers. A clearer presentation regarding the colours would be appreciated.

The contrast is low because not many different index values were used/needed. The color code is an inherent feature of this extended data analysis tool and changing the colors for this particular example would compromise the contrast in more elaborated setups like the one shown in Figure 9 (i.e. Figure 7 in the revised version). Therefore I prefer to leave this Figure unchanged because this is how the Figure is produced by PTRwid.

Figure 10: The order of the headers is not matching the displayed values. Values for mean and median are not displayed. Values following the ion's formulas are not explained.

Fixed.

Structure:
As there are a couple of appendices, they should be ordered the way they are referred to in the text to provide a clearer structure. At the moment Appendix D is referred to first (line 20, page 1632), followed by A, B and C.

Done.

The single procedures are explained later in the text in Section 2.1.3, so a reference to Appendix D is not useful before that section and could be removed on page 1632.

Done.

Figures 1, 7 and 10 do not provide additional information to the text. The functionality of PTRwid can be understood just from the text. However, they are still useful for a future user of the tool, so I would recommend to integrate them into the appendix.

Done.

Lines 13-18, page 1630: Very long sentence. Last part “the ions to be monitored do not need to be selected beforehand” as (iii) or separate sentence.

The last part is not essential and has been deleted.

Technical corrections:
Line 14, page 1633: ". . . works on files that that contain . . .".
Line 7,8, page 1638: unclear structure of sentence, instead e.g. “. . .all peaks with a maximum signal within the following range:. . .”.
Line 21, page 1639: ". . . the bin with increases. . .".
Line 1, page 1642: ". . . of ions trough the TOF . . .".
Line 1, page 1645: ". . . the das phase inlet . . .".
Line 3, page 1647: ". . .on the SumSpectrum; which" (replace ; with ,).
Lines 14, page 1647: too many commas, which are causing confusion. A suggestion: “(ii) a tool to create plots such as van Krevelen diagrams and presentations of desorption thermograms or carbon oxidation state, which. . .”.
Figure 2, line 4: "The range . . . is indicated by a horizontal red lines . . .".
Figure 9, line 8: ". . . the das phase inlet . . .".

All corrected.