The work by Sun et al., presents the analysis of cloud water from Mt. Tianjing in southern China using Fourier transform-ion cyclotron resonance mass spectrometry (FT-ICR MS). The results are very interesting and provide some insight into in-cloud aqueous-phase chemical composition.

I have several comments and suggestions to the authors below.

<u>Minor comments:</u>

Considering the emphasis of the paper, I suggest moving sample preparation and analysis procedure into the main text (not the SI). In places it is not clear how the analysis was performed as incorrect referencing to the SI material section was provided. For example, SPE extraction was referred to Text S3, which does not contain this information, but described in the Text S1. *Please also see relevant comment below.*

The following sentence is not clear – ''The peaks of formulas are intensive within m/z 200-400'', line 139. Please rephrase. What is the impact of these observations?

<u>Major comments:</u>

It is not clear whether the authors used a direct infusion or applied a hyphenated technique for their analysis. This needs to be stated in the manuscript. Advantages and limitations of the applied technique need to be stated in the text as well.

The information on ESI parameters e.g. source type, nebuliser gas pressure, gas velocity and temperatures, and capillary voltages are missing. These parameters are crucial to understand how the data was acquired and for a comparative analysis with the literature. Major MS parameters have to be provided as well. How was the system calibrated **and** tuned? Depending on the system optimisation parameters the analyst would see preferentially one or other type of compounds.

What do the authors mean by the ''*mass spectra*'' calibration? ''*The mass spectra was calibrated externally using measurements of a known homologous series of N1 (neutral nitrogen compounds) and O2 compounds (acids) with high abundance in a petroleum*''. Please provide more details on the utilised petroleum type etc. If the system was optimised (tuned) using petroleum on N and O containing ''compounds'' it should not be a surprise that CHON, aliphatic and olefinic species are the major components in the analysed samples. I do not think it is correct to infer that N-containing compounds, aliphatic and olefinic species are the dominating organic species in the analysed water. It might be the case, but if your system is optimised for N-containing compounds then the analysis would be skewed towards these species. There is nothing wrong with this as there are no perfect analytical tools that would cover all compound classes; however, this needs to be acknowledged in the text, so that it is clear for the reader who are not expert in FTIR-MS.

In addition, there is a clear evidence that the type of SPE extraction (including Strata X cartridges) and ESI source (e.g. HESI, nano-ESI) can skew the recoveries of specific compound classes. It has been demonstrated that SPE sample pretreatment significantly improves ion recoveries for organic species with nonpolar and moderately polar functional groups, but leads to lower recoveries for highly oxygenated molecules. Therefore, while SPE reduced in-source adduct formation, it also limited the range of compounds identified through a single analysis (Kourtchev et al., 2020). So the observed variation of various molecular groups e.g. CHO, CHON presented in the work by Sun et al. work can be influenced by the applied techniques and thus lead to specific compound classes recoveries. How does this affect the interpretation of their data?

The authors identified and present elemental composition in their work but incorrectly refer (numerous times) to these formulae as compounds. This should be avoided as multiple isomers can be associated with a single molecular formula even at the reported by the author achieved <0.3ppm mass error especially for *mz* > 319.

Reference: Kourtchev et al. Comparison of Heated Electrospray Ionization and Nanoelectrospray Ionization Sources Coupled to Ultra-High-Resolution Mass Spectrometry for Analysis of Highly Complex Atmospheric Aerosol Samples, Anal. Chem. 2020, 92, 12, 8396–840, doi: 10.1021/acs.analchem.0c00971