Atmospheric
Measurement
Techniques

Discussions

Orbitool: A software tool for analyzing online Orbitrap mass spectrometry data

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Atmospheric
Measurement
Techniques
Discussions

Abstract

The Orbitrap mass spectrometer has recently been proved to be a powerful instrument to accurately measure gas-phase and particle-phase organic compounds with a greater mass resolving power than other widely-used online mass spectrometers in atmospheric sciences. We develop an open-source software tool (Orbitool,

5   https://orbitrap.catalyse.cnrs.fr) to facilitate the analysis of long-term online Orbitrap data. Orbitool can average long-term data while maintaining the mass accuracy by re-calibrating each mass spectrum, identify chemical compositions and isotopes of measured signals, and export time series and mass defect plots. The noise reduction procedure in Orbitool can separate signal peaks from noise and greatly reduce the computational and storage expenses. Chemical-ionization Orbitrap data from laboratory experiments on ozonolysis of monoterpenes and

10   ambient measurements in urban Shanghai were used to successfully test Orbitool. For the test dataset, the average mass accuracy was improved from < 2 ppm to < 0.5 ppm by mass calibrating each spectrum. The denoising procedure removed 97% of the noise peaks from a spectrum averaged for 30 min while maintaining the signal peaks, greatly helping the automatic identification of unknown species. To illustrate the capabilities of Orbitool, we used the most challenging/complex dataset we have collected so far, which consists of ambient measurements

15   in urban Shanghai. These tests showed that Orbitool was able to automatically separate and identify hundreds of compounds as well as their isotopes with a very high accuracy.

Atmospheric
Measurement
Techniques
Open Access

EGU

Discussions

1 Introduction

Biogenic and anthropogenic emissions constantly produce a wide variety of volatile organic compounds (VOCs) into the atmosphere (Hallquist et al., 2009; Shrivastava et al., 2017). Once emitted, VOCs can quickly react with different atmospheric oxidants (OH radicals, O_3, NO_3 radicals or Cl atoms) yielding a wide variety of oxidized

5   VOCs (OVOCs) spanning a broad range of chemical formulae and, thus, volatilities (Hallquist et al., 2009; Li et al., 2020; Wennberg et al., 2018). OVOCs play a central role in the formation of atmospheric aerosols by either condensing onto pre-existing aerosol particles or by forming new particles (Hallquist et al., 2009; Jimenez et al., 2009; Kirkby et al., 2016; Shrivastava et al., 2017). Generally, the more oxidized OVOCs are, the lower their volatility, and the greater the probability to partition to the particle phase. However, the quantitative evaluation of

10   the impact of aerosol on climate is yet inadequately constrained due to a number of factors, including an incomplete understanding of how VOC oxidation processes contribute to new particle and secondary organic aerosol formation (Glasius and Goldstein, 2016). Indeed, the gas phase oxidation of one single VOC can yield thousands of oxidized products (Glasius and Goldstein, 2016; Goldstein and Galbally, 2007; Li et al., 2020; Riva et al., 2019b). As a result, the chemical variety of OVOCs poses a major challenge in detecting, quantifying, and characterizing such

15   a large number and wide variety of organic compounds.

Over the last decade, mass spectrometric techniques have made extensive improvements and are now well-suited to detect a large range of species simultaneously. This is highlighted by the key role of chemical ionization mass spectrometry (CIMS) in improving our understanding of the atmospheric chemical composition (Breitenlechner et al., 2017; Ehn et al., 2014; Jokinen et al., 2012; Krechmer et al., 2018; Lindinger et al., 1998;

20   Yuan et al., 2017). CI is a soft ionization technique where the analytes are ionized through a clustering process with the reagent ions and undergoes only minimal fragmentation. While CIMS provides very good sensitivities (i.e., as low as 10^4 molecules cm^{-3}) (Jokinen et al., 2012) and is suitable to measure a wide variety of gaseous organic and inorganic compounds, they are mainly associated with time-of-flight (TOF) mass analyzers. The mass

resolving power of a TOF analyzer typically ranges from hundreds to less than 15 000 (Riva et al., 2019b). Although often able to separate between some isobaric species, these mass resolving powers still limit accurate identification and quantification of OVOCs in complex air sample. Existence of multiple overlapping ions yield significant uncertainties (Cubison and Jimenez, 2015; Riva et al., 2019b; Stark et al., 2015). Computational approaches,

5 including ion deconvolution procedures, are required to partly resolve this limitation in order to extract the maximum possible information content (Cubison and Jimenez, 2015; Meija and Caruso, 2004; Zhang et al., 2019a, 2019b). To overcome these limitations, we have coupled a high-resolution mass spectrometer (Orbitrap, Eliuk and Makarov 2015) with a CI source (Riva et al., 2019a, 2020) and an extractive ESI (EESI) inlet (Lee et al., 2020) for online analysis. Similarly, Zuth et al. (2018) have combined an atmospheric pressure chemical ionization (APCI)

10 interface to an Orbitrap and have shown that such a technology can achieve much greater mass resolving power at similar detection limit for the real-time measurement of organic aerosols. As a result, CI, EESI, and/or APCI-Orbitrap represent very promising new techniques for online characterization of the chemical compositions of gaseous and particle phases at a very high mass resolving power.

The demand for a new software tool for analyzing Orbitrap data comes along with applying an Orbitrap in

15 long-term continuous online measurements. The commercial software, Xcalibur[TM] that has been used in our initial studies (Lee et al., 2020; Riva et al., 2019a, 2020), provides an interface for basic data analysis e.g., reading single or averaged scans and exporting the time evolution of selected signal peaks. However, more complicated data analysis is usually needed for investigating the complexity and chemical processes occurring within the atmosphere. Hence, some customized software tools e.g., RawQuant (Kovalchik et al., 2018), RawTool (Kovalchik et al., 2019),

20 and dimspy (Weber and Zhou, 2020) are developed to meet different demands. In atmospheric sciences, due to the extremely low concentrations (< 1 ppt) of some key chemical species (e.g., peroxy radicals) in typical atmospheric environments, the measured spectra must be averaged over a long period to overcome the interference of noise and accumulate signals. This step implies averaging spectra across files while maintaining the mass accuracy. Although

facilitated by the high mass resolution of the Orbitrap, a minor proportion of the detected signal peaks still inevitably overlap with each other. Therefore, peak fitting is needed to separate the overlapped signal peaks. In addition, using a list (i.e., "peak list") of possible species obtained in similar atmospheric environments can greatly reduce the expense for data analysis. The aforementioned features are already realized in existing software tools

5   for analyzing data acquired with CIMS or proton-transfer-reaction (PTR) ToF-MS, e.g., TofTools (Junninen et al., 2010), Tofware and other software developed to analyze PTR-TOF-MS dataset (Holzinger, 2015; Müller et al., 2013). It would seem straightforward to convert the Orbitrap raw data into certain formats and then conduct data analysis using these existing software tools. However, due to the high mass resolution of the Orbitrap compared to TOF mass analyzers, the computational expense will be high if analyzing Orbitrap data using, for example TofTools.

10   This is because the TOF mass spectra are stored on equally spaced grids (with respect to TOF), with data points on the order of 10^4-10^5. For comparison, approximately 10^8 data points are needed to characterize a single Orbitrap spectrum using this grid-based data structure. Instead, saving only the signals with their adjacent zeros will reduce the computational and storing expenses by orders of magnitude. As a result, a new software tool for analyzing Orbitrap data is needed to facilitate its application in atmospheric researches.

15   In this study, we develop a new software tool, named Orbitool, for analyzing online Orbitrap mass spectrometry data. The working principles and features of Orbitool are introduced. Several test examples using both laboratory and atmospheric data are presented to illustrate and validate its features.

2 Orbitool

Orbitool is a software tool with a graphical user interface (GUI) for analyzing online Orbitrap mass spectrometry

20   data. It is optimized for long-term atmospheric measurements and laboratory studies. Flexible input and output interfaces facilitate the coupling between Orbitool and other software. Orbitool's basic working principle is shown in Fig. 1, which includes data reading and averaging, background noise determination and reduction, peak shape determination, mass calibration, chemical composition and signal abundance determination via peak fitting, and

Atmospheric
Measurement
Techniques
Discussions

data output. The details of these features will be elaborated in the following sections. Orbitool is mainly coded in Python with the supports form several third-party libraries (Pedregosa et al., 2011; Goloborodko et al., 2013; Levitsky et al., 2018). To enhance computational speed, the mass spectra are processed using the Numba package (Lam et al., 2015) and chemical composition and signal abundance are determined using the Cython package (Behnel et al., 2011). Orbitool was tested in Python 3.6 on the Microsoft Windows operating system. An executable version of Orbitool and its open-source codes are publicly available (see *Software availability*).

2.1 Data averaging. The data collected by the Orbitrap is stored in a RAW file, containing segmented peak intensities and their corresponding masses of each scan, scan filters, event logs, instrumental information, etc. For minimizing data storage expenses, the RAW file records only the spectra of all the detected peaks rather than an equally spaced spectrum with ~10^8 data points. Before further analyses, raw mass spectrometry data is read and averaged using Orbitool. Since the abundances of most detected species can be extremely low, especially under typical ambient concentrations, proper averaging is needed for identifying these signal peaks against noise. The raw data can be imported into Orbitool as single files or using a file folder. The user can choose to average all the imported files or a subset of them. The average spectra are calculated based on either scan number or time. For the time-based data averaging, Orbitool calculates the average spectrum within each time bin. The beginning and ending times can be specified by the user, while they are by default obtained from the time range of the input data files. The averaging weight for spectra in the same data file is determined by scan number rather than the duration of each single scan. When multiple data files are found in the same time bin, the average spectra of each file are calculated first and then are averaged with respect to time. Peaks close to each other in the averaged spectrum are merged or identified as separated peaks according to the mass resolution of the Orbitrap. To facilitate a quick data analysis, averaging is not conducted until either the user or Orbitool call the averaged spectrum in order to minimize unnecessary expenses. Further, the data averaging can be skipped. In this case, single spectra are used instead of averaged spectra in the following steps. Orbitool also supports filtering data using the charge polarity. For instance,

when the positive polarity is selected, only the positively charged spectra are taken for the averaging while negatively charged spectra are excluded. Hence, this feature can support the analysis of Orbitrap measurements that switch the charge polarity routinely (e.g., every 1 minute) to realize near real-time measurement of both positively and negatively charged compounds.

5 **2.2 Noise determination and reduction.** The background noise is estimated and then removed from the average spectra during this step. Some detected compounds are difficult to be separated from noise in a signal scan due to their very low concentrations. However, after averaging for a sufficiently long period, the signal peaks usually exceed noise peaks because averaging reduces the height of noise peaks but not signal peaks. To estimate the noise level, Orbitool first takes all the detected peaks located in the mass defect range of [0.5, 0.8] Da. Mass defect is the 10 absolute difference between the accurate mass and the nominal mass of the given compound, which is determined by the type and quantity of atoms contained in a compound and its charge polarity. Such a mass defect range is chosen because most of the observed compounds in atmospheric measurements are located outside of this mass range (Zhang et al., 2019a). Then, peaks lower than a certain percentile of the peak heights in this mass defect range (0.5-0.8) are taken as noise peaks. The noise and discriminator levels are determined as μ and $\mu + 3\sigma$, 15 respectively; where μ and σ are the mean and standard deviation of these noise peaks, respectively. The noise and discriminator levels as a function of mass can be exported for further analysis.

Concerning different amounts of noise in an averaged spectrum, Orbitool provides three strategies to deal with the obtained noise: a) remove noise peaks below the discriminator level; b) remove noise peaks below the discriminator level and subtract noise level (μ) from all signals above the discriminator level; c) preserve all the 20 noise peaks. Option a) is the default setting. Option b) is for averaging over a long period so that the signal peaks are likely to be overlapped by noise peaks and hence the abundances of signal peaks have contributions by noise. Option c) is for averaging over a very short period so that it is difficult to separate signals from noise. In addition

to correcting the impact of noise to signal abundance, removing noise peaks reduces the expenses for both peak fitting and data storage. This is because each averaged spectrum in Orbitool is stored as a series of peaks rather than the signal intensities at each given mass grid.

2.3 Single peak shape determination. Although the mass resolution of the Orbitrap (e.g., 140 000 at mass 200
5   Da) is considerably higher than those of conventional online mass spectrometers in atmospheric research (Riva et al., 2019), some peaks (e.g., ^{13}C or ^{18}O isotopes) in an Orbitrap spectrum might still need to be separated via fitting multiple peaks to the measured signals. A known single peak shape is necessary for the peak fitting, where a single peak herein refers to the signals contributed by a single compound (and its isomers). A signal peak hereafter refers to a measured peak, which may be composed of a single ion or multiple different ions. Orbitool uses a normal
10   distribution to characterize the single peak shape (See Fig. 2A). To obtain the standard deviation of the normal distribution at different masses, Orbitool first takes the x highest signal peaks in the spectrum, where x can be set from 1 to 999 and it is 100 by default. The mass resolution of Orbitrap is inversely proportional to $\sqrt{m}$ (Zubarev and Makarov, 2013) where m is mass; hence, the peak width is theoretically proportional to $\sqrt{m}$. According to this relationship, the measured widths of these selected peaks are normalized to 200 Da by dividing them by $\sqrt{m}$. After
15   this normalization, the mass resolution at 200 Da is determined via the least square fitting. The shape of some selected signal peaks composed by multiple ions may deviate from others. The user can remove these peaks manually on the GUI before the fitting. As shown in Fig. 2A, the normalized peaks can be well characterized using a normal distribution and the fitted resolution at 200 Da is close to the instrumental mass resolution.

2.4 Mass calibration. Due to the high mass resolving power of the Orbitrap, determining the mass accurately is
20   critical to identify the chemical composition corresponding to an observed peak. The Orbitrap is able to maintain its mass accuracy (i.e., < 2 ppm) with the help of constantly existing peaks with relatively high abundances, named lock masses (Olsen et al., 2005). Despite of this, additional mass calibrations might be needed, especially for long-

Atmospheric
Measurement
Techniques
Discussions

term measurements, to ensure an optimal identification of the measured compounds across the entire mass range. Orbitool can automatically find the peaks of user-specified calibration species within a given uncertainty range. The mass positions of these calibration species are shown on the top of the averaged spectrum on the GUI to guide eyes. Then, a calibration curve is fitted using a polynomial function and shown on the GUI. The users can set the

5 degree of the polynomial and adjust the calibration curve by using different calibration species. The spectra saved in the same raw data file share the same calibration parameters. The difference between the measured mass and the calibration mass inferred from the chemical formula are shown on the GUI. If the analyzed dataset contains more than one raw file, the trends of these differences for all the calibration species are displayed (Fig. 2B). The calibration information can also be exported for further analysis. Using lock mass(es) during Orbitrap

10 measurements can improve mass accuracy but it requires a constantly existing compound in the measured spectra. When charging compounds by CI, the reagent ion and its dimer are usually in high abundance. Therefore, it is recommended to use the reagent ions as lock masses when using a CI-Orbitrap. During the data analysis with Orbitool, the lock masses are treated as normal signals rather than being excluded from the spectra (i.e., default setting in Xcalibur), since the abundance of the reagent ion is usually a critical parameter to characterize the

15 performance of a CI-mass spectrometer.

2.5 Peak identification. Identifying the abundances and chemical formulae of ions contained in each signal peak is one of the main advantages of Orbitool. Before peak identification, the user can merge the peaks in a given mass range using a customized mass tolerance. A merge sort algorithm (Knuth, 1998) is used to improve computational efficiency. The first step of peak identification is to fit single peaks to the calibrated averaged spectrum. Since the

20 width of a certain single peak is determined by its position (mass), the fitted parameters are only peak position and peak area (which can be converted to peak height). Orbitool usually conducts a default peak fitting to the whole spectra. The number of single peaks used to fit a signal peak is determined automatically according to the number of local maxima of intensities. After a default fitting, the user can look into each signal peak. The signal peak, fitted

single peaks, and fitting residues are shown on the GUI to indicate the quality of the default fitting. Orbitool supports repeating the peak fitting for each signal peak with a user-determined single ion number, and the updated fitting results for the signal peak will replace the default fitting results in the whole spectra.

The possible chemical formulae corresponding to each fitted single peak is retrieved during fitting. Prior to determining the chemical formulae from a given mass, the user can customize the possible elements contained in the detected compounds and the charge polarity. The minimum and maximum numbers of atoms contained in each measured ion, the range of equivalent double bond number, and the maximum tolerance of mass precision are used as boundary conditions. Orbitool searches for all possible chemical formulae satisfying these boundary conditions for a given mass. The nitrogen rule can be applied when only hydrogen, carbon, nitrogen, oxygen, silicon, phosphorus, sulfur, and the halogens are included in the possible element list. An empty string is returned if no possible chemical formula is found under the given conditions. The user can edit the retrieved chemical formulae after this automatic screening. A separate window on the GUI also supports the conversion of chemical formulae to mass at any analyzing step and vice versa. Orbitool also supports identification of isotopes. Hence, the users can adjust the possible isotopes in an isotope list and all the isotopes in this list will be considered. However, it is important to mention that the Orbitrap provides non-linear responses when the concentrations of the analytes are very low (i.e., $< 1 \times 10^6$ molecules cm^{-3}, at a 10-minute integration time). As a result, the calculated isotope abundance may deviate from its true value (Riva et al., 2020).

After identifying all the single peaks, a mass list is generated from the fitted peak position and their corresponding chemical formulae. The user may add all the fitted peaks into the mass list or select only a proportion of them. The unidentified chemical species are shown with empty strings. The mass list can be exported into file. Alternatively, an existing mass list with a certain format can be imported into Orbitool. The new mass list imported from a file or retrieved from a new mass spectrum can either substitute the existing list or merge with it. Orbitool

supports fitting the signal peaks using a mass list instead of fitting all the signal peaks, which greatly reduces the user's workload when analyzing the chemical species in a known system. For instance, when measuring ambient air, the user can average data over a whole day to obtain a mass list. After this, the user may restart data analysis from the beginning and average the raw data with a higher temporal resolution (e.g., 30 min). Then, the user may

5   fit the signals using the former mass list derived from the whole day instead of repeating the default fitting and a manual correction.

2.6 Time series and mass defect. The time series (temporal evolution of abundance) of given chemical species can be calculated based on the measured time-evolving spectra. These chemical species for the time series are usually chosen from the mass list. Due to the unavoidable random error in the measured mass even after mass

10   calibration, Orbitool searches for these chosen peaks within a customized uncertainty range (e.g., 1 or 2 ppm). The time series of all the chosen species are displayed on the GUI and they can be exported into files. The temporal resolution of these time series is configured in the data averaging step. To facilitate a quick analysis, Orbitool can also show the time series of a given compound instead of using a mass list. The input for specifying this compound is either its accurate mass (or its chemical formula which will be automatically converted into accurate mass) with

15   a mass tolerance or a mass range. Using this feature, the user can also obtain the abundance of all the signals within a wide mass range. Orbitool is also able to show the mass defect plot on the GUI for an intuitive and rapid characterization of an averaged spectrum. The size of data points is determined by their intensity, which can be tuned on the GUI. These data points are colored by the number of a chosen element (e.g., C, O, N) or the double bond equivalent. The peaks without identified chemical formulae can either be omitted or displayed in grey.

20   **3 Results and Discussion**

As illustrated in section 2.2, Orbitool estimates the noise level and discriminator level based on the statistics of the measured spectra. Except for the mass defect range of [0.5, 0.8] Da, no prior information is used for determining

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the noise level. This indicates that one cannot unambiguously distinguish every signal peak from the noise, which

may theoretically introduce uncertainties to retrieve compositions and abundances of the measured compounds.

However, such uncertainties are practically negligible after averaging the spectrum. To validate the algorithm used

in Orbitool for estimating the noise level, Fig. 3 shows the total number of peaks in each single or averaged

5   spectrum measured in Shanghai. The noise and discriminator levels were firstly determined using a certain

percentile of peaks in the mass defect range of [0.5, 0.8] Da. Peaks below the determined discriminator level in the

entire mass range were then taken as noise and removed from the spectrum. Considering that some species may

not be detected in a single scan (i.e., present at very low concentration), the total number of peaks in the averaged

spectrum should grow with the increasing averaging time when the period is considerably short, and then it should

10 converge to a certain value when the averaging period is sufficiently long. This is consistent with the observed

trend of the total number of peaks after noise reduction in Fig. 3, in which the total number of peaks after noise

reduction with the 50th percentile is insensitive to the averaging time. In contrast, the total number of peaks without

noise reduction increases gradually as a function of the averaging time, indicating that most of the peaks observed

in the averaged spectrum are noise. In addition, using the 25th, 50th or 70th percentile does not lead to a significant

15 difference in the total number of peaks after noise reduction (within 5-10%), which indicates that the noise level is

governed by the instrument rather than the customized percentile value. Accordingly, Orbitool uses the 70th

percentile as the default value to estimate the noise and discriminator levels.

Combining data averaging and noise reduction, Orbitool can remove most of the noise while maintaining

most of the signal peaks. Figure 4 shows the averaged spectra before and after noise reduction measured from the

20 ozonolysis of monoterpenes in ambient indoor air conditions and ambient air measured in Shanghai. The noise

levels were calculated using the 70th percentile of peaks in the mass defect range of [0.5, 0.8] Da. They can also be

identified by eye in the mass range from 600 Th to 750 Th, where a few signal peaks were detected and noise peaks

are at approximately the same height. The noise level in Fig. 4B is lower than that in Fig. 4A because it was

averaged for a longer period. 97% of the measured peaks in the Shanghai data set after then 30-min averaging were identified as noise and hence removed. Since no significant mass dependencies of noise and discriminator levels were observed, Orbitool uses size-independent noise and discriminator levels. It should be clarified that some signal peaks with low abundances may be mistaken as noise peaks during noise reduction. Even after averaging for a

5   longer period, some detected compounds with extremely low abundances may still be below the discriminator level.

To illustrate the capabilities of Orbitool, measured ions depicted in Fig. 4B were characterized. A total of 1850 ions were identified and their composition retrieved. Figure 5 shows the corresponding mass defect plot of gaseous compounds measured in urban Shanghai, whose data were retrieved and exported by Orbitool. Organic compounds contributed to a major proportion of the measured compounds. The reagent ion (i.e., NO_3^-) is not

10 considered when sorting out the different ions into family groups. Hence the chemical analysis reveals that due to its higher mass resolving power compare to other online mass spectrometers, the CI-Orbitrap identifies a large number of gas-phase signals with elemental composition categories including CHO, CHON, CHONS, CHOS, and others. In addition, inorganic sulfuric acid was observed, which were reported to be the major gaseous precursors for nucleation in Shanghai (Yao et al., 2018). Interestingly, the presence of highly oxygenated CHONS and CHOS

15 species might indicate the existence of uncharted chemical processes.

4 Summary

We developed a publically available software tool named Orbitool for analyzing long-term online Orbitrap mass spectrometry data in atmospheric researches. Orbitool is capable of averaging raw data across files while improving the mass accuracy, distinguishing signal peaks against noise peaks, identifying chemical compounds and their

20 isotopes via peak fitting, and exporting time series and mass defect plots. Compared to similar software tool for atmospheric science studies such as Toftools, Orbitool redesigned the storage method for the measured signals so that it greatly reduces the computational and storage expenses. The data measured in a laboratory study on

Atmospheric
Measurement
Techniques
Discussions

ozonolysis of monoterpenes and in the ambient air of Shanghai were used to successfully test Orbitool. The mass axis uncertainty after calibration using Orbitool was < 0.5 ppm in this test, which is lower than the average uncertainty of 2 ppm calibrated during measurements. The noise reduction was demonstrated to be able to separate signal peaks from noise and greatly reduce the amount of saved data. For instance, the total number of peaks of a

5   test spectrum averaged over 30 min were reduced by 97%. The mass defect plot retrieved using Orbitool indicates that most of the chemical species in urban Shanghai measured by a CI–Orbitrap were organic compounds and reveal the presence of gaseous compounds with unique composition (i.e., CHONS; CHOS).

Orbitool will be open source and freely available for download (see Software availability below), and we hope that it will evolve in the future with added features, optimally as a community effort as Orbitrap mass spectrometers

10   become increasingly utilized as tools for online studies within, and possibly outside, atmospheric sciences.

Software availability

An executable version of Orbitool and its source codes can be found at https://orbitrap.catalyse.cnrs.fr. Orbitool will be continuously updated in the future. It is recommended to contact the corresponding authors for needs on software development.

15   ### *Author contributions*

M.R. initialized this study. Y.L., R.C. and Y.C. wrote the software. D.L., C.D., Y.M., and M.R. conducted the experiments. D.L., C.D., S.P., Y.M., and M.R. tested Orbitool and M.R. analyzed the data. M.F. and L.B. developed the website. R.C. and M.R. wrote the manuscript with the help of all co-authors.

Competing interests

20   The authors declare that they have no conflict of interest.

Atmospheric
Measurement
Techniques
Discussions
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Atmospheric
Measurement
Techniques
Discussions

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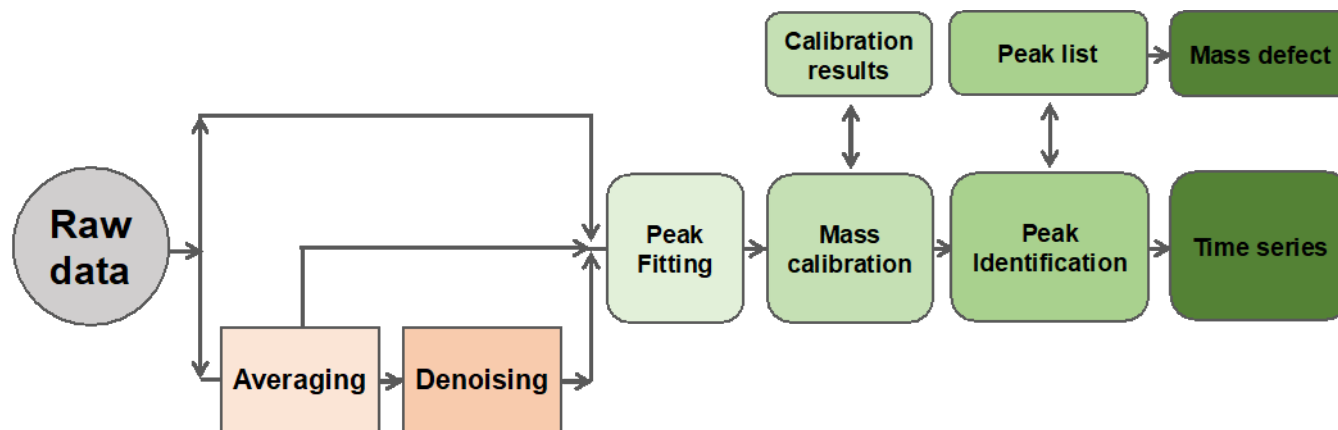25   90(15), 8816–8823, doi:10.1021/acs.analchem.8b00671, 2018.

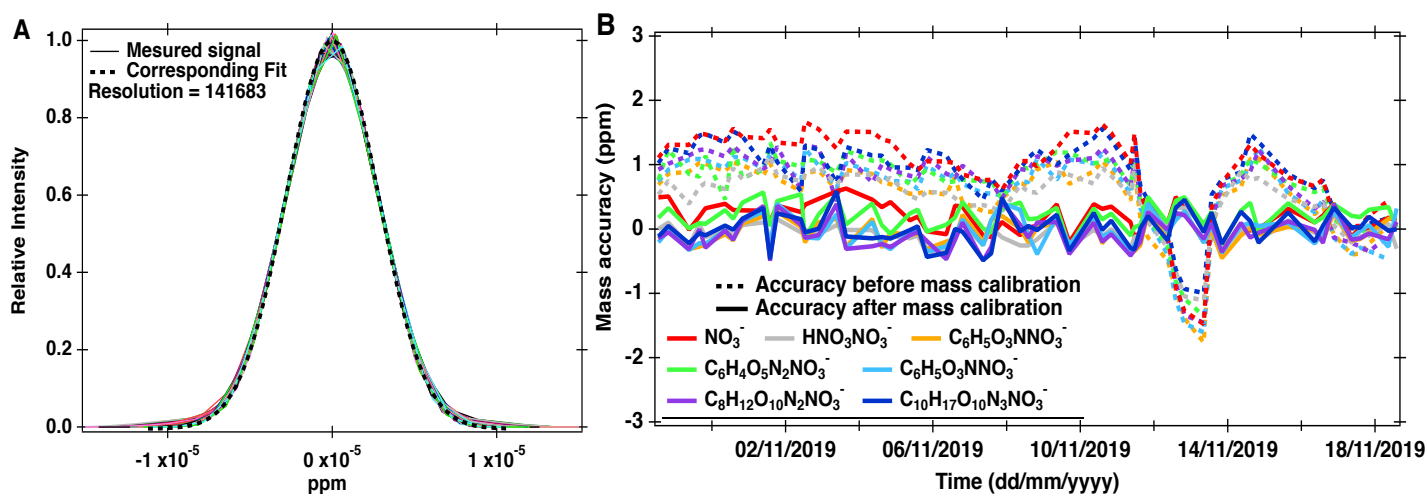**Figure 1:** Simplified schematics of the working principle of Orbitool.

Figure 2. (A) Peak shape determined using the highest 100 peaks observed in the mass spectrometry. The position and width of signal peaks were normalized to 200 Da. The intensity of each signal peak was normalized by dividing by its peak intensity. **(B)** Mass accuracy of product ions at mass (in Da) 62 (red); 125 (grey); 183 (orange); 201 (green); 246 (blue); 358 (purple) and 401 (dark blue) before and after mass calibration. Each data point (as indicated by the fluctuation of the lines) corresponds to a raw data file.
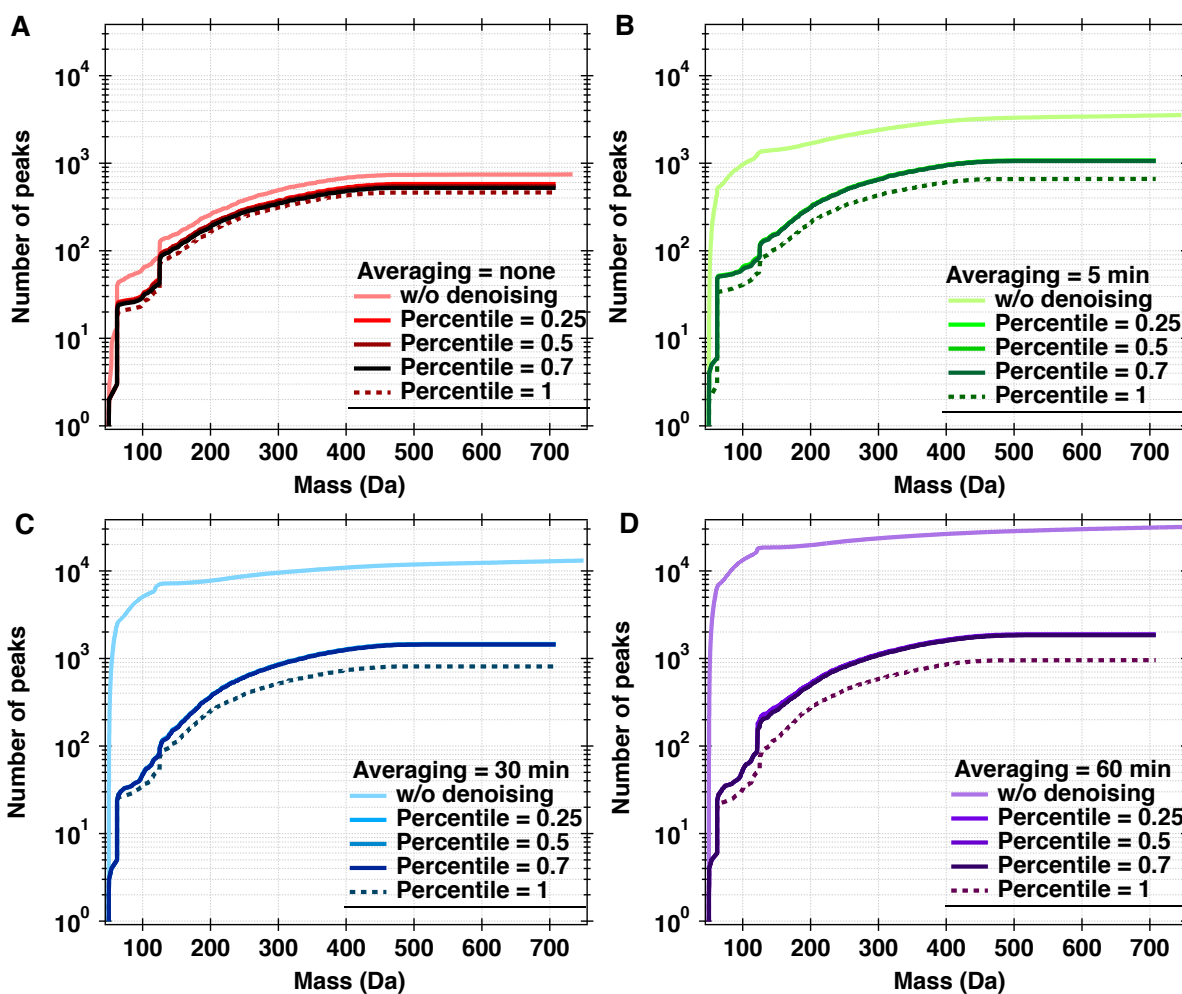
Figure 3. Number of peaks automatically detected in ambient air by Orbitool with and without noise reduction and

for different averaging time. When the percentile = 100%, all the peaks in the mass defect range of [0.5, 0.8] was
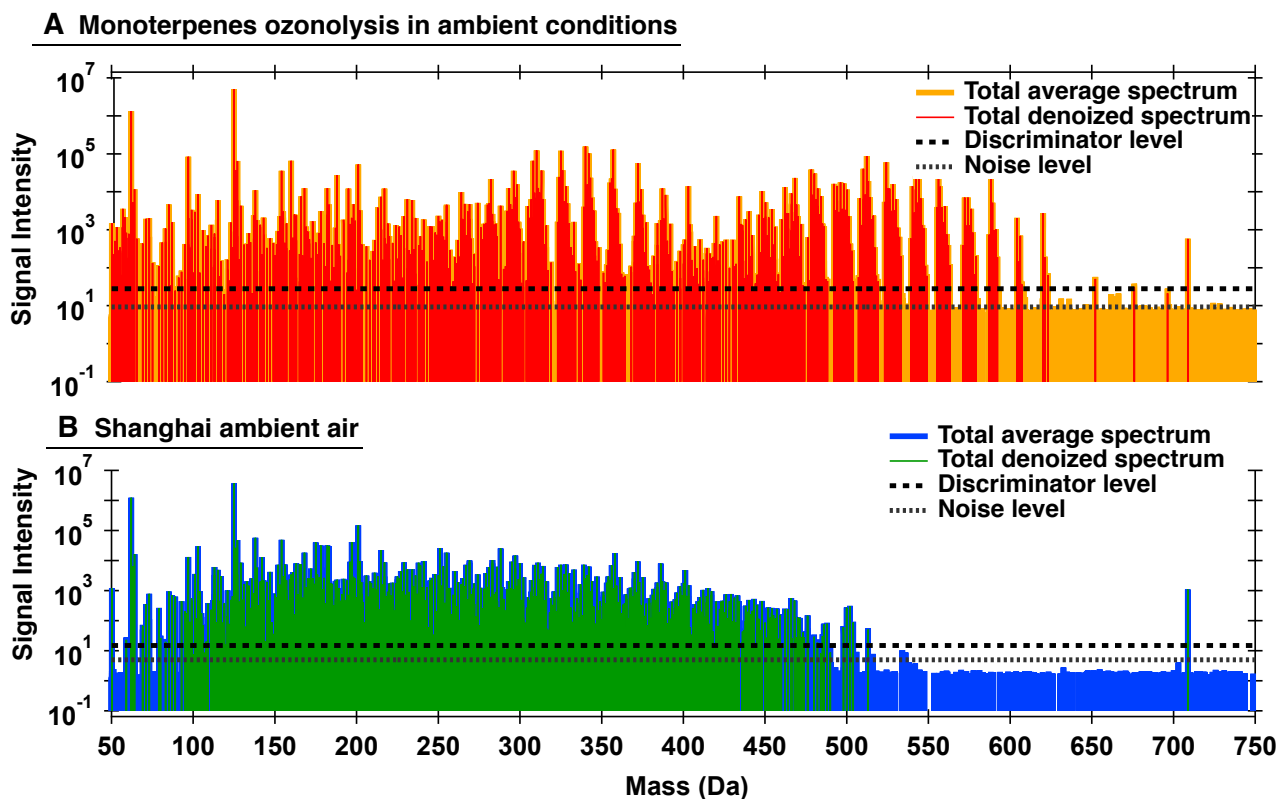
removed.

Figure 4: The noise and discriminator level of mass spectra obtained from the ozonolysis of monoterpenes in **(A)** ambient indoor air conditions (via peeling an orange in front of the Orbitrap) and **(B)** ambient air measured in Shanghai. The averaging span for raw data in **(A)** and **(B)** were 5 and 30 min, respectively. The 70th percentile was used to estimate the noise and discriminator level.

Atmospheric
Measurement
Techniques
Discussions

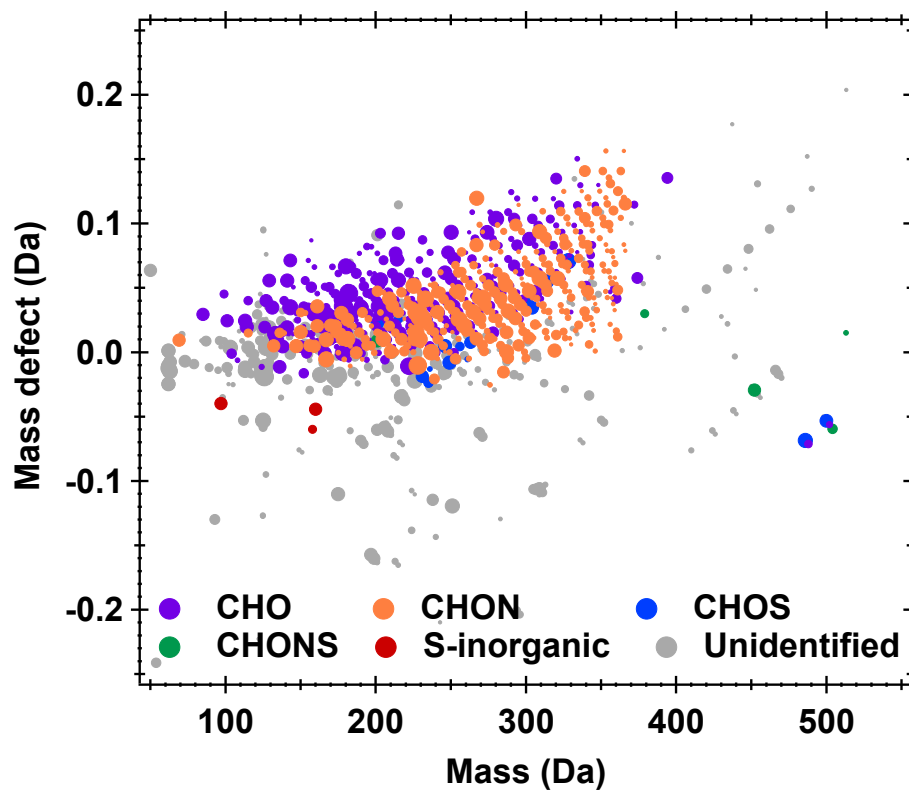**Figure 5.** Mass defect of gaseous compounds observed using the CI-Orbitrap in Shanghai (31/10/2019 between

5   14:00-14:30).