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Automated compound speciation, cluster analysis, and quantification of organic vapours and aerosols using comprehensive two-dimensional gas chromatography and mass spectrometry

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Abstract: The advancement of analytical techniques, such as comprehensive two-dimensional gas chromatography coupled with mass spectrometry (GC×GC-MS), enables the efficient separation of complex organic matrix. Developing innovative methods for data processing and analysis is crucial to unlock the full potential of GC×GC-MS in understanding intricate chemical mixtures. In this study, we proposed an innovative method for the semi-automated identification and quantification of complex organic mixtures using GC×GC-MS. The method was formulated based on self-constructed mass spectrum patterns and the traversal algorithms and was applied to organic vapor and aerosol samples collected from tailpipe emissions of heavy-duty diesel vehicles and the ambient atmosphere. Thousands of compounds were filtered, speciated, and clustered into 26 categories, including aliphatic and cyclic hydrocarbons, aromatic hydrocarbons, aliphatic oxygenated species, phenols and alkyl-phenols, and heteroatom containing species. The identified species accounted for over 80% of all the eluted chromatographic peaks at the molecular level. A comprehensive analysis of quantification uncertainty was undertaken. Using representative compounds, quantification uncertainties were found to be less than 37.67%, 22.54%, and 12.74% for alkanes, polycyclic aromatic hydrocarbons (PAHs), and alkyl-substituted benzenes, respectively, across the GC×GC space, excluding the first and the last time intervals. From source apportionment perspective, adamantane was clearly isolated as a potential tracer for heavy-duty diesel vehicles (HDDVs) emission. The systematic distribution of N-containing compounds in oxidized and reduced valences was discussed and many of them served as critical tracers for secondary nitrate formation processes. The results highlighted the benefits of developing self-constructed model for the enhanced peak identification, automated cluster analysis, robust uncertainty estimation, and source apportionment and achieving the full potential of GC×GC-MS in atmospheric chemistry.

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1 Introduction

Improved sampling strategies, coupled with innovative measurement techniques, are imperative to capture the dynamic nature of atmospheric chemistry, particularly in the context of climate change and health risk (Franklin et al. 2023, Franklin et al. 2022, Huo et al. 2021, Phillips et al. 2018). Comprehensive two-dimensional gas chromatography coupled with mass spectrometry (GC×GC-MS) has emerged as a powerful tool for compound detection and identification, benefitting from the combination of two columns with orthogonal selectivity (Alam et al. 2013, Franklin et al. 2022).

Despite its capabilities, GC×GC-MS encounters formidable challenges in data analysis, which can be extremely complicated and demanding. Efforts have been made to delve into the deluge of data generated by GC×GC-MS. Traditionally, mass spectra were deconvoluted and compared to spectra from the National Institute of Standards and Technology (NIST20) library for peak identification with pre-defined criteria (Guo et al. 2016, Piotrowski et al. 2018). Retention indices (RI) were further introduced to distinguish homologous compounds with resembling mass spectra (Zang et al. 2023). A pioneering and instructive work for searching criteria to classify GC×GC peaks was published in 2003 (Welthagen, Schnelle-Kreis and Zimmermann 2003). Welthagen (2003) incorporated the mass fragmentation patterns to classify compounds in atmospheric aerosol samples. Compounds belonging to the same chemical group related to one another in the GC×GC space and distributed in a structured pattern. They successfully identified seven groups of compounds, including alkanes, alkenes and cycloalkanes, alkyl substituted benzenes, alkyl substituted polar benzenes, hydrated naphthalenes and alkenyl benzenes, alkylated naphthalenes, and alkane acids, occupying more than 60% of the total peak area. This work set a good example of how user-defined rule could facilitate the identification of specific compound groups. Recent advances in chemometric tools for GC×GC-MS analysis involving machine learning and deep learning renovate multi-dimensional chromatography fields (Stefanuto, Smolinska and Focant 2021). Bendik (2021) developed a programming suite for high-confidence and fast compound identification using GC×GC coupled with time-of-flight mass spectrometry (TOF-MS) (Bendik et al. 2021). He (2022) extracted featured mass spectrometric information of the intermediate-volatility and semi-volatile organic compounds (I/SVOCs) by integrating algorithmic language into GC×GC-MS data (He et al. 2022a, He et al. 2022b). A novel pixel-based multiway principal component analysis method was utilized in Song (2023) to identify key tracers during incense burning (Song et al. 2023). Nevertheless, the

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interpretation of GC×GC-MS data demands advanced computational tools and expertise, and the investigation of unknown compounds remains scarce due to the inadequate validation procedures, overreliance on manual data processing, limited access to computational capabilities, and the lacked expertise to handle the complex chromatographic data effectively.

Bridging this gap requires further development of sophisticated algorithms and analytical approaches to unlock the full potential of GC×GC. This study proposed a bottom-up method for cluster analysis and quantification of organic vapours and aerosols within complex atmospheric mixtures. The scripts were initiated with the recognition of the common mass spectra features of specific species and tailored to a wide range of compound clusters. The scripts were then trained, iterated, and optimized incorporating real sample data until robust outputs were achieved. The new strategy reduced the ambiguity that is often associated with identifying compounds in complex mixtures.

The proliferation of heavy-duty diesel vehicles (HDDVs) has raised significant concerns, with an escalating demand for freight transport and in various industrial operations (Yan et al. 2022, Cheng et al. 2022). Despite a low retention rate, HDDVs release massive amounts of particulate matter, nitrogen oxides, ammonia, and carbon monoxide into the atmosphere, compared with other vehicle types (Wang et al. 2023, Silva et al. 2023, Chang et al. 2022, Stanimirova et al. 2023, Hamilton and Harley 2021, 2021, Kruve et al. 2014). Given this, the gas and aerosol samples from representative HDDV tailpipes and the ambient environment were collected and analyzed by GC×GC-MS. The proposed bottom-up method was applied for a comprehensive analysis of the complex organic mixtures, resolving 26 compound categories including hydrocarbons in multiple forms, oxygenated components, and heteroatom containing species. Over 80% of all the chromatographic peaks were identified and assigned to a compound cluster using proposed method, leaving a minor portion of organic matrix unresolved. Different compound clusters occupied separate positions in the GC×GC space, and distinctive distribution patterns within diverse samples and their contribution fractions were revealed. Quantification uncertainties were addressed thoroughly and the significant potential deviation when using n-alkanes as semi-quantification surrogates was proved. Overall, the integration of automated algorithms and GC×GC data analysis holds significant implications for advancing our understanding of atmospheric chemistry, improving secondary organic aerosol (SOA) estimation, and thus guiding the implementation of environmental policies.

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2 Materials and methods

2.1 Sample collection, treatment, and instrumental analysis

For the collection of HDDVs tailpipe emission, chassis dynamometer experiments were conducted at the China Automotive Technology & Research Center (CATARC) in Guangzhou, China. Exhaust emissions from HDDVs were diluted in a constant volume sampler (CVS, CVS-ONE-MV-HE, Horiba), following the China heavy-duty commercial vehicle test cycle for tractor trailers (CHTC-TT) driving cycles. The average temperature in the sampling train was precisely controlled at 47 °C, and airflow, relative humidity, and airflow, relative humidity, and pressure were monitored simultaneously. The speed trace and characteristics of CHTC-TT are shown in Figure S1.

Gaseous exhausts were collected by two adsorbent thermal desorption (TD) tubes in series (Tenax TA, C1-AXXX-5003, Markes International) after being filtered by a Teflon filter. Particulate exhausts were deposited on a 47 mm quartz filter (Grade QM-A, Whatman). Ambient $PM_{2.5}$ filter samples were collected on the rooftop of a 5-story building on the campus of Shenzhen University (22.60°N, 114.00°E) in western Shenzhen, approximately 25 m above the ground. The sampling site was surrounded by campus, residential areas, greenbelts, and a golf park and, the location map is shown in Figure S2. Previous studies demonstrated that the $PM_{2.5}$ concentration in this aera represented the average pollution scheme in Shenzhen (Huang et al. 2018, Yu et al. 2020). Sampling strategy followed a regular schedule of one 24-h sample every day using a high-volume sampler (Th-1000c II, Wuhan Tianhong Environmental Protection Industry Co., Ltd). TD samples were kept dry at room temperature, and quartz filters were stored frozen at −18 °C before analysis. All sampling materials were pre-baked thoroughly to remove potential carbonaceous contamination.

TD samples were injected with 2 μL of deuterated internal standard (IS) mixing solution through a mild N_2 blow (CSLR, Markes International). A precious portion of 1 cm^2 (1 cm × 1 cm) filter sample was isolated and cut into strips. They were spiked with 2 μL of IS mixing solution and inserted into a passivated quartz tube. All TD samples and quartz tubes were loaded onto a thermal desorption autosampler (ULTRA-xr, Markes International), thermally desorbed (UNITY-xr, Markes International), and subjected to GC×GC separation (Agilent 8890, Agilent Technologies; Solid State Modulator1810, *J&X* Technologies) and mass spectrometry detection (Agilent 5977B, Agilent Technologies).

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The thermal desorption system heated the TD tubes to 320 °C (quartz tubes to 330 °C) for 20 min, while the trap remained at 20 °C. Following tube desorption, the trap temperature was raised to 330 °C (340 °C for quartz tubes measurement) for 5 min at the maximum heating rate, and the vaporized analytes were purged into the 1st GC column with a desorb split flow of 6 mL/min. Separation of the analytes was carried out using a DB-5ms capillary column (30 m × 0.25 mm × 0.25 µm, Agilent Technologies) as the primary column and a DB-17MS capillary column (1.2 m × 0.18 mm × 0.18 µm, Agilent Technologies) as the secondary column. The modulation column consisted of a VF-1MS capillary column (0.7 m × 0.25 mm × 0.10 µm, Agilent Technologies) connecting to the 1st column and an Ultimate Plus deactivated fused silica tubing (0.6 m × 0.25 mm, Agilent Technologies) connecting to the 2nd column.

Initially, the GC oven was set at 50 °C for a 3-min duration, followed by a gradual increase at a rate of 5 °C/min until it reached 310 °C, where it was maintained for an additional 5 minutes. The entry and exit hot zones were +10 °C higher than the GC oven temperature, and the trap zone was maintained at -50 °C. The modulation cycle had a period of 4 s. Carrier gas flow was set at 1.2 mL/min. The ion source was kept at 250 °C and scanned over a range of 20 – 350 amu.

2.2 Data collection, alignment, and parsing

GC×GC-MS data acquisition was conducted using Enhanced MassHunter (version 10.0, Agilent Technologies) and SSCenter (version 2.4.0.0, *J&X* Technologies). All data utilized to develop and test the scripts were processed by Canvas Browser (version 2.5, *J&X* Technologies) for basic preprocessing, such as baseline correction, mass spectra deconvolution, and peak smoothing. The application of baseline correction and peak smoothing allowed for an increased signal-to-noise ratio (S/N) and improved overall data quality. Chromatographic peaks were filtered according to the filtering rules: baseline noise = 150, S/N $>$ 50. For each individual sample, after isolating all compounds of interest, a peak table in 1st retention time (RT) sequential order with 1st RT and 2nd RT, peak area, peak height, peak width, and deconvoluted mass spectra was exported. These quantitative variables were further processed for targeted and non-targeted “omics” oriented analysis.

As anticipated, the chromatographic variables experienced RT shifts due to column degradation, routine maintenance (e.g., cutting column), and system fluctuation (e.g., carrier gas pressure variation). The initial RT shifting tolerance for adaptive cluster matching was set to be 1 period of modulation in the 1st dimension and 0.1 s in the 2nd dimension. Additionally, a 2D shift cluster consisting of $C_{16}D_{34}$, $C_{24}D_{50}$,

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and $C_{32}D_{66}$, with the merit of correcting 2nd RT shift, was configured. Data correction or data alignment is crucial for accurate and consistent peak integration.

2.3 Algorithmic development

EI spectra are typically characterized by a molecular ion (M^+) peak plus a collection of fragment ion peaks. The M^+ may dominate the mass spectrum in some cases (e.g., un-substituted polycyclic aromatic hydrocarbons (PAHs)), and more frequently presents at a relatively low intensity. The EI spectra are highly comparable among different instrument systems and experimental conditions, making them an excellent measure to identify compounds. The characteristic ions and their relative intensities depend on the intrinsic nature of the targeted compounds, necessitating knowledge of basic rules and common fragmentation routes to interpret EI mass spectra. Figure 1 illustrates the workflow for establishing computational strategies for robust and reproducible GC×GC-MS data processing.

Functional groups have significant effects the fragmentation patterns observed in mass spectrometry, and some ions are typical of given structures. Isotopic peaks (e.g., hydrogen and chlorine) provide additional information about the molecules (Du and Angeletti 2006, Fernandez-de-Cossio et al. 2004). These pieces of information formed the foundation for building up the model for cluster analysis and are addressed in greater detail in the supporting information (S1). These indicative reaction schemes have been incorporated into the model development. Each critical step of model construction and validation is described thoroughly. The quantitative variables in the data alignment table, combining the chromatographic and MS information are properly exploited and determine the overall speciation capacities. Traditionally, compound identification relies on the electron ionization-based fragmentogram and the deconvoluted mass spectra. Empirically speaking, one-by-one compound identification would be greatly intervened by neighbouring peaks, especially those with similar structures, and introduce considerable uncertainties. A good example is the assignment of homologous *n*-alkanes, of which the fragmentogram bears a close resemblance (Figure S5). In such cases, the similarity score (the measure of similarity between the observed mass spectrum and the NIST library hit) could be erroneously inflated to 850 (out of 999) or higher. In contrast, cluster analysis or “omics” oriented analysis involves the comprehensive analysis of a specific type of compounds on a large scale, aiming to provide a holistic understanding of the distribution and transformation of the specific compound cluster being investigated.

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Due to the complexity and remarkable peak capacities, sophisticated and detailed scripts for cluster identification were constructed. Heteroatom containing species, e.g., amides and amines, were carefully examined. The scripts began by recognition of the common mass spectra features of compound cluster of interest and are addressed in more details as follows:

1. The Boolean value of characteristic ions.
2. The intensity sequence of abundant ions in the whole spectra.
3. The retention time window restriction for certain compound groups.
4. The pattern of mass spectrometry variation with the increased number of substituents or the extension of the carbon chain.
5. Iteration framework that involved repetitive cycles among all the tested samples.

The scripts were then trained, iterated, and optimized incorporating real sample data, and the parameters were adjusted accordingly until a robust output was achieved. The extractor function built in the Canvas software was activated, and all the scripts were imported to facilitate automated cluster analysis. The scripts parsed all the files in the given directory into the required structure and generated three reports in the form of .pdf, .csv, and .bmp. The .csv file contained key information including the compound name, compound cluster, 1^{st} and 2^{nd} RTs, and peak area (based on total ion current (TIC)).

Once exported, the peaks were further processed for quantification/semi-quantification following the steps below. First, calibration curves were prepared by spiking different volumes of the standard solution mixture onto the blank TD tubes and blank filters, respectively. Peak area ratios, i.e., peak area of authentic standards over that of the internal standards, were used to build the linear relationship, with the merit of correcting system fluctuation. The selection of authentic standards prioritizes their wide distribution across the entire chromatogram space, ranging from high to low volatility and weak to strong polarity, and meanwhile encompassing a broader range of functional groups and heteroatoms. The distribution and performance of all authentic standards are summarized in Table S1 and Figure S6. Second, for the un-quantified peaks, their complied information (X, Y, Z) corresponding to (1^{st} RT, 2^{nd} RT, compound cluster) is looped through the list of all authentic standards in the following descriptive algorithm framework (note that the statements do not conform to the grammar rule and it is for illustrative purpose only) until the optimal authentic standard to semi-quantity the target peaks is exported. It should be emphasized that the un-quantified peak and the corresponding authentic standards to semi-quantify it must belong to the same group, due to their physics-chemical similarities.

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```
For (i = 1 to n) # n equals the number of authentic standards and is a known variable.
    If (ZM = Zi) # M is the un-quantified peak and i refers to the authentic standard that is selected in a certain loop.
        Ai = Min (an array of ((XM – Xi)^2 + (YM – Yi)^2)) # This sentence dose not conform to the grammar rule of Visual Basic for Applications in Excel, and it is for illustrative purpose only.
        Export Zi, (Xi, Yi, Zi), its peak area, and its linear calibration relationship.
    End if
Next i
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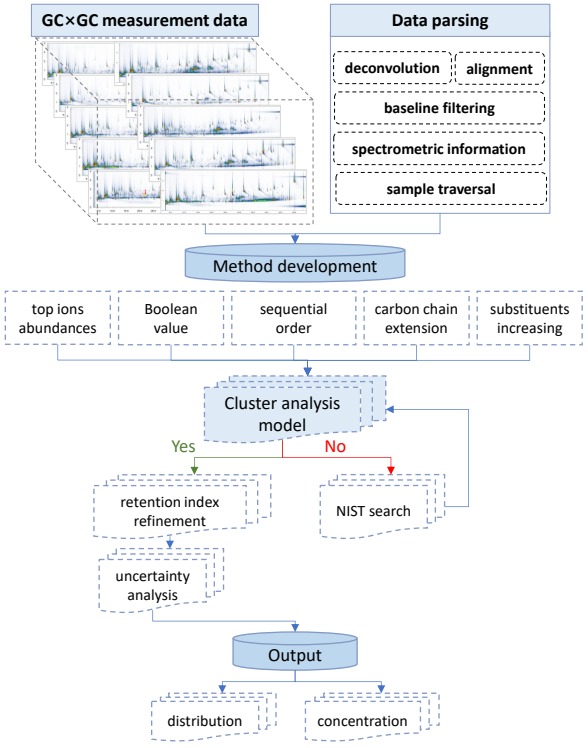

Figure 1. Flow diagram illustrating the multistep data processing for establishing computational strategies for cluster analysis and quantification of organic vapours and aerosols using GC×GC-MS data.

2.4 Quality assurance/control and uncertainty evaluation

It is common for thermal decomposition to occur in analytical methods involving heating processes, potentially leading to the erroneous detection of compounds that are either not present in real samples or

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present in low concentrations. Such artifacts need careful scrutiny, and the availability of authentic standards covering the GC×GC space range is essential for validation. The thermal programs used in this study were highly similar to those employed by Franklin (2023), who observed low chromatographic signals of decomposition products (Franklin et al. 2023). Nevertheless, the possibility that some observed analytes are decomposition products cannot be entirely ruled out. Peaks of ISs were traced across all samples to monitor the variation of several modules, and the results are presented in Figure S7. Excellent stability was clearly observed, demonstrating the robustness of the testing system. Strong linear correlations were achieved for this set of authentic standards, with Pearson's R ranging from 0.97 to 0.99. Routine blank tests were conducted to prevent unexpected contamination.

3 Results and discussion

3.1 Overall performance of the algorithm and compound identification

The optimization of component identification remains a challenging issue, and this work involves converting known chemical compounds into molecular descriptors and utilizing cluster analysis to predict the relationship between these descriptors and structural information. After continuous trails to improve reliability and data processing speed, a final solution of 26 compound clusters stands out with high accuracy and repeatability:

- Aliphatic hydrocarbons, including *n*-/*i*- alkanes and alkenes
- Cycloalkanes
- Alkyl-substituted benzenes, including C_1 – C_6 alkyl-substituted benzenes
- Admantanes
- Hopanes
- 2 – 5 ring PAHs
- Acids
- Aliphatic alcohols
- Aliphatic aldehydes and ketones
- Oxy-PAHs
- Phthalates
- Phenols and alkyl-substituted phenols

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- Phenol ethers
- Amides
- Amines
- Pyridines
- Nitros, including organic nitrates and organic nitrites

Validation of the model output using field diesel samples has been conducted and has shown high estimation accuracy and integrity. Generally, over 82% of the peaks have been successfully classified and assigned to the corresponding compound groups and their distribution in an example GC×GC plot is shown in Figure 2. To confirm the tentatively identified heteroatom groups, their raw chromatogram, mass spectra, and chemical structures of representative species are displayed in Figures S9-S15. Less than 18% of the chromatographic peaks were identified as unresolved components. Basically, aliphatic hydrocarbons were located in the lowest position in a GC×GC space except column bleedings (Figure 2a-c and Figure S8), and their 2^{nd} RT drift was less than 1s from the far-left to the far-right side. N-containing compounds in oxidized and reduced valences, including amides, amines, pyridines, and nitros, were resolved simultaneously under respective filtering rules, and they occupied a slightly higher position in the GC×GC space (Figure 2f). Amines and pyridines were more volatile species and eluted at early stages, whereas nitros and amides were eluted at middle and late stages sequentially. Due to their high volatility, C_2-C_6 alkyl-substituted benzenes also presented at the beginning of the GC×GC space and they partitioned dominantly into the gas phase. Their 2^{nd} RTs were comparable to those of pyridines and amides, and the 2^{nd} RT drift was negligible. Aliphatic O-containing compounds, including acids, alcohols, and ketones, were found to be in the middle region and covered a wide volatility rang. Aliphatic O-containing compounds affect the acidity of the atmosphere, participate in aqueous phase reactions, and contribute significantly to the formation of SOA (Cope et al. 2021, Xu et al. 2022). Phenols with one or more hydroxyl groups attached to an aromatic benzene ring were observed in the middle of the GC×GC space. Oxy-PAHs and PAHs presented in the upper middle of GC×GC space, and the volatility range stretched to the low volatility end, for which a clear trend tilting to the upper right corner was observed, suggesting that the aromaticity played a significant role in the retention in the secondary dimension.

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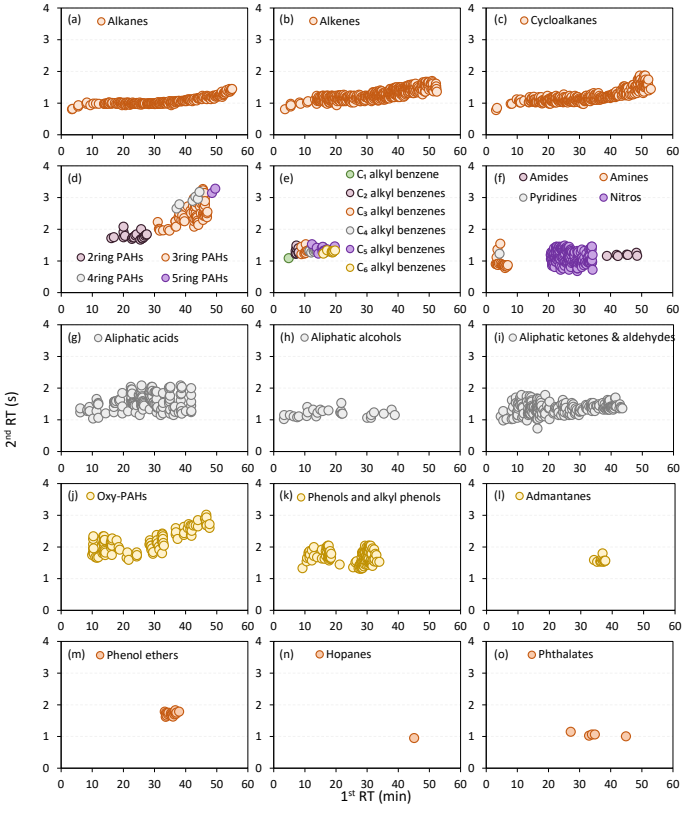

Figure 2. The distribution of the 26 compound groups in an example GC×GC plot. For clear visualization, different compound groups are displayed separately, except for 2 – 5 ring PAHs, C_2 – C_6 alkyl-substituted benzenes, and N-containing species. Nitros include organic nitrates and organic nitrites, due to the co-existence of the characteristic ions at m/z 30 (NO^+) and m/z 46 (NO_2^+).

3.2 Model uncertainty estimation

We conducted a systematic evaluation of the model output, and the results are shown in Figure 3 and Figure 4. To address this issue comprehensively and accurately, we selected three types of standards including C_7 – C_{37} *n*-alkanes, C_2 – C_6 alkyl-substituted benzenes, and 2 – 4 ring PAHs, representing a full range of low to high polarity and various functionalities. The quantification deviation was computed according to the principles of the model. Chromatographic peaks were quantified by either their authentic standards or the surrogates that fell within the same compound category after being classified to one of the 26 compound classes. For example, if the mass spectrum of a chromatographic peak followed the pattern of the compound class of alkanes, it would be assigned into the alkane group and quantified by its authentic standard if any, or by the *n*-alkane (*n*-alkane serving as the semi-quantification surrogate in

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this case) that was closest to it spatially. Similarly, if the mass spectrum of a chromatographic peak followed the pattern of C_x alkyl-substituted benzenes, it would be assigned into the C_x alkyl-substituted benzene group and quantified by its authentic standard if any, or by the alkyl-substituted benzene (alkyl-substituted benzenes serving as the semi-quantification surrogate) that was closest to it spatially. In light of the explanation, the deviation of the slopes of the calibration curves of any pair of the adjacent authentic standards that fell within the same compound category was computed to represent the ceiling of the semi-quantification uncertainty. Uncertainties are computed using the following Eq. (1):

$$Uncertainty\ (\%) = \frac{Abs(S_p - S_s)}{Smaller\ (S_p, S_s)} * 100 \quad (1)$$

where S_p and S_s are the slopes of the previous and subsequent compounds, respectively.

The slopes increased rapidly from 3.13 (C_7 *n*-alkane) to 8.21 (C_9 *n*-alkane), fluctuated slightly from 8.85 to 11.8 in the range of C_9 to C_{27} *n*-alkanes, and decreased gradually after C_{28} *n*-alkane to the end of C_{37} *n*-alkane. In the whole volatility range of C_9 – C_{37} *n*-alkanes, the uncertainties were less than 37.67%, except for one time interval between C_8 and C_9 *n*-alkanes, where the quantification deviation reached 142%. A similar trend was observed for PAHs, with uncertainties less than 22.54%, except for the first- and last-time intervals, where the quantification deviations were 55.44% and 81.59%, as shown in Figure 3. Stable responses of C_2 – C_6 alkyl-substituted benzenes were monitored, and the uncertainties were less than 12.74%. In other words, for any given peak, it would be quantified/semi-quantified by one authentic standard, and the upper limit of quantification uncertainty originated from any pair of the adjacent authentic standards was as discussed earlier.

It made sense that the uncertainty ranges of alkyl-substituted benzenes were less than those of *n*-alkanes and PAHs, given that alkyl-substituted benzenes were eluted early at the front half, whereas alkanes and PAHs covered the whole volatility range. The trends illustrated that the responses of GC×GC to the analysts were sensitive to the volatility distribution and region for accurate quantification fell in the middle part. It also highlighted the utility of introducing more authentic standards and the benefits of enriching compound categories. We could speculate that the quantification uncertainty would be further reduced with the augmentation of standard compounds.

Furthermore, we delved into the uncertainty estimation of dividing the whole chromatogram into bins based on retention time, and all the species in the same bin were quantified, referring to the mass-to-signal responses of the C_n *n*-alkanes (Zhao et al. 2015, Zhao et al. 2014). This approach corrected the

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signal variation of hydrocarbons in the GC-MS and was widely adopted for quantifying unresolved complex mixtures (UCMs) (Shen et al. 2023, Zhao et al. 2022). We chose four types of standards belonging to different compound categories with similar 1st RTs and different 2nd RTs, including $C_{19}H_{40}$ (1st RT = 34.6 min, 2nd RT = 1.03 s), 9,10-anthracenedione (1st RT = 36.07 min, 2nd RT = 3.85 s), $C_{19}H_{40}$ (1st RT = 36.54 min, 2nd RT = 1.07 s), and fluoranthene (1st RT = 37.00 min, 2nd RT = 3.04 s), and assessed the deviation of slopes of each pair of the standards. Results in Figure 4 show that the deviation between the three pairs of standards was 1809% (C_{19} *n*-alkane vs. 9,10-anthracenedione), 1903% (9,10-anthracenedione vs. C_{20} *n*-alkane), and 105% (C_{20} *n*-alkane vs. fluoranthene), respectively. The quantitative errors in quantifying unidentified chromatographic peaks using responses of *n*-alkanes could reach three orders of magnitude, especially for O-containing species, and those errors in quantifying aromatic components, e.g., PAHs, also exceeded 100% in some cases.

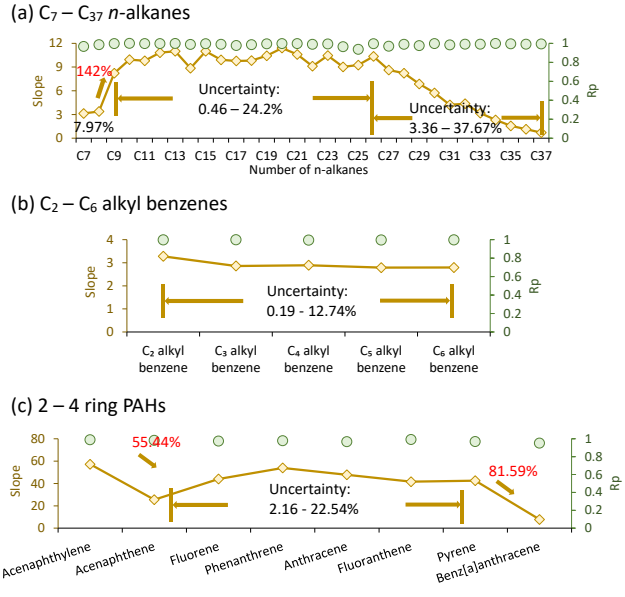

Figure 3. Slope and Pearson correlation variation of (a) C_7 – C_{37} *n*-alkanes, (b) C_2 – C_6 alkyl-substituted benzenes, and (c) 2 – 4 ring PAHs. Brown diamond dots represent slopes of different species and are referenced to the left-axis. Green circles denote the Pearson correlation of individual species and are referenced to the right-axis. Pearson correlation values of *n*-alkanes, C_2 – C_6 alkyl-substituted benzenes, and 2 – 4 ring PAHs range from 0.936 to 0.999, 0.994 to 0.998, and 0.952 to 0.992, respectively. Uncertainties are computed using the equation provided in the main text.

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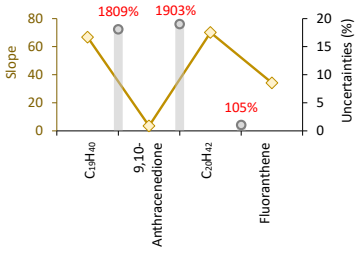

Figure 4. Slopes and uncertainty estimation of example compounds with close 1st RTs and different 2nd RTs: $C_{19}H_{40}$ (1st RT = 34.6 min, 2nd RT = 1.03 s), 9,10-anthracenedione (1st RT = 36.07 min, 2nd RT = 3.85 s), $C_{20}H_{42}$ (1st RT = 36.54 min, 2nd RT = 1.07 s), and fluoranthene (1st RT = 37.00 min, 2nd RT = 3.04 s). Brown diamond dots represent slopes of different species and are referenced to the left-axis. Gray bars denote the uncertainty estimation of example compounds and are referenced to the right-axis.

3.3 Cluster analysis in organic vapor and aerosol samples

The model was applied to organic vapor samples from HDDV tailpipe emission (HDDV vapours for short), aerosol samples from HDDV tailpipe emission (HDDV aerosols for short), and atmospheric aerosol samples (ambient aerosols for short) for cluster analysis. The results are shown in Figure S16, displaying the top few species' distribution with a contribution fraction exceeding 5%, and in Figure 5, showing the mass stacking. Overall, the speciated chromatographic peaks accounted for 85%, 82%, and 99% for HDDV vapor, HDDV aerosol, and ambient aerosol samples, respectively. The unidentified peaks were less than 20% and addressed in greater details in the supporting information (S1).

Distinct cluster distribution features could be extracted. For ambient aerosol samples, six compound clusters were filtered, and aliphatic ketones were the most abundant cluster, contributing to 27% of all the peak signals, followed by alkanes and alkenes. A notable fraction of 15.2% of organic nitros was observed in ambient samples exclusively, indicating significant secondary nitrate formation processes under atmospheric conditions. Aliphatic acids and oxy-PAHs were also detected at an abundant level, and the top six groups accounted for over 95% of the total classified peak signals. Minor but non-negligible fractions included cycloalkane, aliphatic alcohols, and phenols and alkyl-substituted phenols. Similarly, aliphatic ketones ranked first for HDDV aerosol samples, with the mass intensity reaching 46% of the total signals, followed by alkanes. Aliphatic alcohols and oxy-PAHs were detected at an abundant level, and the top four groups accounted for over 88% of the total classified peak signals. Cycloalkanes, amides, phenols and alkyl-substituted phenols, and alkenes were compound clusters with lower abundance ranging from 1-4%.

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For HDDV vapours, the most abundant group was phenols and alkyl-substituted phenols, constituting 34% of the total peak signals. Compared with previous results where the most abundant group was reported to be alkanes,(Wang et al. 2022, Alam et al. 2019) the adoption of the innovative model contributed to resolving the oxygenated factions and reduced inaccuracies in SOA simulation due to the lack of species information. The compound cluster is confirmed by 1) the retention time window including 1^{st} RT and 2^{nd} RT, and 2) the mass spectra. Detailed information is displayed in Figure S15. The 2^{nd} RTs of the identified phenols and alkyl-substituted phenols range from 1.45 to 1.78 s, well above the hydrocarbon regions, of which the 2^{nd} RTs fall within the range of 1.0 to 1.15 s approximately. Their mass spectra also feature with the typical phenol ions at m/z = 94, 107, 121, 135, 149, and 191. Alkanes ranked as the second top species, followed by C_1 alkyl-substituted benzene. C_1 – C_6 alkyl-substituted benzenes were negligible in both ambient and HDDV aerosol samples, whereas in notable abundance in HDDV vapor samples. This distribution aligned with their placement in the GC×GC plot, indicating they were relatively volatile species and partitioned predominantly into the gas phase. Oxy-PAHs and aliphatic ketones contributed to 6% of the total identified peak intensities, followed by some minor fractions, including C_2 alkyl-substituted benzene, cycloalkanes, and alkenes.

The model output illustrates the overall distribution of compound clusters in various gas and aerosol samples, providing comparative insights. Carboxylic acids indicated a higher oxidation state than other compound clusters and were exclusively observed at a notable level in ambient samples compared with "freshly emitted" source samples. The oxidation state of dominant compounds in HDDV samples was comparatively low. For example, a significant ketone fraction was observed in HDDV samples, with the majority partitioning into the aerosol phase due to the long chain carbon skeleton and thus low volatility. Phenols and alkyl-substituted phenols were the leading species in HDDV gas samples. He (2022) reported that the oxygenated I/SVOCs accounted for over 20% of the total I/SVOCs mass in HDDV tailpipe emissions (He et al. 2022a). With the refinement and improvement of model performance, e.g., further splitting mixed mixtures, the oxygenated fraction was elevated to over 50%.

This study highlighted the systematic presence and distribution of N-containing compounds in oxidized valences (including nitros) and reduced valences (including amides, amines, pyridines). Among them, amines and amides were key precursors for new particle formation processes in a polluted atmosphere (Saeki et al. 2022, Cai et al. 2021), and pyridines, with the N atom in the aromatic ring, were readily dissolved in water, participating in the global N cycle in ecosystems (Kosyakov et al. 2020). Nitros

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covered a wide range of organic compounds with NO or NO_2 substituents and served as critical tracers for secondary nitrate formation processes. Amines and pyridines were volatile species occupying the early section of the GC×GC space, while nitros and amides were distributed in the middle and rear space. Individual N-containing species were at trace levels under atmospheric conditions and were hardly detectable. Moreover, authentic standards or high-resolution mass spectrometry were required to identify and quantify each compound (Zhang et al. 2018). With the establishment of an algorithmic solution, we were able to conduct a full scan of N-containing compound clusters.

In addition to common features, specific compounds were identified in separate samples and could potentially serve as markers or tracers for primary emission. Adamantane and its derivatives, with the fusion of three cyclohexane rings (chemical structure and mass spectrum shown in Figure S17a), were natural products in petroleum (Stout and Douglas 2004). They were volatile and had previously been isolated using GC×GC-ToF-MS in crude oil (Wang et al. 2013). Adamantanes were observed in HDDV vapor samples, contributing 1.4% to the identified peaks. Hopane (chemical structure and mass spectrum shown in Figure S17b) was also a natural product in petroleum and bitumen, and it was an important marker for vehicle emissions due to its persistency and stability (He et al. 2022b, Wong et al. 2021). Hopane was reported to survive heat treatment up to 460 °C and was exclusively detected in HDDV aerosol samples, with an intensity fraction of 0.3% (Wu and Geng 2016).

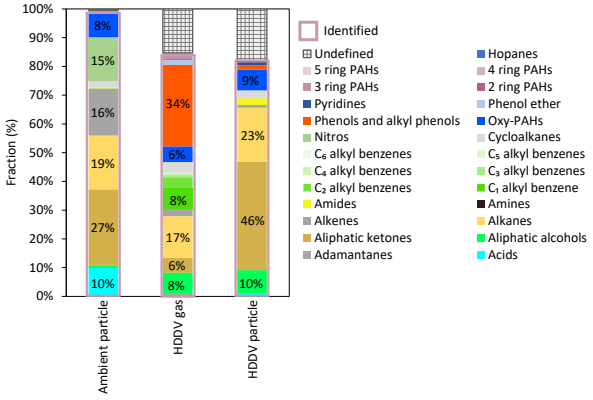

Figure 5. The fraction distributions of different compound clusters in ambient aerosol samples, HDDV tailpipe vapours, and HDDV tailpipe aerosols. Numbers labelled on each column represent the fractions of the top few groups in different samples. Identified clusters are outlined in light purple.

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4 Conclusions and outlook

We presented an innovative method for optimizing the separation and identification of organic vapours and aerosols, with a focus on establishing molecular descriptors and cluster analysis algorithms. The model outputs were validated using field samples with high accuracy and integrity. Less than 20% of the peaks were unresolved components. The retention patterns of various compound groups and their distribution in the GC×GC plot were resolved, and the influence of functional groups on fragmentation was thoroughly addressed. We also provided a comprehensive analysis of the quantification uncertainties of this new approach and highlighted the significant quantitative errors when using *n*-alkanes as semi-quantification surrogates. This model was applied to various types of field samples, and the results revealed distinctive distribution patterns of compound clusters and contribution fractions, providing valuable insights into the compositions of organic vapours and aerosols, and offering potential markers for specific emission sources.

Compound speciation in atmospheric chemistry continues to be a dynamic and challenging field. Speciated compounds enable models to consider the diversity of organic species and dynamic chemical transformation in the atmosphere, contributing to more accurate SOA simulation results. It also allows for a more refined description of the dispersion of pollutants, thereby assisting in the development of localized air quality management strategies, as we strive for a more accurate and broad understanding of atmospheric chemistry.

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Author contribution:

X.H.: Conceptualization, formal analysis, model development, data validation, writing−original draft, funding acquisition; X.Z.: Writing−reviewing and editing, project administration, supervision, funding acquisition; S.G: Experiment; L.Z., T.C., B.Y., and S.X.: Experiment; Q.W., Z.L., Y.Y., S.Z., and Y.W.: Data validation, writing−reviewing and editing.

Competing interests:

The authors declare that they have no conflict of interest.

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