Variation in chemical composition and volatility of oxygenated organic aerosol in different rural, urban, and ~~remote~~ mountain environments

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Abstract. The apparent volatility of atmospheric organic aerosol (OA) particles is determined by their chemical composition and environmental conditions (e.g., ambient temperature). A quantitative, experimental assessment

30   of volatility and the respective importance of these two factors remains challenging, especially in ambient measurements. We present molecular composition and volatility of oxygenated OA (OOA) particles in different rural, urban, and ~~remote~~ mountain environments ~~across the globe~~ (including Chacaltaya, Bolivia; Alabama, U.S.; Hyytiälä, Finland; Stuttgart and Karlsruhe, Germany; and Delhi, India) based on deployments of a filter inlet for gases and aerosols coupled to a high-resolution time-of-flight chemical ionization mass spectrometer (FIGAERO-

35   CIMS). We find on average larger carbon numbers (nC) and lower oxygen-to-carbon (O:C) ratios at the urban sites (nC: 9.8±0.7; O:C: 0.76±0.03; average ± 1 standard deviation), compared to the rural (nC: 8.8±0.6; O:C: 0.80±0.05) and ~~remote~~ mountain stations (nC: 8.1±0.8; O:C: 0.91±0.07), indicative of different emission sources and chemistry. Compounds containing only carbon, hydrogen, and oxygen atoms (CHO) contribute highest to the total OOA mass at the rural sites (79.9±5.2%), in accordance with their proximity to forested areas (66.2±5.5% at the

40   mountain sites and 72.6±4.3% at the urban sites). The largest contribution of nitrogen-containing compounds (CHON) are found at the urban stations (27.1±4.3%), consistent with their higher NO_x levels. Besides, we parametrize OOA volatility (saturation mass concentrations, C_{sat}) using molecular composition information and compare it with the bulk apparent volatility derived from thermal desorption of the OOA particles within the FIGAERO. We find differences in C_{sat} values of up to ~3 orders of magnitude, and variation in thermal desorption

45   profiles (thermograms) across different locations and systems. From our study, we draw the general conclusion that environmental conditions (e.g., ambient temperature) do not directly affect OOA apparent volatility, but rather indirectly by influencing the sources and chemistry of the environment and thus the chemical composition. The comprehensive ~~global~~ dataset provides results that show the complex thermodynamics and chemistry of OOA and their changes during its lifetime in the atmosphere, and that generally the chemical description of OOA suffices to

50   predict its apparent volatility, at least qualitatively. Our study thus provides new insights that will help guide choices of e.g. descriptions of OOA volatility in different model frameworks ~~which has been previously simplified~~ ~~due to challenges to measure and represent it in models~~, such as air quality models and cloud parcel models.

1 Introduction

Chemical composition and volatility of atmospheric organic aerosol (OA) particles are interconnected.

55   Functionalization of organic molecules can modify their vapor pressure by several orders of magnitude (Pankow and Asher, 2008;Donahue et al., 2011;Graham et al., 2023;Isaacman-VanWertz and Aumont, 2021;Kroll and Seinfeld, 2008). Volatility determines whether a compound partitions into or evaporates from the particle phase and thus influences particulate mass and lifetime in the atmosphere. Accurate predictions of atmospheric organic particle mass thus require a quantitative understanding of the chemical nature and volatility of its components.

60   This is of special importance for oxygenated organic aerosol (OOA), most of which is of secondary origin (i.e., SOA) (Jimenez et al., 2009) and involves phase transitions and chemical reactions in all phases. Further, the conditions of the atmosphere, e.g., temperature, play a critical role. A semi-volatile compound may be in the gas phase in the boundary layer at 25 °C but condense at an altitude of ~4.5 km where the ambient temperature is ~20 °C lower, and consequently its apparent volatility is lower by up to ~2 orders of magnitude (Bardakov et al.,

65   2021;Donahue et al., 2011;Epstein et al., 2010;Stolzenburg et al., 2018). The complex thermodynamics and chemistry of OOA and their changes during its lifetime in the atmosphere are challenging to measure and represent

in modelling frameworks, resulting in simplified descriptions of volatility (Nozière et al., 2015;Hallquist et al., 2009).

The development of the filter inlet for gases and aerosols coupled to a time-of-flight chemical ionization mass spectrometer (FIGAERO-CIMS) has enabled the combined analysis of molecular composition and volatility of OOA particles in near-real time (Thornton et al., 2020;Lopez-Hilfiker et al., 2014). OOA volatility can be derived in two ways from the FIGAERO-CIMS:

1) The molecular information of OOA can be used to parametrize volatility via calculations of the effective saturation mass concentrations (C_{sat}) of different organic compounds (Donahue et al., 2011;Li et al., 2016;Mohr et al., 2019;Isaacman-VanWertz and Aumont, 2021;Graham et al., 2023). There are various parametrization methods to calculate C_{sat}, based on different assumptions, training datasets, or structure-based estimation methods (Isaacman-VanWertz and Aumont, 2021). However, calculated C_{sat} from different parametrizations may vary among each other: while modified Li method (Li et al., 2016;Isaacman-VanWertz and Aumont, 2021) tends to estimate higher vapor pressures than expected for low-volatility species, Daumit method (Daumit et al., 2013) and Donahue method (Donahue et al., 2011) (also the updated Mohr method (Mohr et al., 2019)) are found to estimate lower vapor pressures (Isaacman-VanWertz and Aumont, 2021). The discrepancy in C_{sat} among different parametrizations can span several orders of magnitude and become even larger for compounds with increasing nitrogen numbers, especially for organonitrates with multiple nitrate groups (Wu et al., 2021;Isaacman-VanWertz and Aumont, 2021;Graham et al., 2023). This could induce uncertainties associated with volatility estimates particularly for the complex ambient particle matrix (O'Meara et al., 2014), in addition to the potential divergence from the sum of individual parametrized C_{sat} due to non-ideal intermolecular interactions (Compernolle et al., 2011;Isaacman-VanWertz and Aumont, 2021).

2) While the particles are thermally desorbed within the FIGAERO for molecular composition analysis with CIMS, the instrument also yields a qualitative measure of particle volatility through the signal evolution as a function of desorption temperature (i.e., thermograms) (Lopez-Hilfiker et al., 2014;Lopez-Hilfiker et al., 2015). A model framework has also been developed to reproduce the shape of thermograms (Schobesberger et al., 2018). The desorption temperature at which a compound exhibits maximum signal (T_{max}) correlates with the compound's enthalpy of sublimation and can be used to infer its saturation vapor pressure (Lopez-Hilfiker et al., 2015;Mohr et al., 2017). Evaporative behavior, and hence thermogram shape, T_{max} and inferred volatility of a particle-bound compound are subject to artefacts from thermal decomposition (Lopez-Hilfiker et al., 2015;Yang et al., 2021), heating rate (Yang et al., 2021;Ylisirniö et al., 2021;Thornton et al., 2020;Schobesberger et al., 2018), FIGAERO geometry (Ylisirniö et al., 2021), the presence of isomers (Thompson et al., 2017;Masoud and Ruiz, 2021), and particle-phase diffusivity and viscosity (Yli-Juuti et al., 2017;Huang et al., 2018). As a consequence, thermogram shape and T_{max} for an individual compound can vary among different chamber studies (D'Ambro et al., 2017;Huang et al., 2018;Wang and Ruiz, 2018) and field measurements (Thompson et al., 2017;Huang et al., 2019b;Gaston et al., 2016), which could also induce uncertainties associated with volatility estimates, similar to parametrization methods.

Overall, the relationship between molecular composition-derived volatility and thermal-desorption-derived volatility is not always straight forward given the rather large uncertainties of both methods (Isaacman-VanWertz and Aumont, 2021;Voliotis et al., 2021;Masoud and Ruiz, 2021;Wu et al., 2021). Huang et al. (2019b) found consistent results of bulk volatility for OOA particles measured in Stuttgart, Germany, when using volatility parametrizations and thermograms, indicative of the connection between chemical composition and volatility. Wu

et al. (2021) found a qualitative agreement between T_{max} and C_{sat} for individual compounds of SOA particles in their chamber studies, but varying results for the bulk volatility when using different parametrizations and thermograms. Further comprehensive investigations of the relationship between volatility and chemical composition of OOA particles are warranted, particularly for ambient measurements.

In this study, we present an overview of the chemical composition of OOA and OOA volatility derived from both molecular composition measurements and thermogram analyses for a number of ambient FIGAERO-CIMS datasets ~~across the globe~~ (Chacaltaya, Bolivia; Alabama, U.S.; Hyytiälä, Finland; Stuttgart and Karlsruhe, Germany; Delhi, India). We assess how different environments (e.g., emission sources and meteorological parameters) influence the particle chemical composition and volatility derived from these two methods, discuss the reasons for differences and similarities, and the relationship between volatility and chemical composition for the different locations.

2 Methodology

2.1 Measurement sites

The measurement sites of this study are listed in Table 1. The list includes one ~~remote~~ mountain site (MCC, 16°21'00.0" S, 68°07'48.0" W), located at the GAW (Global Atmosphere Watch) high altitude research station Chacaltaya (~5240 m a.s.l.), ~25 km northeast of La Paz city (~3640 m a.s.l.), Bolivia (Bianchi et al., 2022); three rural sites, the first one located in the Rhine river valley near Eggenstein-Leopoldshafen, ~12 km north of the city of Karlsruhe, Germany (REL, 49°6′10.54″ N, 8°24′26.07″ E) (Huang et al., 2019a), the second one in the boreal forest of Hyytiälä, Finland (RHT, 61°50'47.2" N, 24°17'43.3" E) (Mohr et al., 2017;Mohr et al., 2019), and the third one located near Centreville, Alabama, United States (RAB, 33°10'48.0" N, 86°46'48.0" W) (Lopez-Hilfiker et al., 2016); and three urban sites, the first one located in a park in the city of Stuttgart, Germany (UST, 48°47′55.1" N, 9°12′13.5" E) (Huang et al., 2019b); the second one right next to a road crossing the city center of Karlsruhe, Germany (UKA, 49°00'35.0" N, 8°25'02.8" E), and the third one on a university campus in the city of Delhi, India (UDL, 28°32'48.8" N, 77°011'26.8" E). For MCC, UST, and UKA, measurements from different seasons were included to investigate the influence of seasonal variation in emission sources and/or chemistry on OOA composition and volatility. The campaign-average values for co-located measurements of meteorological parameters (temperature (T) and relative humidity (RH)), trace gases (O_3, NO_2, and SO_2), equivalent black carbon (eBC), and total non-refractory particulate mass are listed in Table S1.

Table 1. Overview of the measurement sites included in this study, their locations, and the measurement periods.

Abbreviation	Location	Measurement period	Description
MCC	Chacaltaya, Bolivia	April 9-26, 2018 (transition season); May 7-June 2, 2018 (dry season)	Mountain site
REL	near Eggenstein-Leopoldshafen, Germany	August 18-Sept. 1, 2016	Rural site
RAB	near Centreville, Alabama, U.S.	June 4-July 16, 2013	Rural site
RHT	Hyytiälä, Finland	April 11-June 3, 2014	Rural site
UST	Stuttgart, Germany	July 5-August 17, 2017 (summer); February 5-March 5, 2018 (winter)	Urban background site
UKA	Karlsruhe, Germany	June 28-July 29, 2019 (summer); February 22-March 30, 2020 (winter)	Urban curb site
UDL	Delhi, India	January 11-February 5, 2019	Urban background site

2.2 Measurements and volatility determination of OOA particles

2.2.1 Measurements of OOA particles

140   Particulate oxygenated organic compounds were measured with a FIGAERO-CIMS (Aerodyne Research Inc. or from the University of Washington (Lopez-Hilfiker et al., 2014)) using iodide (I^-) as the reagent ion. Iodide-CIMS is sensitive to more polar oxygenated organic compounds with three to eight oxygen atoms (Lee et al., 2014;Riva et al., 2019;Huang et al., 2019a). Inlet flow and residence time, particle deposition time, mass loadings on the filter, and instrumental parameters for the different campaigns are summarized in Table S2. Differences in instrumental

145   parameters such as IMR (ion molecule reaction chamber) pressure, ion source, the ratio of sample and ionizer flow, and the voltage settings of the mass spectrometer can affect the sensitivities of organic compounds and therefore their measured distribution. Here we simply use mass fractions of compounds calculated using sensitivities assumed or assessed for the individual campaigns/instruments, since the focus of this study is not to report and compare absolute mass concentrations of OOA at different locations. An in-depth analysis of the differences in

150   instrumental parameters among different campaigns, and how they affect the measured OOA composition, is beyond the scope of this paper. Data were analyzed with the software packages "tofTools" (developed by Junninen et al. (Junninen et al., 2010)) or "Tofware" (provided by Tofwerk Ltd.).

For REL, RHT, RAB, MCC, and UDL, aerosol particles were measured in-situ with the FIGAERO-CIMS (Huang et al., 2018;Mohr et al., 2019;Lopez-Hilfiker et al., 2016;Bianchi et al., 2022). Particle-phase backgrounds

155   were assessed in regular intervals by placing an additional Teflon (Polytetrafluoroethylene, PTFE) filter upstream of the normal filter and using the same deposition procedure as for the ambient measurements. These data were then used for background subtraction.

For UST and UKA, aerosol particles were deposited on Teflon filters and analyzed later in the laboratory with FIGAERO-CIMS ("offline mode"; see Table S2) (Huang et al., 2019b;Cai et al., 2023). Filters were kept frozen

160   until analysis. Deposition times were varied (see Table S2) based on ambient organic mass concentrations measured by a concurrent high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS, Aerodyne

Research Inc.) in order to achieve similar organic mass loadings on the filter and to avoid mass loading effects (Huang et al., 2018;Wang and Ruiz, 2018). A total of 21 (10) and 29 (23) filter samples were collected in summer (winter) at UST and UKA, respectively. Particle-phase backgrounds were assessed by placing prebaked clean
165 filters in the filter holder at the measurement sites with the deposition flow switched off. These field blank samples were also analyzed by FIGAERO-CIMS in the laboratory like the samples and used for background subtraction.

2.2.2 Volatility determination of OOA particles

OOA volatility was determined for all sites based on FIGAERO-CIMS thermograms and C_{sat} parametrizations. Different temperature ramp rates affect T_{max} (Schobesberger et al., 2018;Yang et al., 2021;Ylisirniö et al.,
170 2021;Thornton et al., 2020). The ramp rates for all measurements shown here varied between 6.7 and 13.3 ºC/min (see Table S2), inducing a T_{max} difference of up to 5 ºC (Schobesberger et al., 2018;Ylisirniö et al., 2021;Thornton et al., 2020). Since for most locations no calibrations of the relationship between T_{max} and C_{sat} are available (Wang et al., 2020;Ylisirniö et al., 2021), we present and discuss here only relative variations in thermogram shapes and T_{max}, including the variations caused by different ramp rates, and compare them qualitatively to the variation in
175 C_{sat} determined from parametrization.

C_{sat} (298 K) was calculated ~~for all sites~~ using the approach by Li et al. (2016) as in equation (1) for all sites in order to not introduce more bias:

$$\log_{10} C_{sat} (298 \text{ K}) = (n_C^0 - n_C) \times b_C - n_O \times b_O - 2 \times \frac{n_C \times n_O}{(n_C + n_O)} \times b_{CO} - n_N \times b_N - n_S \times b_S \tag{1}$$

where n_C, n_O, n_N, and n_S are the number of carbon, oxygen, nitrogen, and sulfur atoms in the organic compound,
180 respectively; n_C^0 is the reference carbon number; b_C, b_O, b_N, and b_S are the contribution of each atom to $\log_{10} C_{sat}$, respectively; b_{CO} is the carbon–oxygen nonideality (Donahue et al., 2011). Since the empirical approach by Li et al. (2016) was derived with very few organonitrates, we modified the C_{sat} (298 K) of CHON compounds by treating all NO_3 groups like OH groups following the approach by Daumit et al. (Daumit et al., 2013;Isaacman-VanWertz and Aumont, 2021). A recent study however found that the parametrization of C_{sat} for nitrate groups is highly
185 uncertain (Graham et al., 2023). Even for different biogenic terpene+NO_3 systems, none of the four parametrizations Graham et al. (2023) investigated performed perfectly for all systems, as parametrizations which are developed based on different datasets comprising different compounds with different functionalities can yield different results for the same dataset (e.g., Graham et al., 2023). For example, the Mohr et al. (2019) parametrization method, which was tuned for -OOH functional groups, was found to work better for α-pinene+O_3
190 system and thus it was speculated that the α-pinene+O_3 system has more -OOH functional groups. The Daumit et al. (2013) parametrization method, which assumes all oxygen atoms except those from -NO_3 are from -OH and =O functional groups, was found to work better for α-pinene+NO_3 system and thus the α-pinene+NO_3 system is speculated to have more -OH and =O groups (Graham et al., 2023). These results underline again the complexity (and with that also the limitations) of assessments of the volatility (especially at the quantitative level) through
195 parametrizations using the molecular composition as input, as already shown for laboratory measurements (Graham et al., 2023), and even more so for complex ambient data from different locations and periods.

We also adjusted the C_{sat} (298 K) to the measured ambient temperature, C_{sat} (T), using the approach by Donahue et al. (2011) and Epstein et al. (2010) as in equations (2) and (3):

$$\log_{10} C_{\text{sat}}(T) = \log_{10} C_{\text{sat}}(298 \text{ K}) + \frac{\Delta H_{\text{vap}}}{R\ln(10)} \times \left(\frac{1}{298} - \frac{1}{T}\right), \tag{2}$$

$$\Delta H_{\text{vap}}(\text{kJ mol}^{-1}) = -11 \times \log_{10} C_{\text{sat}}(298 \text{ K}) + 129 \tag{3}$$

where T is the temperature in Kelvin; C_{sat} (298 K) is the saturation mass concentration at 298 K; ΔH_{vap} is the vaporization enthalpy; and R is the gas constant (8.3143 J K^{-1} mol^{-1}). We have added a comparison of the results from using the parametrization by Donahue et al. (2011) (Figure S1a) if making a simple assumption about predominant aliphatic/aromatic OOA at urban sites in winter (i.e., UST-w, UKA-w, and UDL) and predominant isoprene OOA in MCC-t and RAB (Nie et al., 2022). The $\log_{10}C_{\text{sat}}$ (T) shows a similar trend for both parametrizations; however, the C_{sat} (T) using the Donahue et al. (2011) parametrization is on average 4 to 8 orders of magnitude lower, with the largest difference for UKA-w and smallest for UDL (Figure S1b). The discrepancies seem to be correlated with the average number of oxygen atoms (nO) in the bulk aerosol of the different environments (Pearson's R: 0.85; Figure S1b), confirming the influence of different functional groups on parametrization results. Our discussion of volatility results in this study is therefore mostly qualitative.

3 Results and discussion

3.1 Bulk molecular composition of OOA particles

3.1.1 Average number of carbon and oxygen atoms and oxygen-to-carbon ratios

We focus our analysis of the bulk molecular composition of OOA from the different locations here on the average number of carbon (nC) and oxygen atoms (nO) as they affect the parametrized C_{sat}, and ~~also could be used to indicate~~give an indication of potential precursor sources (Huang et al., 2019a) and oxidation processes, respectively. Figure 1a shows the average mass-weighted nO vs. nC for all compounds with the molecular formula $C_{x\geq1}H_{y\geq1}O_{z\geq1}X_{0-n}$ (CHOX; X are different atoms such as N, S, Cl, or a combination thereof) measured by FIGAERO-CIMS for each campaign. The markers are color-coded by the average mass-weighted oxygen-to-carbon (O:C) ratios. The observed average nC and nO range from 7.7 to 11.2 and from 4.9 to 7.1, respectively. There is an overall trend of increasing nO with increasing nC (Figure 1a), with the spring-time OOA at the rural station Hyytiälä, Finland (RHT), and the wintertime OOA at the urban station Delhi, India (UDL) deviating from that general trend (see discussions below). The overall trend shows the effect of the length of carbon backbone on the number of potential oxygen atoms that can be added to the carbon chain (Huang et al., 2019a).

Generally, at the urban sites, OOA particles exhibit on average larger nC (9.8±0.7; average ± 1 standard deviation) compared to the rural (8.8±0.6) and mountain stations (8.1±0.8), indicative of different emission sources and OOA precursors (Huang et al., 2019b).

At the ~~remote~~ mountain site Chacaltaya, Bolivia, OOA has a relatively longer carbon backbone (nC: 8.4±0.8) in the transition season (MCC-t) than in the dry season (MCC-d, nC: 7.7±0.7). The air masses arriving at Chacaltaya present a diverse mixture from various sources, which vary significantly between the transition and the dry seasons (Aliaga et al. 2021). While air masses arriving at Chacaltaya during the dry season are more affected by volcanic SO$_2$ emissions as well as ~~the~~ anthropogenic ~~sources~~ compounds such as toluene (also seen in the slightly higher contributions of C$_7$ compounds in Figure S2) (Bianchi et al., 2022;Zha et al., 2023b), air masses

reaching Chacaltaya during the transition season have more influence from ~~e.g.~~ the Amazon Basin (Aliaga et al.,

235   2021;Zha et al., 2023b)~~,; and~~ hence~~,~~ a higher contribution of monoterpene ($C_{10}H_{16}$) and especially isoprene (C_5H_8) oxidation products ~~are~~ is expected (also reflected in the clear peak of C_5 compounds and the second hump of C_{8-10} compounds in Figure ~~S1~~S2) (Zha et al., 2023a).

Rural Alabama in U.S. (RAB) and rural Hyytiälä in Finland (RHT), which are both forested stations albeit in different biomes, show respective OOA composition with nC of 8.0±0.4 at RAB and 9.1±0.6 at RHT. This is likely

240   due to the different distributions of terpene emissions with more isoprene at RAB (Lopez-Hilfiker et al., 2016;Lee et al., 2016) and mostly monoterpenes at RHT (Li et al., 2020;Huang et al., 2021). It is also seen in the higher contributions of C_{8-10} compounds for RHT, and comparable contributions of C_5 and C_{8-10} compounds for RAB (Zhang et al., 2018;Massoli et al., 2018) (Figure ~~S1~~S2). The third rural site, REL, which is situated at a location with substantial anthropogenic as well as biogenic influence dominated by monoterpene emissions (Huang et al.,

245   2019a), has a comparable nC (9.2±0.8) to RHT and again shows a relatively higher contributions of C_{8-10} compounds (Figure ~~S1~~S2).

For the urban sites, the curb site in Karlsruhe, Germany (UKA) has a larger nC (summer: 10.7±0.8; winter: 11.2±0.8) compared to the urban background site in the nearby city of Stuttgart (UST, summer: 8.8±0.4; winter: 8.7±0.9). The nC for wintertime Delhi in India (UDL, 9.4±0.4) is between that of UKA and UST. Such differences

250   are likely due to the UKA and UDL measurement locations being more directly impacted by traffic emissions (Kumar et al., 2022) with higher contributions of larger aromatic compounds (Zheng et al., 2017;Lim et al., 1999). This is substantiated by the observed elevated contributions of C_{11-18} compounds (Figure ~~S1~~S2) and higher DBE (double bond equivalent) values (Table S1). In addition, all three urban sites, despite their very different locations, show a similar seasonal pattern, with higher contributions of C_{8-10} compounds in summer from biogenic emissions,

255   and higher contributions of C_6 compounds (e.g., levoglucosan, $C_6H_{10}O_5$) in winter due to biomass burning emissions (Figure ~~S1~~S2) (Huang et al., 2019b;Kumar et al., 2022).

Whereas the nC values may give some indication of OOA precursor emission sources, the average nO and O:C ratios are linked to different aging processes and/or varying distance from the sources (Jimenez et al., 2009). The urban stations exhibit on average the lowest O:C ratios (0.76±0.03), compared to the rural (0.80±0.05) and ~~remote~~

260   mountain stations (0.91±0.07).

OOA particles during the transition season at the mountain site Chacaltaya, Bolivia (MCC-t), have relatively larger nO (6.2±0.3), but slightly lower O:C ratio (0.89±0.08) compared to the dry season (MCC-d; nO: 5.8±0.3; O:C: 0.94±0.05). For two of the rural stations (RAB in the southeastern U.S. and RHT in Finland), nO is comparable (RAB: 5.7±0.2; RHT: 5.7±0.3), but O:C is slightly higher at RAB (0.81±0.04; RHT: 0.77±0.05). This

265   may again be due to the difference in dominating terpene sources (isoprene for RAB (Lopez-Hilfiker et al., 2016) and monoterpenes for RHT (Li et al., 2020); also reflected in Figure ~~S1~~S2). The third rural site, REL in Germany (during summertime with substantial anthropogenic and biogenic influence) (Huang et al., 2019a), has higher nO (6.6±0.5) and O:C (0.83±0.06) compared to RAB and RHT, despite the fairly large nC (9.2±0.8). This could be related to more intense photochemistry/oxidation with higher temperature and/or solar radiation at this site (Table

270   S1). Lower temperature and solar radiation could also be the reason for RHT deviating from the general trend of nO and nC in Figure 1a.

The urban sites in Germany (Karlsruhe, UKA, and Stuttgart, UST) have similar nO in summer and in winter (UKA: summer: 7.0±0.4; winter: 7.1±0.4; UST: summer: 6.4±0.2; winter: 6.7±0.2). In comparison, nO for the winter Delhi site (UDL) is 4.9±0.1 due to the dominance of primary OA (Kumar et al., 2022), resulting in its

deviation from the general trend of nO and nC (Figure 1a). Besides, O:C ratios are lower for UKA (summer: 0.73±0.02; winter: 0.73±0.04) and UDL (0.66±0.02) compared to UST (summer: 0.82±0.02; winter: 0.89±0.06), which relates back to its larger nC (see Figure 1a) as a result of its high proximity to traffic emissions (Kumar et al., 2022) with more larger aromatic compounds (Lim et al., 1999;Zheng et al., 2017) (see discussions above and Figure S1S2). Despite the influence of different OOA sources in summer and winter (biogenic emissions vs. biomass burning contributions) for both German urban sites UKA and UST (Huang et al., 2019b), only UST exhibits higher O:C ratios in winter than summer. This could be due to the complex topography of the city of Stuttgart, resulting in stronger surface temperature inversions and consequently longer aging time of air masses (Huang et al., 2019b;Baumbach and Vogt, 2003).
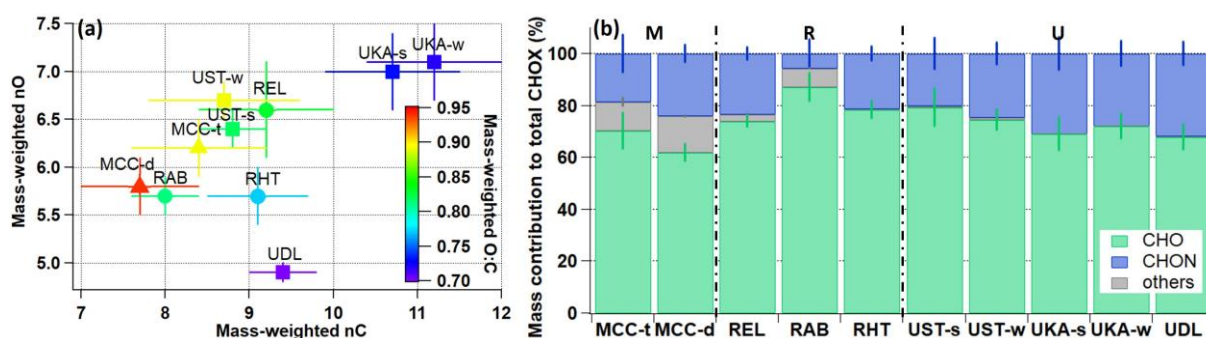
Figure 1. (a) Campaign-average mass-weighted number of oxygen atoms (nO) vs. number of carbon atoms (nC) at the different locations and seasons (Mountain sites in triangles, Rural sites in circles, and Urban sites in squares; for a list of nC and nO values see Table S1), with the markers colored by the corresponding campaign-average mass-weighted oxygen-to-carbon (O:C) ratios; **(b)** Campaign-average mass contributions of organic compounds (separated into CHO, CHON, and other compounds) for the different campaigns (M = mountain sites, R = rural sites, U = urban sites) and seasons (s = summer, w = winter, t = transition, d = dry).

3.1.2 Mass contribution of organonitrates

The presence of NO_x during the oxidation of volatile organic compounds (VOC) can lead to the formation of organonitrates, either via reactions with peroxy radicals or formation of NO_3 radicals acting as VOC oxidants, and influence SOA yields and properties of OOA (D'Ambro et al., 2017;Ng et al., 2007;Faxon et al., 2018;Wu et al., 2021). Organonitrates have been found to make up an important fraction of total OA particle mass globally (Kiendler-Scharr et al., 2016;Huang et al., 2019a;Lee et al., 2018). Due to their connection to emissions from fossil fuel burning, they can be indicators of the anthropogenic influence of a particular location. To a lesser extent, also lightning is a source of atmospheric NO_x (Murray, 2016). Here we simply group all organic compounds containing at least one nitrogen atom (CHON) and loosely define them as organonitrates (Lee et al., 2016;Huang et al., 2019a). Compounds containing only carbon, hydrogen, and oxygen atoms are grouped as CHO.

Average mass contributions of CHO and CHON for the different locations are shown in Figure 1b. Overall, CHO compounds clearly dominate the OOA mass at all locations (62.0–87.1%). CHO contributions are on average higher at the rural sites (79.9±5.2%) compared to the mountain (66.2±5.5%) and urban sites (72.6±4.3%), in accordance with their proximity to forested areas. The nitrogen-containing compounds (CHON) contribute 18.7–31.8% to the total OOA mass, except . A low CHON fraction is observed at the rural station in southeastern U.S. (RAB; 5.6±2.6%). This low contribution could be possibly due to the less efficient production rates of CHON

and/or their faster loss rates caused by hydrolysis under the high RH conditions there (83.1±15.2%; Table S1) (Lee et al., 2020;Hu et al., 2011;Lee et al., 2016;Pye et al., 2015). At the mountain site Chacaltaya, Bolivia, CHON contributes more (23.9±4.1%) in the dry season (MCC-d) than in the transition season (MCC-t, 18.7±5.9%), as a result of enhanced transport of anthropogenic pollutants from the nearby La Paz–El Alto metropolitan area during the daytime in the dry season (Bianchi et al., 2022;Aliaga et al., 2021;Zha et al., 2023b). As expected, the largest contributions of CHON compounds are found at the urban stations (27.1±4.3%), coinciding with their higher NO_x levels (15.8±8.7 ppbv; Table S1), but overall, differences between stations and seasons are small.

The compounds labelled as "others" in Figure 1b are mostly identified as CHOS or CHONS compounds, making up 0.1–14.1% of the total OOA mass. Sulfur-containing compounds exhibit non-negligible contributions for MCC, REL, and RAB. This is likely due to varying sources for these locations: The mountain site in Bolivia (MCC) was influenced by volcanic emissions during the campaign (Bianchi et al., 2022), the rural sites in central Europe (REL) and southeastern U.S. (RAB) by nearby refineries and/or power plants (Huang et al., 2019a;Fry et al., 2018).

3.2 Volatility of OOA particles

3.2.1 Volatility derived from molecular composition

For each campaign we calculated C_{sat} (T) for each compound based on its molecular composition (see more details in section 2.2.2) (Donahue et al., 2011;Isaacman-VanWertz and Aumont, 2021;Li et al., 2016;Mohr et al., 2019) and grouped all compounds into a 25-bin VBS (volatility basis set; Figure S2S3) (Donahue et al., 2011;Donahue et al., 2012). The 25 volatility bins were then further aggregated into extremely low-volatile organic compounds (ELVOC, C_{sat} (T) lower than $10^{-4.5}$ µg m^{-3}), low-volatile organic compounds (LVOC, C_{sat} (T) between $10^{-4.5}$ and $10^{-0.5}$ µg m^{-3}), semi-volatile organic compounds (SVOC, C_{sat} (T) between $10^{-0.5}$ and $10^{2.5}$ µg m^{-3}), and intermediate-volatility organic compounds (IVOC, C_{sat} (T) between $10^{2.5}$ and $10^{6.5}$ µg m^{-3}) (Donahue et al., 2009). The average contributions of different volatility groups to total OOA are shown in Figure 2, together with the average mass-weighted $\log_{10}C_{sat}$ (T). Note that the bulk apparent volatility of OOA particles, i.e., average mass-weighted $\log_{10}C_{sat}$ (T), which represents the overall observed $\log_{10}C_{sat}$ (T) of the OOA as a whole (D'Ambro et al., 2018), is different from the $\log_{10}C_{sat}$ (T) and volatility of the (pure) compounds detected.

We find that the more volatile species with C_{sat} (T) between 10^0 and 10^4 µg m^{-3} make up the biggest mass contributions at all locations (47.7–83.8%); LVOC and ELVOC contribute substantially (13.4–42.1%; Figure 2 and S2S3). In general, the VBS distribution pattern does not seem to have huge differences across different systems and environments, despite that a large (though not all) fraction of OOA can be detected by iodide-CIMS (Riva et al., 2019;Huang et al., 2021). Whereas LVOC and ELVOC may be important for the early stages of atmospheric new particle formation, they certainly do not dominate the OOA mass. Note that thermal decomposition of larger organic compounds during particle desorption with the FIGAERO could contribute, in particular, to the IVOC fraction (Huang et al., 2019b;Lopez-Hilfiker et al., 2016). Resolving and subtracting the thermal decomposition compounds using multi-peak fitting methods (Lutz et al., 2019) or with the help of positive matrix factorization (Buchholz et al., 2020) may, however, introduce uncertainties due to some ambiguity during the implementation and interpretation (Graham et al., 2023;Voliotis et al., 2021). Using the thermal decomposition estimation approach by Wu et al. (2021) the decomposition fraction is estimated to be 5.8–35.9% (see more discussions below), which is close to the reported thermal fragmentation contributions (1–27%) for nitrate SOA in a recent chamber study

(Graham et al., 2023). This has ~~however~~ an insignificant effect on the bulk molecular composition of OOA particles, ~~which is~~and e.g. within the corresponding standard deviation range of nC, nO, and O:C ratios. If we remove the fraction of signal from potential decomposition products (which is still not ideal), the change in C_{sat} is within the uncertainties of the parametrization method (Isaacman-VanWertz and Aumont, 2021). However, please note that the decomposition estimation approach we used in our study was initially used for controlled laboratory studies by Wu et al. (2021), and thus remains a conservative approach for ambient particle matrix with complex VOCs.

The mountain site in Bolivia exhibits slightly higher contributions from the more volatile species (i.e., IVOC) in the dry season (MCC-d, 31.2±3.9%) compared to the transition season (MCC-t, 20.0±5.0%). Consistently, also the average mass-weighted $\log_{10}C_{sat}$ (T) value is higher for MCC-d (0.58±0.35 µg m^{-3}) than MCC-t (-0.18±0.43 µg m^{-3}). In addition to the higher thermal decomposition contribution for MCC-d (~34.3%) compared to MCC-t (~26.3%), higher contributions of CHON and sulfur-containing organic compounds during the dry season (see also Figure 1b) could also play a role (Peräkylä et al., 2020). Even though the addition of a NO_3 functional group is assumed to decrease a compound's vapor pressure by up to several orders of magnitude (Donahue et al., 2011;Graham et al., 2023;Pankow and Asher, 2008), CHON compounds with the same nC and nO as a CHO compound (e.g., $C_{10}H_{15}NO_7$ vs. $C_{10}H_{16}O_7$), are expected to have a higher vapor pressure (Donahue et al., 2011;Lee et al., 2018;Pankow and Asher, 2008). Different origin of air masses and hence atmospheric processing time and chemistry may be another reason for the slight differences in OOA volatility between the seasons (Aliaga et al., 2021;Bianchi et al., 2022).

Among the rural sites in Germany (REL), Finland (RHT), and southeastern U.S. (RAB), RAB shows the highest volatility (IVOC: 49.2±4.9%; ELVOC: 2.4±1.3%; $\log_{10}C_{sat}$ (T): 2.0±0.4 µg m^{-3}) compared to REL (IVOC: 38.8±6.3%; ELVOC: 12.5±5.4%; $\log_{10}C_{sat}$ (T): 0.67±0.67 µg m^{-3}) and RHT (IVOC: 32.7±6.1%; ELVOC: 5.5±2.1%; $\log_{10}C_{sat}$ (T): 1.0±0.5 µg m^{-3}). RAB is the southernmost station of all rural sites, with the highest RH (also temperature; Table S1) and high emissions of isoprene, and thus the reactive uptake of IEPOX (isoprene-epoxydiol) in aqueous aerosol is likely a more important SOA pathway compared to REL and RHT. This result again shows that the interpretation of OOA volatility derived from molecular composition is complex, and warrants careful consideration of various parameters (Graham et al., 2023;Voliotis et al., 2021).

The urban site in Delhi, India (UDL) exhibits the lowest LVOC and lowest ELVOC mass fractions (13.4% in total), highest IVOC mass fractions (54.5±3.4%) and mass-weighted $\log_{10}C_{sat}$ (T) values (2.3±0.3 µg m^{-3}; also consistent with its lowest O:C ratios, see Figure 1a), compared to the two urban sites in Germany (UKA: LVOC+ELVOC: 18.4–42.1%; IVOC: 20.5–42.8%; $\log_{10}C_{sat}$ (T): -0.37–1.6 µg m^{-3}; UST: LVOC+ELVOC: 27.9–41.9%; IVOC: 23.8–32.5%; $\log_{10}C_{sat}$ (T): -0.50–0.63 µg m^{-3}). The relatively higher volatility of OOA in Delhi compared to that in the German cities may be likely related to the dominance of primary OA with very high biomass burning (also reflected in the large peak of C_6 compounds in Figure ~~S1~~S2) and traffic emissions (Kumar et al., 2022). The biomass burning vapors have been found to be responsible for the nighttime particle growth at UDL (Mishra et al., 2023). As for UKA and UST, higher LVOC and ELVOC mass fractions (41.9–42.1%) and lower mass-weighted $\log_{10}C_{sat}$ (T) values (-0.50--0.37 µg m^{-3}) are observed in winter compared to summer (18.4–27.9% and 0.63–1.6 µg m^{-3}, respectively), indicating that the bulk winter OOA is less volatile. Similar results were also observed in Zurich, Switzerland based on AMS data (Canonaco et al., 2015). Higher O:C ratios (Figure 1a) could be part of the reason for the less volatile OOA in winter in Stuttgart (UST) compared to summer (Huang et al., 2019b). For the Karlsruhe curb site (UKA), the O:C ratios are quite similar for winter and summer (Figure 1a) and therefore other factors, such as the relatively higher contributions of larger molecules (nC >16; Figure ~~S1~~S2)

as well as the reduced volatility of OOA from biomass burning due to aging processes (Keller and Burtscher, 2017) (see also the higher O:C ratios in Figure 1a compared to UDL with more primary emissions (Kumar et al., 2022)), might play a role.
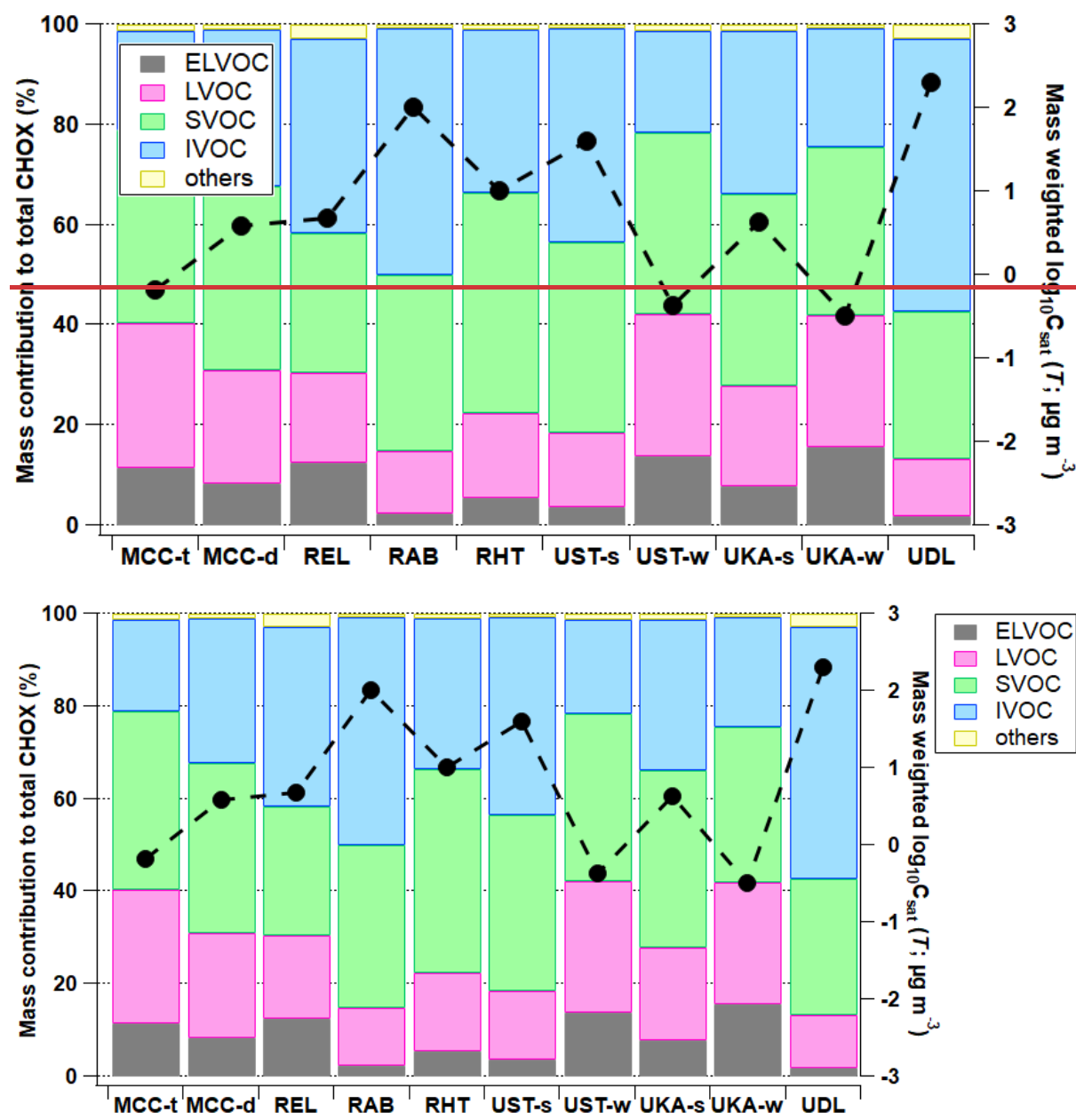
Figure 2. Campaign-average contribution (%) to total organics of different volatility groups resulting from VBS calculations (colored in bars) and campaign-average mass-weighted $\log_{10}C_{sat}$ (T) values (in black markers) for different campaigns with the modified Li et al. (2016) parametrization method (Daumit et al., 2013; Isaacman-VanWertz and Aumont, 2021). Compounds more volatile than IVOC with C_{sat} (T) higher than $10^{6.5}$ µg m^{-3} (labelled as "others") contributed negligibly (0.8−2.9%).

The mass-weighted $\log_{10}C_{sat}$ (T) shows a qualitatively similar distribution as the ambient temperature (Pearson's R: 0.58; Figure S3 S4 and S4S5). This makes sense insofar as on the one hand the $\log_{10}C_{sat}$ (T) calculated using molecular composition is shifted based on ambient temperature (compare Eq. 2) - the same compound exhibits a higher apparent volatility under warmer conditions and vice versa; on the other hand, a higher apparent

volatility is also expected at higher ambient temperatures due to higher local emissions of biogenic precursors. In addition, we find a positive correlation between $\log_{10}C_{sat}$ (T) and humidity (Pearson's R for RH and absolute humidity: 0.57 and 0.68, respectively; Figure S4S5), indicating potential hydrolysis effects on OOA particles (forming smaller and more volatile compounds) caused by potentially high aerosol liquid water content at higher humidity levels (Lee et al., 2020;Hu et al., 2011;Hinks et al., 2018). Negative correlations are found between $\log_{10}C_{sat}$ (T) vs. nO (Pearson's R: -0.72) and the average mass-weighted molecular weight (MW) of CHOX compounds (Pearson's R: -0.56), following the parametrization assumption of the oxidation effect on volatility and of lower volatility for larger and complex molecules (Donahue et al., 2011).

3.2.2 Volatility derived from thermograms

We further investigate the volatility derived from FIGAERO thermograms qualitatively for the different sites and compare it to the volatility derived from the molecular composition measurements. It is important to note that, similar to D'Ambro et al. (2018), the term "volatility" we discuss here refers to the effective volatility of bulk OOA particles, which combines the impacts of diffusion limitations and thermal decomposition of lower-volatility species. We focus the bulk OOA volatility analysis here on the shape and distribution of sum thermograms, which are found to give representative qualitative volatility estimations as they take into account the whole signal distribution and reduce potential artefacts from thermal decomposition of individual compounds (Voliotis et al., 2021).

Campaign-average sum thermograms of CHOX compounds (i.e., the sum of mass spectral signal evolution of all CHOX compounds as a function of desorption temperature) for the different locations are shown in Figure 3, normalized to their maximum values. Sum Tthermogram shapes vary for different environments, and they exhibit maximum signal at temperatures (sumT_{max}) ranging from 80.5 to 146.3 °C (see also Figure S5S6). Such differences of sumT_{max} of >60 °C across different systems and environments are hardly surprising, given the large spread in T_{max} for all compounds in one single mass spectrum (Huang et al., 2019b;Wang and Ruiz, 2018), in T_{max} calibrations with different instrumental settings, experimental procedures or calibrants (Wang et al., 2020;Ylisirniö et al., 2021), as well as for one compound with the same molecular formula between day vs. night (Thompson et al., 2017;Gaston et al., 2016), field vs. laboratory (Thompson et al., 2017), or over a whole campaign period using the same instrument and operating conditions (Thompson et al., 2017) (see an example of $C_6H_{10}O_5$, the molecular formula corresponding to levoglucosan, in Figure S6S7). However, T_{max} variation due to different instruments or operating conditions is generally smaller than that from the difference in monomers and dimers (Wu et al., 2021) and other factors like the presence of isomers (Thompson et al., 2017;Masoud and Ruiz, 2021) and particle-phase diffusivity, viscosity and matrix effects (Huang et al., 2018;Ren et al., 2022). Different FIGAERO geometry was speculated to not induce significant T_{max} changes (Ylisirniö et al., 2021). The ramp rates for all measurements shown in the present study varied between 6.7 and 13.3 °C/min (see Table S2), inducing a T_{max} difference of maximum 5 °C (Schobesberger et al., 2018;Ylisirniö et al., 2021;Thornton et al., 2020). Correction of the T_{max} values to a filter mass loading of 1 µg following our approach outlined earlier (Huang et al., 2018) only leads to a T_{max} change of <5 °C. It is also worth noting that thermal decomposition of larger organic compounds during particle desorption with the FIGAERO could form products with lower masses and lower T_{max} values, and hence higher effective volatility. Although the calculated decomposition fraction has a minor effect on the molecular composition of OOA particles (see more details in section 3.2.1), the contribution of fragments to their parent compounds and the impact on the "original" volatility should not be ignored.

The mountain site in Bolivia in the transition season (MCC-t) exhibits some of the lowest sumT$_{max}$ values of all stations (81.7 °C), indicating relatively higher bulk volatility. In contrast, during the dry season, the bulk OOA appears less volatile (MCC-d sumT$_{max}$: 107.7 °C). This trend is in disagreement with $\log_{10}C_{sat}$ (T), which is higher for MCC-d (i.e. higher volatility) than MCC-t. The discrepancy could be due to thermal fragmentation of larger oligomeric molecules, which bias the C_{sat} results towards higher volatilities and the sum thermogram shape to a lesser extent due to the dominance of monomer species (i.e., ending up with a "tail"). Compared to MCC-t (~26.6%), MCC-d exhibits a higher contribution of thermal fragmentation (~35.9%; also reflected in the higher IVOC fractions in Figure 2a), with multi-mode thermograms showing elevated signals at high desorption temperatures (~150 °C), i.e., with long "tails" (see also Figure S~~5~~6a–b).

The rural sites in Germany (REL) and southeastern U.S. (RAB) have similar sumT$_{max}$ values of ~100°C. Both also show contributions (up to 21%) from thermal fragmentation through multi-mode thermograms or long tails at high desorption temperatures (~150 °C; see also Figure S~~5~~6c–d; similar to the dry season for the mountain site MCC-d). The lowest sumT$_{max}$ value (94.5 °C) at RAB is consistent with its highest average $\log_{10}C_{sat}$ (T) value (2.0±0.4 µg m^{-3}) among the rural stations. The rural site in Finland (RHT) exhibits a high sumT$_{max}$ value of 146.3 °C with a thermogram shape reaching a plateau after 120 °C and the signal only starting to decrease at a desorption temperature >180 °C (see also Figure S~~5~~6e). This might be related to an older age (D'Ambro et al., 2018) and/or a more viscous phase state of the OOA particles at RHT caused by its lowest temperature and RH of all rural stations (Table S1) (Shiraiwa et al., 2011), affecting the evaporative behavior and inferred volatility of the particle-bound compounds (Yli-Juuti et al., 2017;Huang et al., 2018).

The urban sites in Germany (UKA and UST) exhibit similar trends in sumT$_{max}$, with relatively higher values in winter (106.1–112.5 °C) compared to summer (80.5–102.0 °C). Such a seasonal trend is mirrored in their average $\log_{10}C_{sat}$ (T) values. Differences in sumT$_{max}$ between summer and winter are found to be larger for Stuttgart (UST; ~32 °C) than for Karlsruhe (UKA; ~4 °C). This could be due to the differences in measurement environments and topography. The topography at UST prevents dispersion (Huang et al., 2019b;Baumbach and Vogt, 2003), and thus the formation of more oxygenated molecules in winter at UST can be expected due to longer residence time of the air masses (Buchholz et al., 2019) (also reflected in the higher O:C ratios; see Figure 1a). The UKA site is a curb site with more influence from direct traffic emissions (Kumar et al., 2022) including larger aromatic compounds (Lim et al., 1999;Zheng et al., 2017) (see above-mentioned discussions and Figure S~~1~~S2), and smaller differences for summer vs. winter are therefore expected. The winter Delhi site in India (UDL) exhibits a similar sumT$_{max}$ value (113.0 °C) as UST and UKA in winter (106.1–112.5 °C). All three urban locations show indication of substantial contribution (up to 14%) of thermal fragmentation in their thermograms (see also Figure S~~5~~6f–j), which might also be the reason for the highest sumT$_{max}$ value not corresponding to the lowest $\log_{10}C_{sat}$ (T) value, similar to MCC.

As shown in earlier publications (Huang et al., 2018;Ylisirniö et al., 2021), the connection between T$_{max}$ and volatility is complex, and direct relationships between T$_{max}$ and vapor pressures can only be established for solutions of pure or few compound(s) (Wang et al., 2020;Ylisirniö et al., 2021;Ren et al., 2022). For the complex ambient particle matrix, other factors than the pure compounds' vapor pressures come into play, such as the presence of isomers with different vapor pressures (Thompson et al., 2017), thermal decomposition contributions of larger molecules (Lopez-Hilfiker et al., 2015), and matrix effects and viscosity (Huang et al., 2018;D'Ambro et al., 2017;Wang and Ruiz, 2018) even for same compounds in solutions mixed with different species (Ren et al., 2022). This is exemplified here showing varying T$_{max}$ values for compounds with the same molecular formula

across different campaigns (with an average T_{max} difference of 55.0±24.3 °C), such as $C_5H_{12}O_4$ (molecular formula corresponding to 2-methyltetrol, a tracer of isoprene oxidation products (D'Ambro et al., 2019)), $C_6H_{10}O_5$ (molecular formula corresponding to levoglucosan, a tracer for biomass burning (Saarnio et al., 2010)), $C_8H_{10}O_5$ (identified in the laboratory as a monoterpene oxidation product (Hammes et al., 2019)), $C_8H_{12}O_5$ (molecular formula corresponding to 2-hydroxyterpenylic acid identified in α-pinene SOA (Claeys et al., 2009)), $C_{10}H_{15}NO_7$ (identified in the laboratory as a monoterpene oxidation product (Boyd et al., 2015;Faxon et al., 2018)), and $C_{17}H_{24}O_6$ (identified in the laboratory as a monoterpene oxidation product (Kenseth et al., 2020); Figure ~~S7~~S8). Such variation~~s~~ may be due to actual changes in effective volatilities of the observed OOA components, due to experimental factors, or both. ~~For example, correction of the T_{max} values to a filter mass loading of 1 µg following our approach outlined earlier (Huang et al., 2018) only leads to a T_{max} change of <5 °C, which is not enough to explain the T_{max} differences alone.~~ However, as we discussed earlier, T_{max} variation due to different instruments or operating conditions is generally smaller compared to those due to changes in physico-chemical properties. Therefore, the relative variations in thermogram shapes and T_{max} we present and discuss here in our study are dominated by the presence of isomers (Thompson et al., 2017;Masoud and Ruiz, 2021) and particle-phase diffusivity, viscosity and matrix effects (Huang et al., 2018;Ren et al., 2022). Due to unavailable calibrations of the relationship between T_{max} and C_{sat} (Wang et al., 2020; Ylisirniöet al., 2021) for most locations, ~~We conclude that~~ the analysis and interpretation of OOA volatility based on FIGAERO-CIMS thermograms is challenging and, in the absence of additional constraints on OOA composition and thermal behavior, currently remains at the qualitative level (Graham et al., 2023;Voliotis et al., 2021), especially for complex field data.

Similar to $\log_{10}C_{sat}$ (T), we also compare the $\text{sum}T_{max}$ with various environmental and measurement parameters (Figure ~~S8~~S9). Correlations of $\text{sum}T_{max}$ values with other parameters (e.g., meteorology, trace gases) are weak (Pearson's R within ±0.3)~~, except for SO₂ (Pearson's R: 0.67). However, this could be artificial as SO₂ would not react/condense directly onto aerosol particles and also too few SO₂ data points were available for this correlation (see also Table S1). Levels of sulfur-containing organics (CHOS and CHONS) and non-refractory particulate sulfate show no correlations with $\text{sum}T_{max}$ values as well~~. These results further show the complexity in assessing the effective volatility derived from thermogram behavior and T_{max}, especially for a diverse set of field data. Contributing to the lack of clear correlations in this analysis may be potential effects of experimental parameters on the FIGAERO thermograms (Table S2) (Thornton et al., 2020), as well as open questions in their interpretation, as noted above.
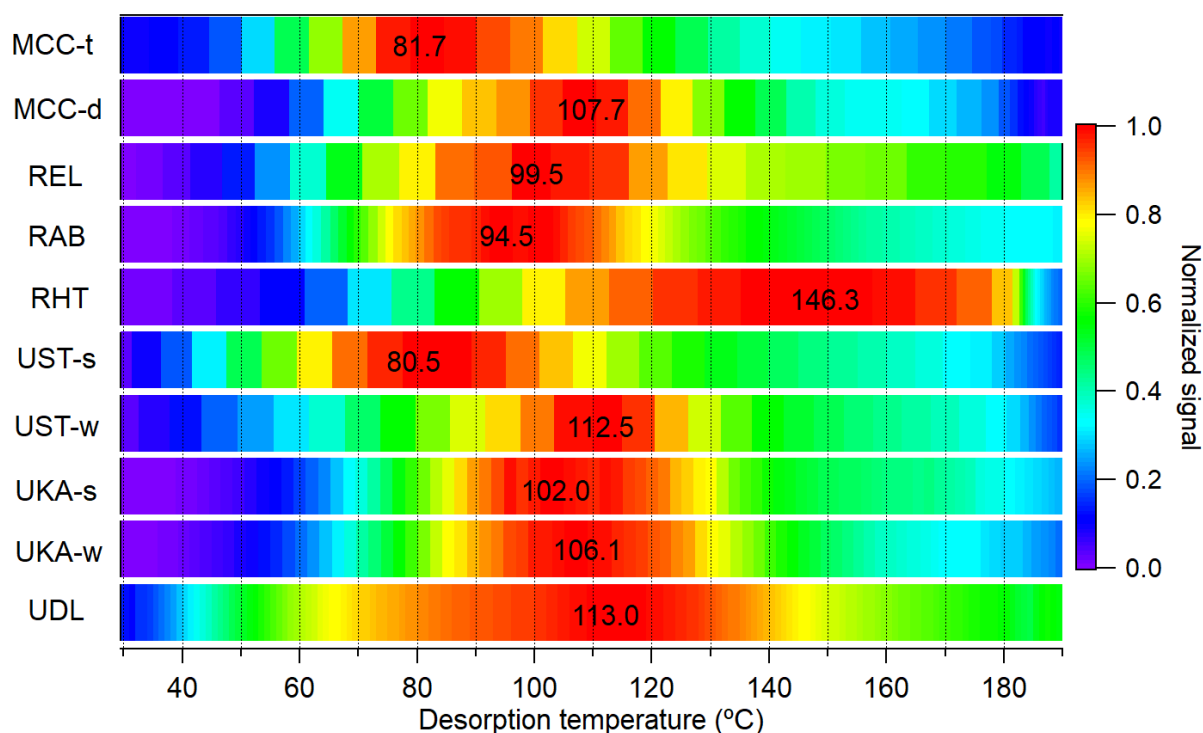
Figure 3. Campaign-average sum thermograms of CHOX compounds (normalized to their maximum values) for all campaigns with corresponding sumT$_{max}$ values labeled on the plot.

3.3 Relationship between thermal desorption-derived volatility and molecular composition-derived volatility

In order to investigate whether there is consistency in the bulk OOA volatility derived from molecular composition and thermograms, we compare the average $\log_{10}C_{sat}$ (i.e, molecular composition-derived volatility) with the sumT$_{max}$ (i.e., thermal desorption-derived volatility) in Figure 4 and Figure ~~S9~~S10. The gray area covers the previously reported calibration fit curves of $\log_{10}C_{sat}$ (298 K) vs. calibrant T$_{max}$ values in colored dashed lines. The As we can see from Figure 4, overall the $\log_{10}C_{sat}$ (298 K) values from different locations are close to the range given by the calibration curves. However, it is important to note that this does not suggest T$_{max}$ calibrations are not needed for field measurements (unavailable for our datasets). Although we cannot find a correlation between $\log_{10}C_{sat}$ (298 K) and sumT$_{max}$ with all data points included, that correlation might be to some extent improved with laboratory T$_{max}$ calibrations. This underlines again the complexity of assessments of the volatility through either method, as already shown for laboratory measurements (Graham et al., 2023), but even more so for comparisons of complex ambient data from different locations and periods, and different instrument versions (see Table S2).

If we only focus on the datasets collected with the same FIGAERO setup (REL, UST-s, UST-w, UKA-s, and UKA-w) assuming similar calibration factors, a negative correlation (Pearson's R: -0.54) is observed between $\log_{10}C_{sat}$ (298 K) and sumT$_{max}$. And the correlation still holds between ambient temperature-corrected $\log_{10}C_{sat}$ and sumT$_{max}$ (Pearson's R: -0.92). Although C_{sat} values can be biased by orders of magnitude using other parametrization methods (Graham et al., 2023), the general slope and trend is similar to the calibration curves or to that using other parametrization methods such as Donahue et al. (2011) method (Figure S1). The results hence provide an overall broad qualitative agreement between bulk volatility derived from thermograms and composition.
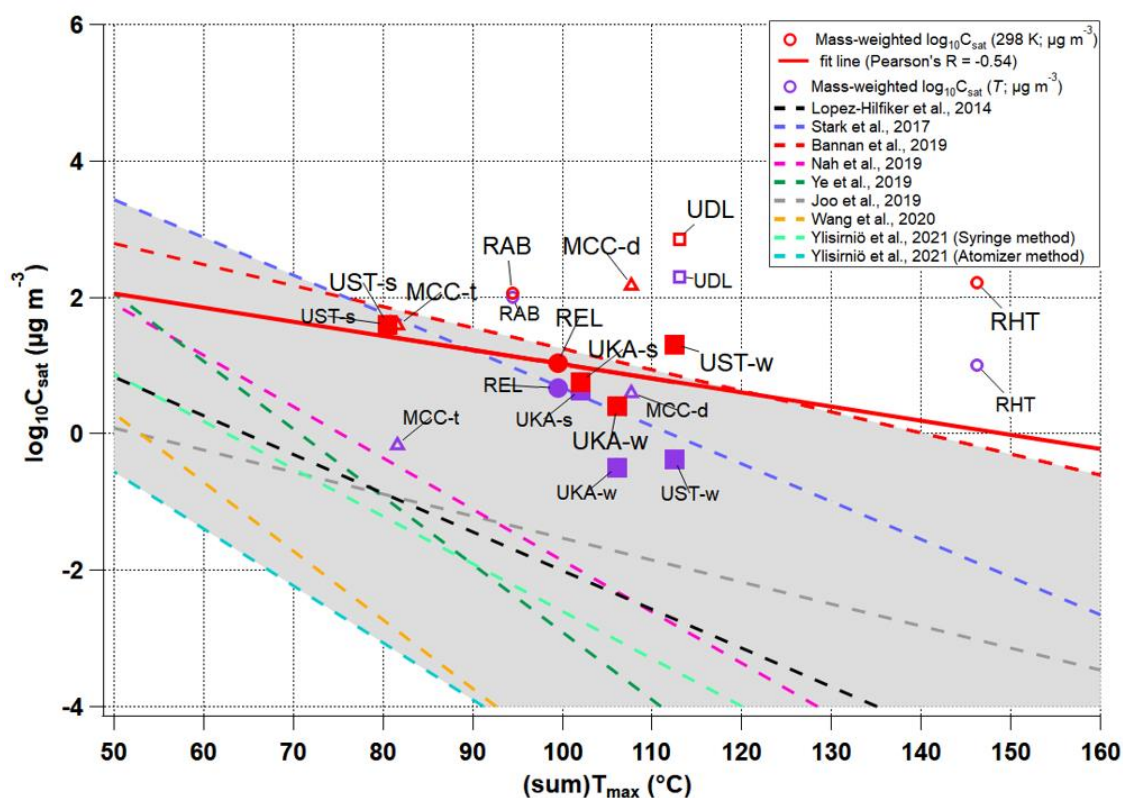
Figure 4. Comparison of the campaign-average mass-weighted $\log_{10}C_{sat}$ and sumT$_{max}$ values for different locations and seasons (Mountain sites in triangles, Rural sites in circles, and Urban sites in squares), with mass-weighted $\log_{10}C_{sat}$ (298 K) in red and mass-weighted $\log_{10}C_{sat}$ (T) in purple. The red solid line is the fit line for the red solid markers only, the data of which are from the same FIGAERO setup. The gray area covers the previously reported calibrations of $\log_{10}C_{sat}$ (298 K) vs. calibrant T$_{max}$ values in colored dashed lines. The wide spread of these calibration lines is believed to result from variations in instrument designs, experimental procedures, and the ranges of used calibration compounds (Ylisirniö et al., 2021).

Other than the effects of different FIGAERO geometries (Ylisirniö et al., 2021), parameters affecting the correlation between $\log_{10}C_{sat}$ and sumT$_{max}$ are manifold and the correlation is subject to uncertainties and artefacts for both methods. On the one hand, molecular composition-derived volatility is limited by its incapability in differentiating isomers with different vapor pressures since it is solely based on molecular formula (Graham et al., 2023), and the bulk OOA volatility for the complex ambient particle matrix may also diverge from the sum of individual parametrized C_{sat} due to non-ideal intermolecular interactions (Compernolle et al., 2011;Isaacman-VanWertz and Aumont, 2021), in addition to the highly uncertain parametrization of C_{sat} for organonitrates with multiple nitrate groups (Graham et al., 2023). On the other hand, thermal desorption-derived volatility can suffer from artefacts from oligomer content, viscosity, and possible mutual interactions between them (i.e., oligomer content vs. viscosity) (Huang et al., 2018;D'Ambro et al., 2017;Wang and Ruiz, 2018). Thermal decomposition of larger oligomeric molecules can bias the C_{sat} towards higher volatilities and the sum thermogram shape and sumT$_{max}$ to a lesser extent due to the dominance of monomer species (i.e., ending up with a longer tail). There have been attempts to separate the thermal decomposition contribution for individual thermograms (Lutz et al., 2019;D'Ambro et al., 2018;Buchholz et al., 2020;Wu et al., 2021), but this poses the threat for introducing new uncertainties due to the difficulty in e.g. differentiating isomers from thermal decomposition products, and monomers from dimers in ambient samples with complex VOC precursors (Graham et al., 2023;Voliotis et al.,

2021). Overall, however, for a limited number of our datasets from the exact same instrument, the lower apparent volatility (i.e., higher sumT$_{max}$) agrees qualitatively with the lower log$_{10}$C$_{sat}$ values, corroborating potential relationships and interconnections between volatility and chemical composition across different environments and systems despite the large uncertainties and artefacts of both methods.

4 Conclusions and atmospheric implications

In this paper, the molecular composition and volatility of OOA particles at different rural, urban, and ~~remote~~ mountain environments ~~across the globe~~ were investigated with the deployments of FIGAERO-CIMS. We find distinct molecular composition for different environments: OOA particles exhibit on average larger nC and lower O:C ratios at the urban sites (nC: 9.8±0.7; O:C: 0.76±0.03), followed by the rural (nC: 8.8±0.6; O:C: 0.80±0.05) and ~~remote~~ mountain stations (nC: 8.1±0.8; O:C: 0.91±0.07), indicative of different emission sources and chemistry. While the CHO contributions are on average higher (79.9±5.2%) compared to the mountain (66.2±5.5%) and urban sites (72.6±4.3%), in accordance with their proximity to forested areas, the largest contributions of CHON compounds are found at the urban stations (27.1±4.3%), consistent with their higher NO$_x$ levels.

Besides, the bulk OOA volatility differences are found in C$_{sat}$ values by up to ~3 orders of magnitude, and in thermogram shapes with average sumT$_{max}$ values by up to 60 °C across different locations and systems. Despite of the uncertainties/limitations for volatility derived from both sumT$_{max}$ and molecular formula as well as the translated uncertainties in the relationship between them, sumT$_{max}$ are found to exhibit an overall negative correlation with molecular formula based C$_{sat}$, suggesting a potential relationship/interlink between the volatility and chemical composition for the different locations and systems.

Here, using FIGAERO-CIMS measurements of OOA particles from various locations ~~across the globe~~, we achieve a comprehensive picture of the relationship/interconnection between volatility and chemical composition of OOA particles in different rural, urban, and mountain~~remote~~ environments, which are characterized by different ambient meteorological parameters, trace gas levels, emission sources/chemistry, and resulting distinct OOA molecular composition and volatility. Our study shows a connection between chemical composition and thermal desorption behavior, but also the limitations of using measurements of either for the assessment of volatility. Thermal decomposition has been a well-known issue for FIGAERO-CIMS measurements, however, the effects on the bulk molecular composition and sum thermograms of all detected OOA compounds for most sites studied here are ~~small~~ not significant as these thermally-unstable oligomers do not dominate the OOA mass. For some locations with multi-mode thermograms dominated by the second mode (e.g., MCC-d, RHT, and UDL; see Figure S6), the effects would be larger. Still, alternative approaches need to be developed for more quantitative estimations of volatility from FIGAERO-CIMS measurements.

Overall we find that it is clearly the chemical composition of OOA that determines its apparent volatility, and that environmental conditions (e.g., ambient temperature) play a lesser, secondary role through their influence on sources and chemistry of a particular environment, such as seasonal patterns of biogenic emissions and human behavior (e.g., residential heating). For example, summer OOA particles tend to be more volatile than the winter OOA particles due to higher ambient temperatures in summer and consequently higher local emissions of biogenic precursors and higher reaction rates. In winter, OOA particles are subject to higher biomass burning emissions and/or traffic emissions from human activities. Therefore, the importance of chemical composition and environmental conditions (e.g., ambient temperature) on the apparent volatility of OOA particles is different, with

the chemical composition (i.e., sources and chemistry) being a more direct and important factor than the environmental conditions. The comprehensive ~~global~~ dataset from our results shows the complex thermodynamics and chemistry of OOA and their changes during its lifetime in the atmosphere, and that the chemical description of OOA generally suffices to predict its apparent volatility, at least qualitatively. Considering the major contribution of OA to total aerosol mass concentrations and implications for both human health and climate change (Jimenez et al., 2009;Nel, 2005;IPCC, 2021), ~~O~~our study ~~thus~~ provides new insights that will help guide choices of e.g. descriptions of OOA volatility in different model frameworks~~, which has been previously simplified due to challenges to measure and represent it in models~~. For example, with a better constraint on the volatility of condensable vapors and the associated particles using e.g. the up-to-date CIMS measurements, the study could contribute to understanding the underlying oxidative chemistry and a better OA representation in air quality models. The potential contribution of co-condensation of organic vapors to aerosol forcing or to future cloud radiative effects could also be better accounted for in cloud parcel models (Heikkinen et al., 2023). A better understanding of the chemical nature and volatility of OA components can thus ultimately improve predictions of atmospheric organic particle mass and climate effects of atmospheric OA.

Data availability

The data that are involved in the figures can be found at https://doi.org/10.5281/zenodo.7983797 (Huang, 2023).

Author contributions

JT, HS, DG, and CM designed the research; WH, CW, LG, YG, SLH, FDL, BHL, JS, XS, RR, SNT, DG, FJ, MV, and CM conducted field measurements; WH, CW, LG, SLH, FDL, BHL, JS, HS, XS, SNT, DG, and CM analysed the data; CW, LG, YG, SLH, JT, SS, TY, JS, HS, XS, MV, and CM provided suggestions for the data analysis, interpretation, and discussion; WH and CM wrote the paper with contributions of all authors. All authors have given approval to the final text.

Competing interests

At least one of the (co-)authors is a member of the editorial board of Atmospheric Chemistry and Physics.

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