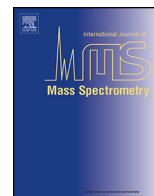




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Review

Isotope ratio studies of atmospheric organic compounds: Principles, methods, applications and potential

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ABSTRACT

In the atmosphere, both gas and particle phase organic trace compounds (OTC) have multiple effects on air quality and climate. Gaps exist in a fundamental understanding of the sources and sinks of organics and thus, knowledge needed to steer regulatory purposes is far from complete. Isotopes provide specific “fingerprints” in OTC. These fingerprints result from the isotopic composition at emission, as well as from chemical and physical processes in the atmosphere. Compound specific isotope ratio mass spectrometry (IRMS) in atmospheric OTC is therefore a promising tool to improve our understanding of sources and the atmospheric fate of OTC. Due to analytical challenges originating from the small sample amounts and a huge variety of physical and chemical properties of OTC present in the atmosphere, such measurements are not routinely performed. We present an overview of basic concepts as well as instrumental and measurement procedures used for compound specific IRMS in atmospheric OTC. Concepts for the interpretation of ambient observations are reviewed together with available literature data on source specific and ambient $\delta^{13}\text{C}$ values of gas and particle phase OTC. Full deployment of the IRMS potential in future atmospheric studies will depend on the availability of laboratory kinetic data. Further method developments, such as increasing sensitivity and accuracy, as well as techniques for simultaneous isotope ratio measurement of multiple atoms are expected to further extend the potential use of isotope ratios for studies of atmospheric OTC.

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1. Introduction

The atmosphere contains a wide range of different groups of organic trace compounds (OTC), which undergo complex chemical and physico-chemical processes [1]. Organic compounds are emitted in large quantities into the atmosphere either in the form of volatile organic compounds (VOC), or as part of suspended particulate matter (PM). Substances with high vapor pressures are typically found exclusively in the gas phase and substances with very low vapor pressures in the particulate phase. Compounds with intermediate vapor pressures, generally called semi-volatile organic compounds (SVOC), are found in both gas and particulate phase. Organic compounds in the atmosphere can have significant impact in a number of areas. Some compounds such as polyaromatic hydrocarbons (PAH), phenols, or polychlorinated biphenyls (PCB) are toxic or mutagenic [2]. Chlorofluorocarbons and hydrochlorofluorocarbons have an adverse influence on stratospheric ozone [3], while many other VOC, such as alkenes, isoprene, terpenes, and aromatic substances, play an important role in the formation of tropospheric ozone [4,5]. Atmospheric suspended particulate matter (aerosols) can impact human health [6] and influence directly, or indirectly via their role as cloud condensation nuclei, the earth's radiation budget [7]. In the atmosphere, organic compounds undergo a variety of reactions, which result in the removal of these substances from the atmosphere. During this process, a variety of secondary organic substances can be formed, which, similar to primary emission, can have a significant impact on human health or climate.

The largest emissions of organic compounds into the atmosphere are in the form of VOC and methane [8], in total between 1500 Tg yr^{-1} and 2200 Tg yr^{-1} . Approximately 10% of these emissions are directly man made, but the by far dominating emissions are from vegetation [8,9]. Emissions of organic compounds include substances with a wide range of reactivity and chemical structures. The atmospheric burden of OTC consists of a wide range of different chemical species with high spatial and temporal variability. For several decades, the sources, sinks, atmospheric distribution and reactions of organic compounds in the atmosphere have been the subject of numerous studies [10] and references therein]. However, due to the complexity of chemical composition and reactions, there are still substantial gaps in our understanding of the atmospheric chemistry of organic compounds.

In many areas of science, stable isotope ratio measurements have been used to gain additional insight into complex problems and the atmospheric chemistry of organic compounds is no exception. In 1997, a methodology to determine compound specific stable carbon isotope ratios for VOC in the atmosphere was developed by Rudolph et al. [11]. Subsequently, a number of studies have been published, presenting methods to measure isotope ratios of atmospheric organic compounds as well as ambient measurements and concepts for the interpretation of such measurements [12–15] and references therein]. There are also several publications presenting information required to interpret ambient isotope ratios measurements for organic compounds such as kinetic isotope effects for atmospheric reactions and isotopic composition of emissions of organic compounds [15] and references therein]. Nevertheless, there are currently very few studies that provide new insight into atmospheric chemical and physical processes based on ambient measurement of isotope ratios. This is partly due to significant experimental difficulties to accurately measure compound specific stable isotope ratios for organic trace compounds in the atmosphere. However, an equally important problem stems from the limited amount of available basic information such as isotope effects for atmospheric reactions or isotopic composition of emissions, which is required to evaluate such measurements.

In this paper, we will provide an overview over existing methods for compound specific analysis of atmospheric organic trace components and for methods that allow determination of isotope ratio specific information required to interpret atmospheric measurements of the isotope ratio of organic compounds. We will also briefly discuss concepts for the interpretation of such measurements since this determines required measurement accuracy as well as type and extent of basic information needed to interpret ambient measurements. We will then provide an overview of existing observations of gas and particle phase organic compounds. As gas phase measurements have been the focus of review before [14,15], we will concentrate on information on gas phase VOC for 2007–2013 as well as on primary and secondary organic compounds in particles. In the conclusions section we will point out new promising approaches and future directions in stable isotope analysis of atmospheric organic compounds.

Currently, most studies of stable isotope ratios of atmospheric organic compounds focus on carbon and, to a lesser extent, on hydrogen. We will therefore concentrate on carbon and hydrogen isotope ratio measurements. This is due to the very limited number of atmospheric measurements of compound specific isotope ratios measurements for organic hetero atoms such as oxygen, nitrogen, sulfur or halogens and does not reflect the potential usefulness and value of such measurements.

2. Basic Concepts

The basic principles of using isotope ratios for studies of atmospheric organic compounds are in several aspects similar to studies of atmospheric organic trace components in general. To avoid misunderstandings, the approach discussed here is based on measurement of naturally occurring isotope ratios, not on labeling by artificial isotope enrichment or depletion. Isotope ratio studies of atmospheric OTC make use of the small variations in the isotope abundance that result from small differences in chemical or physical equilibria or reaction rates, the isotope effects. Molecules where one or more atoms are replaced by a different isotope are called isotopologues. It should be noted that for carbon, hydrogen and oxygen the very low abundance of the heavier isotope results in a very low probability of multiply labeled isotopologues of small molecules. For many molecules isotope labeling is possible at more than one position. Molecules which differ in the position of the heavy isotope, but are otherwise identical are referred to as isotopomers.

Isotope ratios are typically expressed in the form of δ values relative to a reference isotope ratio.

$$\delta^{13}\text{C} = \frac{\left(^{13}\text{C}/^{12}\text{C}\right)_{\text{sample}} - \left(^{13}\text{C}/^{12}\text{C}\right)_{\text{VPDB}}}{\left(^{13}\text{C}/^{12}\text{C}\right)_{\text{VPDB}}} \times 1000 \text{ ‰} \quad (1)$$

This uses carbon as an example. The convention is to use the ratio of less abundant (e.g. ^{13}C) over most abundant (e.g. ^{12}C) isotope. In order to ensure compatibility of measurements from different research groups, data are always reported relative to an established reference point, which is in the case of carbon Vienna Pee Dee Belemnite (VPDB) with $\left(^{13}\text{C}/^{12}\text{C}\right)_{\text{VPDB}} = 0.0112372$ [16]. For the sake of convenience isotope ratios are usually given as ‰.

Kinetic isotope effects (KIE) which occur during irreversible chemical reactions, are defined as ratios of the reaction rate constant of a molecule containing only the light isotopologues (when using carbon as example k_{12}) over reaction rate constant for the heavy isotopologue (k_{13}):

$$\text{KIE} = \frac{k_{12}}{k_{13}} \quad (2)$$

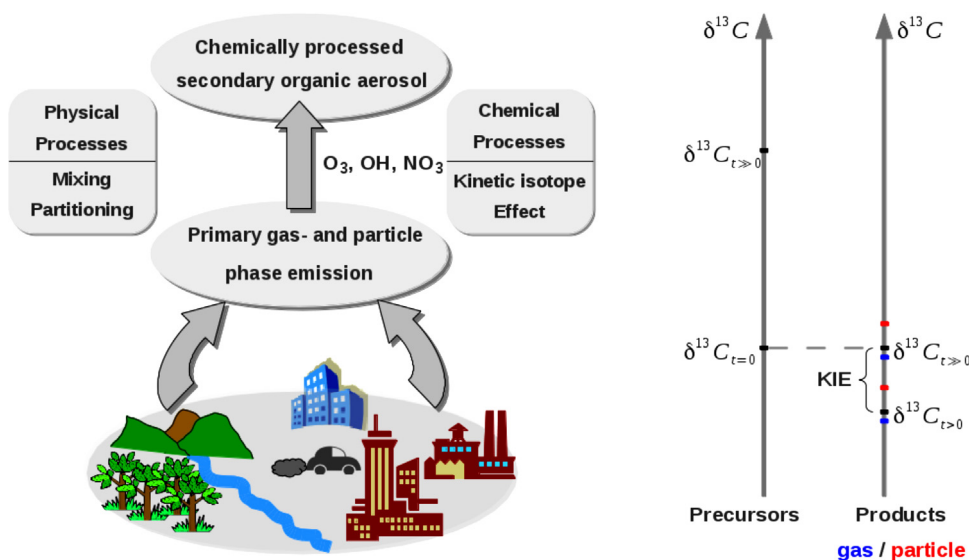


Fig. 1. Schematic of the determining factors of ambient $\delta^{13}\text{C}$ values of VOC. Generally speaking KIE will increase the $\delta^{13}\text{C}$ of a precursor. Reaction products are initially depleted in ^{13}C for $\text{KIE} > 1$ and then become heavier due to the ongoing increase of the precursor $\delta^{13}\text{C}$. Secondary OTC can undergo further reactions in the atmosphere, in which case additional change in $\delta^{13}\text{C}$ occurs, depending on the KIE of the reaction. In equilibrium, partitioning between the gas and particle phase results in larger $\delta^{13}\text{C}$ of particle phase OTC than the corresponding gas phase OTC. If the partitioning between the phases is determined by physical processes such as adsorption or absorption the difference will be small.

Since isotope effects are small, they are, similar to changes in isotope composition, often expressed as ϵ values in ‰ relative difference:

$$\epsilon = \frac{k_{12} - k_{13}}{k_{13}} \times 1000 \text{ ‰} = (\text{KIE} - 1) \times 1000 \text{ ‰} \quad (3)$$

The isotope ratios of atmospheric VOC are determined by two components; (i) isotopic composition of emissions and (ii) changes in isotope ratio resulting from reactions in the atmosphere, as schematically shown in Fig. 1. Therefore in atmospheric chemistry, stable isotope ratio measurements of trace components are predominantly used to identify contributions from different sources (source reconciliation and atmospheric trace gas budgets) and to quantify atmospheric processing [17]. For substances that are formed by reaction of precursors (secondary pollutants), isotope ratio measurements can also provide information on formation mechanisms [18–21].

For meaningful interpretation of compound specific measurement of isotope ratios of atmospheric organic compounds, in addition to knowledge of the isotopic composition of emissions, also quantitative understanding of the isotope fractionation for atmospheric reactions is required. With the exception of distribution between different phases such as gas phase and suspended particles or cloud droplets, most physico-chemical processes of atmospheric organic compounds are irreversible and determined by kinetic parameters. Isotope effects for most purely physical processes, such as distribution between phases are typically small and much lower than isotope effects for chemical reactions (see Fig. 1 for a schematic illustration of expected $\delta^{13}\text{C}$ values of precursor and product pairs). Therefore isotope fractionation of organic compounds in the atmosphere is usually dominated by the KIE of loss or formation reactions.

VOC are mainly removed from the atmosphere by reaction with the OH-radical. VOC containing double bonds also react with ozone. At night, reaction with the nitrate radical (NO_3) can be important and under certain conditions reaction with the Cl-atom may contribute to VOC removal. For some VOC, such as alcohols, light carbonic acids or carbonyls, deposition from the gas phase can contribute to their removal. Photolysis can also be an important reaction for some VOC such as aldehydes. However, photolysis is

most important for VOC that are not efficiently removed in the troposphere and thus can be transported to the stratosphere where photolysis is an efficient loss process. Oxidation products of VOC often have lower vapor pressures than the precursor VOC and therefore, depending on their vapor pressure, can partition into the particulate phase, forming so called secondary organic aerosol (SOA) [22]. Organic compounds in particulate matter (Particulate Organic Matter, POM) are removed from the atmosphere by deposition. Particle deposition does not result in isotope fractionation. However, reactions within particles can result in changes of isotope ratios for individual organic compounds. These reactions are currently poorly understood.

The use of isotope ratio measurements to study atmospheric OTC requires in principle three types of compound specific studies, (i) the isotope ratio analysis of atmospheric OTC, (ii) measurement of the isotope ratio of OTC emissions, and (iii) understanding the isotope fractionation resulting from atmospheric processing of OTC, including formation of secondary OTC for compounds that can be formed by atmospheric OTC reactions. A common challenge for all three types of studies is the vast amount of different OTC present in the atmosphere. Interpretation of atmospheric OTC isotope ratios is complicated by the complex interaction of atmospheric mixing and chemical processing, which requires development of conceptual or numerical tools specific for the atmosphere.

3. Instrumentation and measurement procedures

Since OTC consist of a very wide range of different chemical elements, it is essential that measurements are compound specific. The by far most widely used measurement technique for isotope ratios of atmospheric OTC is gas chromatography coupled on-line to isotope ratio mass spectrometry (GC-IRMS). As schematically shown in Fig. 2 after chromatographic separation of the individual organic compounds, prompt high temperature conversion into CO_2 , H_2 , N_2 , or CO is required for stable isotopic measurements of C, H, N, and O, respectively. Part of the effluent from the conversion interface is continuously fed into an isotope ratio mass spectrometer (IRMS), which determines the isotopologues of CO_2 , H_2 , N_2 , or CO . This results in chromatographic traces for each of the

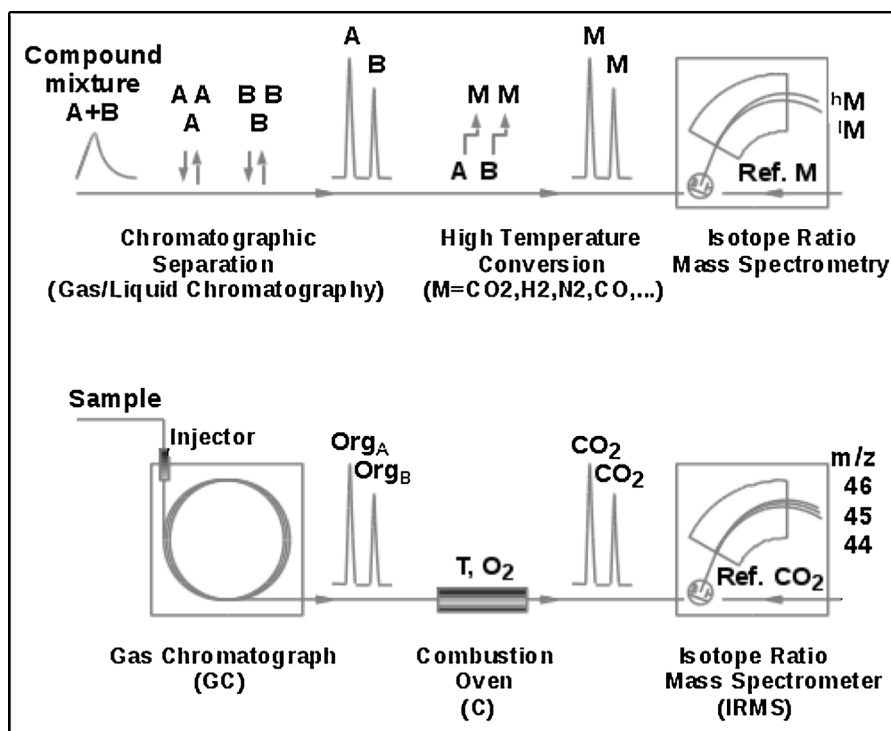


Fig. 2. Schematic illustration adapted from [23] of the analytical steps involved in compound specific measurements of stable isotopic composition (upper panel) and example of $\delta^{13}\text{C}$ analysis in atmospheric samples containing organics (lower part). Mixtures of compounds undergo separation by gas- or liquid chromatography before individual compound peaks are converted into species M for high precision isotope ratio mass spectrometry. In the case of $\delta^{13}\text{C}$ studies, combustion to CO_2 leads to isotopologues at m/z 44 ($^{12}\text{C}^{16}\text{O}^{16}\text{O}$), 45 ($^{13}\text{C}^{16}\text{O}^{16}\text{O}$ or $^{12}\text{C}^{17}\text{O}^{16}\text{O}$), and 46 ($^{13}\text{C}^{17}\text{O}^{16}\text{O}$ or $^{12}\text{C}^{18}\text{O}^{16}\text{O}$ or $^{12}\text{C}^{17}\text{O}^{17}\text{O}$). Reference gases are typically directly introduced into the ion source of the IRMS, bypassing chromatographic separation and high temperature conversion.

isotopologues, which can be analyzed for integrated peaks and used for calculation of compound specific isotope ratios. Critical aspects that determine accuracy and precision of compound specific IRMS for organic compounds include (i) chromatographic performance, (ii) the maintenance of peak separation in the chemical conversion and interface, and (iii) characterization of isotopic fractionation in the sample collection and treatment procedure. Challenges in compound specific isotope analysis of environmental samples have been reviewed recently [23] and references therein]. Here we focus on challenges specific to atmospheric measurements.

Sampling of gas phase VOC as well as OTC in suspended particulate matter (aerosols) can create bias or decrease the measurement reproducibility. This becomes more severe for the isotope ratio measurements, due to the necessity of collecting OTC from very large air volumes. Atmospheric levels of individual OTC are typically less than $1 \mu\text{g m}^{-3}$ and often in the ng m^{-3} range or lower. Precise isotope ratio analysis requires samples in the range of several ng or higher per measurement. Consequently, sampled air volumes for isotope ratio analysis of atmospheric OTC range from several litres to several thousand m^3 at standard temperature and pressure (STP) depending on atmospheric concentration and isotope studied. For measurement of the isotope ratio of OTC in primary emissions or during laboratory studies on isotope fractionation in OTC reactions, sample volumes are often lower due to the higher OTC concentrations.

Sampling methods for OTC differ substantially between analysis of VOC, collection of suspended particulate matter, or sampling of SVOC. A problem specific to SVOC analysis is separation between the gas phase and particle phase fraction. Selective sampling of either phase can change the distribution between the two phases and thus create positive or negative artefacts. Methods for sampling and sample processing for isotope ratio analysis of atmospheric OTC are generally derived from methods developed for concentration

analysis, which are modified to allow OTC collection from very large air volumes.

3.1. Measurement techniques for atmospheric VOC

Detailed summaries of measurement techniques for compounds specific isotope ratios of atmospheric VOC have been given by Goldstein and Shaw [14] and Rudolph [15]. Therefore only a brief overview and recent developments will be presented here. Sampling techniques can be divided into whole air sampling and selective sampling.

For whole air sampling, air is collected in the field in various types of containers, pressurized or at ambient pressure, and transferred to the laboratory for analysis. Most widely used for this purpose are stainless steel canisters with metal bellow valves. Very often the interior surface of the canisters is treated to avoid loss of VOC due to surface reactions or contamination of the sample. Prior to GC–IRMS measurement, the VOC in the collected air samples are concentrated by one or several adsorption–desorption steps. Typically two or three enrichment steps are used to concentrate VOC from large sample volumes in the range of 5–15 L (STP) into a very small final volume suitable for transfer to the gas chromatographic column. The use of several sample concentration steps is one of the major differences between VOC concentration and isotope ratio measurement techniques.

Whole air sampling in stainless steel canisters was used for the first reported measurements of carbon isotope ratios of VOC in the atmosphere [11] and many later studies used very similar sampling and sample processing methods [15] and references therein [24–27]. These methods typically allow carbon isotope ratio measurement with a precision in the range of 0.3–1% for atmospheric concentrations in the range of 10 ng m^{-3} . Depending on molecular weight of the VOC, this corresponds to mixing ratios of

approximately 0.1 nmol mol⁻¹. For substantially lower atmospheric mixing ratios, the reproducibility of the measurements decreases rapidly [15] and references therein [26].

The practical limitations for air volumes that can be collected as whole air samples and the resulting limitations triggered the development of selective sampling techniques to allow collection of VOC from larger sample volumes. The use of cryogenic enrichment allows collection of VOC from very large volumes of air, sometimes exceeding 100 L, and therefore measurement of carbon isotope ratio of atmospheric VOC at mixing ratios in the low pmol mol⁻¹ range [28–33]. However, cryogenic sampling requires substantial logistic effort for field measurements, which may limit its applicability. Turner et al. [34] and von Eckstaedt et al. [35] reported that TenaxTA packed stainless steel tubes can be used for sampling of a range of VOC and subsequent δ D or δ^{13} C analyses. The VOC were sampled from volumes in the range of 0.5–3 L (STP) and it was found that breakthrough could significantly impact the mass of sampled VOC. Although these studies showed that breakthrough did not cause a measurable change in isotopic composition of the sampled VOC, this reduced the mass collected, which makes the method well suitable for isotope ratio measurement of VOC emissions, but limits its applicability for ambient measurements. Very recently, a similar sampling method, using Carboxene 569 instead of TenaxTA as adsorbent was reported [36]. This allowed sampling of VOC from volumes in the range of 50 L and carbon isotope ratio measurement of light aromatic VOC and alkanes at atmospheric mixing ratios in the low pmol mol⁻¹ range with a precision between 0.5% and 1%.

Some sampling techniques use selective chemisorption instead of physical adsorption in order to improve the selectivity as well as the stability of sampled reactive VOC such as formaldehyde or other carbonyls [37–39]. Sampling cartridges are packed with adsorbents coated with reactants such as 2,4-dinitrophenylhydrazine (DNPH) or NaHSO₃, which selectively react with formaldehyde or other carbonyls. The samples are extracted with small volumes of solvents and the solutions are analyzed by GC–IRMS, generally after reducing the extract volume. When using DNPH coated cartridges the formed DNPH derivatives can be analyzed directly. When NaHSO₃-coated adsorbents are used, a derivatization step with cysteine is applied to form compounds that can be analyzed by GC–IRMS.

For sampling of SVOC, a methodology using high volume filters coated with an adsorbent (XAD-4) was recently employed [19]. The method was developed and tested for sampling of phenols, but can in principle be used for a wide range of SVOC. Filters, on which phenols have been collected from some thousand m³ air, were extracted. The extract volume was reduced and the bis(trimethylsilyl) trifluoroacetamide (BSTFA) derivatives of the phenols were analyzed by GC–IRMS. The advantage of this sampling technique is the possibility to collect VOC from very large volumes of air. The limitation is that compounds with high volatility cannot be efficiently sampled. Furthermore, sampling on filters also collects particulate matter and therefore does not differentiate between particle phase and gas phase OTC.

For ambient measurements and emission studies, most currently published isotopic methods use a combustion interface for carbon isotope ratio determination [40]. More recently, GC coupled to a pyrolysis interface [41] has been used for analysis of the stable hydrogen isotope ratio of VOC in emissions as well as in heavily polluted air masses [35,42–44]. Gas chromatography–quadrupole mass spectrometry (GC–qMS) has been used for measurement of the bromine isotope ratio in atmospheric methyl bromide [33] and this technique is promising to extend the range of isotopes for studies of atmospheric VOC.

The very complex composition of many atmospheric samples sometimes requires modifications to improve the selectivity of the separation. Similar to concentration measurements, this is often

done by partial two-dimensional GC separations [29,45]. Also pre-columns, removing specific groups of VOC from the sample, have been used to reduce problems resulting from incomplete chromatographic separation [46]. The combination of two GC-columns also provides the possibility to analyse VOC with a very wide range of volatility in one measurement [13,47].

Isotope ratios are typically determined by comparison with calibration gas injections into the IRMS before, during or after the chromatographic separations. There are several studies using gas mixtures containing VOC with known isotope ratios to evaluate the accuracy of on-line measurements. The gas mixtures are prepared pure from bulk compounds which are analyzed for isotope ratios using conventional off-line techniques. There are several studies demonstrating that isotope ratios determined from on-line and off-line measurements agree within the uncertainty of the on-line analysis [11,15,19,20,26,34]. However, due to the lack of readily available gas mixtures containing VOC with known isotope ratios, not all published measurements of isotope ratios of atmospheric VOC or VOC emissions use such comparison to evaluate measurement accuracy. In this case comparison between results from different laboratories may be subject to bias due to uncertainty in measurement accuracy.

3.2. Measurement techniques for OTC in atmospheric particulate matter

For compound specific measurements of OTC in atmospheric particulate matter, individual compounds have to be transferred from the solid or liquid phase particles to gas- or liquid phase concentrated species. As total aerosol concentrations are regulated by air quality legislation, ambient particulate mass concentration is often in the range of few to tens of μ g m⁻³, with the sum of organic compounds typically accounting for 10–80% of total particulate mass [22]. Considering that particulate organics are composed of thousands of individual species [9], resulting individual OTC concentrations far from individual sources are in the sub ng m⁻³ or ng m⁻³ range. Atmospheric PM samples are commonly collected on pre-combusted quartz fiber filters by using high-volume air samplers, collecting particles from several m³ of air (STP). The sampling from large air volumes usually results in low (days) time resolution. It has been argued that these high sampling volumes insure establishing of equilibrium conditions between the gas and particle phase of condensable organics [48]. Thus, collection artefacts which might lead to isotopic fractionation of the targeted compounds are likely avoided or reduced. However, to our knowledge there are no tests of sampling atmospheric PM for CSIA of OTC using denuder-filter pack combinations, a methodology that is widely used to test the integrity of sampling methods for concentration measurements. An overview on generic aerosol sampling systems with recommendations how to develop individual configurations depending on specific purposes is given elsewhere [49]. To prevent particle losses, after sampling, filters are stored at temperatures lower than –18 °C until they are analyzed offline in the lab. The OTC can be directly transferred from the filter to the GC by thermal desorption (TD) or extracted in an adequate solvent and analyzed with GC- or LC–IRMS, depending on the chemical and physical properties of the targeted compounds.

In IRMS applications, thermal desorption [50] is an emerging technology in which a small section of the filter can be placed directly into a thermal desorption unit (TDU) and heated. Organic compounds are thus volatilized and subsequently concentrated before releasing them into the GC. This refocusing step is necessary to reduce the elute volume and can be achieved by cold trapping or capillary cryo-focusing. Similar to VOC measurements, due to limitations concerning the filter loadings, the pre-concentration unit

was specifically developed to allow cryogenic enrichment of OTC volatilized from large filter pieces.

When thermal desorption of less volatile compounds or complex matrices from filters proves difficult, solvent extraction is performed to dissolve the target analytes in an appropriate solvent, thus removing interfering compounds. For instance, aliphatic hydrocarbons can co-elute with PAHs during GC separation. To increase the performances of IRMS analyses of individual substances, the two compound classes have to be initially separated by extraction with solvents of different polarities. The solvents are selected according to the 'like dissolves like' principle, using e.g. n-hexane for the aliphatic fraction and the higher polar toluene for PAHs [51]. Higher polar OTC, such as fatty acids are extracted with a mixture of methanol/dichloromethane (DCM). Extracts are saponified with methanol/KOH and then again extracted with DCM. After methylation by BF_3 /methanol, the monocarboxylic fatty acid methyl esters are separated using silica-gel-column chromatography [52]. The most suitable solvent for very polar dicarboxylic acids or anhydrosugars is the water. The aqueous extracts are pre-concentrated to small volumes by evaporation and separated by liquid chromatography (LC) [53,54]. When separation is performed by GC, water injection should be avoided. Therefore, solvent exchange by cryo-drying of samples is necessary, followed by solvation in n-butanol [55].

The separation of compounds containing highly polar functional groups (OH, COOH) is a challenge for one-dimensional gas chromatography. To improve the peak form and resolution and reduce sample loss, polar compounds are analyzed as less polar derivatives. The principles and critical aspects introduced by this supplementary sample treatment are discussed in detail elsewhere [23,56]. In brief, when applying derivatization one needs to (i) characterize and take into account the isotopic signature of atoms introduced through derivatization, (ii) ensure stability of derivatives throughout the subsequent separation process, and (iii) determine isotopic fractionation and elemental dilution of the derivatization process [23,57]. An improved separation of complex aerosol matrices was also obtained by two-dimensional heart-cutting gas chromatography. There, target compounds eluting from the first column are cryo-trapped and subsequently separated on the second column with a different polarity [50].

Measurements should ideally prevent isotopic fractionation during sampling, sample pre-treatment and separation. Typically literature lacks a detailed description of the influence of aerosol sampling and filter storage on the isotopic composition of OTC. In particular, in the case of semi-volatile species, handling procedures may introduce positive or negative artefacts, which in addition to influencing observed concentrations, may also affect species isotopic composition.

4. Isotope fractionation for atmospheric reactions of VOC

Laboratory measurements of KIEs for gas phase reactions of VOC with natural isotope abundance typically use methods similar to relative rate constant measurements [58,59]. Relative rate constant experiments determine the reaction rate of a VOC relative to that of a VOC with a known rate constant. The rate constant then is determined from the ratio of the two rates. In KIE measurements, the change of concentrations of different VOC isotopologues is measured. Since the difference in reaction rates between isotopologues is usually small, the change in isotope ratio is measured by GC-IRMS instead of directly measuring the concentration of the different isotopologues. When using artificially labeled VOC, optical spectroscopy can be used for measuring KIEs of reactions of small molecules [60–62].

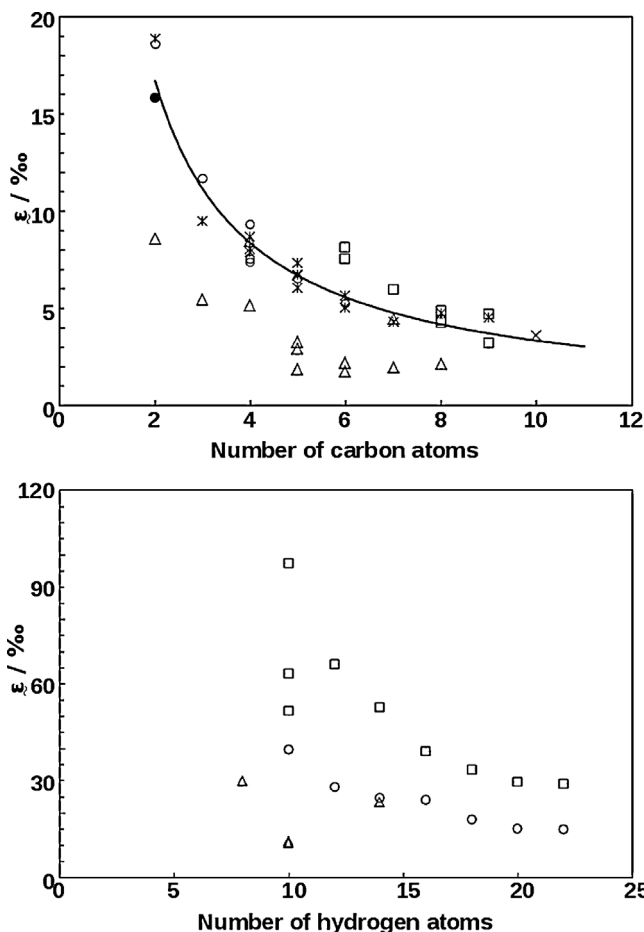


Fig. 3. Summary of results from kinetic isotope effect studied for $\delta^{13}\text{C}$ (upper panel) and δD (lower panel). The increase of ε with decreasing number of C-atoms is observed for reactions of OH with alkenes (Δ), alkenes (\circ), and aromatics (\square), as well as for reactions of O_3 with alkenes ($*$). Individual data for reactions of OH with ethyne (\bullet) and O_3 with b-pinene (\times) are given, as well as a prediction for the O_3 KIE (-----). The dependence of ε on number of H-atoms is presented for OH-alkane (\square), Cl-alkane (\circ), and OH-unsaturated VOC (Δ) reactions. Data were taken from [59,63–68]. The solid line in the upper panel is a fit to a semi-empirical dependence between KIE for alkene ozonolysis reactions and carbon number [64].

KIEs for atmospheric reactions relevant for VOC have been subject of a large number of studies [15,63]. Carbon and hydrogen KIEs for reactions of non-methane hydrocarbons (NMHC) with OH-radicals, ozone and Cl-atoms in the gas phase have been studied in detail and are well understood. There are several semi-empirical relationships that allow estimates of KIEs based on chemical structure. As example, Fig. 3 shows the dependence between the number of carbon atoms and carbon-KIEs (upper panel) as well as number of hydrogen atoms and hydrogen KIEs (lower panel). For most types of reactions such as hydrogen abstraction by OH-radicals, addition of OH-radicals to a double bond, or ozonolysis of alkenes this simple semi-empirical dependencies provide good first order estimates. For instance, the measured KIE for ozonolysis of β -pinene [63] at 303 K fully agrees with a prediction based on the semi-empirical dependence between KIE and number of carbon atoms [64].

Nevertheless, KIEs also depend on details of the NMHC's chemical structure. The concept of structure-reactivity relationships (SRR), originally developed by Greiner [69] and further refined by Kwok and Atkinson [70], has been modified to include deuterium labeled NMHC [71–75]. This concept has more recently been extended to include carbon KIEs for NMHC reactions [59,66,68]. Based on the isotope SRR, the KIEs for individual isotopomers of

labeled NMHC can be calculated and the effective KIE for NMHC with natural isotope abundance can be determined from reactivity weighted averages of the KIEs for isotopomers. Strictly speaking, this requires knowledge of the site specific labeling for naturally occurring NMHC, information that is seldom available. However, it has been shown that KIEs calculated for equal distribution of ^{13}C or D among different positions of a molecule are, within the precision of KIE measurements, identical to results of calculations for site specific enrichment, as long as the site specific enrichment is within the range of naturally occurring isotope enrichment [64,66].

In addition to KIEs for reactions of NMHC, there is a substantial number of carbon or hydrogen KIE measurements for reactions of oxygenated VOC (OVOC) containing one or two carbon atoms [15] and references therein]. The KIEs for reaction of methacrolein and methyl vinyl ketone with ozone and the OH-radical have been recently measured [76,77]. It was found that isotope SRR derived for NMHC correctly predicts the measured KIEs. However, there are no measurements of KIEs relevant for atmospheric reactions of heavier OVOC to test the general validity of this concept.

There are very few measurements of KIEs for gas phase reactions of halogenated VOC (HVOC). Carbon and hydrogen KIEs for reaction of methyl chloride with the OH-radical and Cl-atoms in the gas phase have been reported [62]. The KIEs for photolysis of CFC-11 (CFC13) and CFC-12 (CF₂Cl₂) in the UV, a reaction that is highly relevant for the removal of CFC in the stratosphere, have been recently measured [78]. One of the reasons for the limited information on KIEs for HVOC is the difficulty to accurately measure KIEs for slow reactions. Most HVOC are by far less reactive than NMHC or OVOC. Determination of KIEs for compounds with natural isotope abundance requires precise measurement of the change in isotope ratio resulting from the investigated reaction. In laboratory studies the concentration of the reactant, especially in the case of OH-radical reactions, is often limited by practical considerations. Consequently, during an experiment, the change in concentration and isotope ratio for VOC with low reactivity is often small, resulting in increased uncertainty of the KIE measurement [65]. It should be noted that this is not only due to uncertainty in isotope ratio measurements. For slow reactions, also artefact formation or interfering reactions can create substantially biased results.

Available information on temperature dependence of KIE for reactions of atmospheric VOC is limited. For most NMHC, the change in carbon KIE between 288 K and 373 K is less than the uncertainty of KIE measurements [58]. For reactions of alkylbenzenes with the OH-radical at temperatures exceeding 373 K a significant change in KIE was observed, which was explained by the known change in the reaction pathway for OH-radical reactions of alkylbenzenes at elevated temperature. However, the temperature range at which this occurs is not relevant for reactions of VOC in the atmosphere. Most of the available information indicates that the impact of the temperature dependence of KIEs in the temperature range relevant for VOC reactions in the atmosphere is marginal [15]. An exception was recently reported, with a substantial change in the carbon KIE for the reaction of β -pinene with ozone between 273 K and 258 K [63]. Using a global numerical model it was demonstrated that this can, under specific conditions, have a measurable impact on the carbon isotope ratio of β -pinene in the atmosphere.

The isotope fractionation for deposition processes of VOC has been investigated by Jardine et al. [79]. They observed a kinetic isotope effect for the uptake of acetaldehyde by vegetation, with $\varepsilon = 5.1 \pm 0.3\%$. This value is explained by the mass dependence of the diffusion coefficient for different isotopologues. Based on this, a significant isotope fractionation can be expected for deposition of VOC with low molecular mass, although the number of available studies is still too small to generalize this finding. A substantial KIE

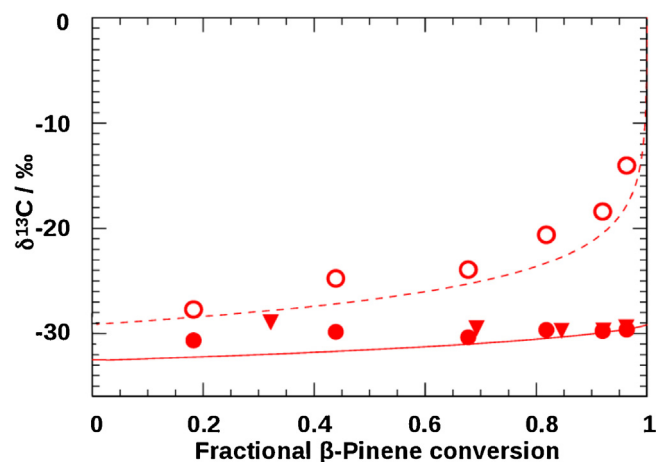


Fig. 4. Evolution of $\delta^{13}\text{C}$ for β -pinene (\square) and its main ozonolysis product nopinone in both gas (\bullet) and particle phase (\blacktriangledown), as function of fractional β -pinene conversion. Also given are modeled $\delta^{13}\text{C}$ for β -pinene and nopinone when applying the KIE for β -pinene ozonolysis, adapted from [63].

for VOC deposition can have a major impact on the atmospheric isotope ratios of molecules that are subject to deposition, for example OVOC with high solubility in the aqueous phase. KIEs for deposition reactions can also have important consequences for VOC that are subject to bidirectional exchange between a reservoir and the atmosphere, even if the net flux is small. This includes, but is not limited to biogenic sources of OVOC.

Isotope fractionation for formation of secondary OTC from gas phase reactions of VOC has been rarely studied [18,20,80,81]. The carbon isotope ratios of methyl vinyl ketone and methacrolein formed by the reaction of isoprene with OH-radicals or ozone has been studied [80]. Relative to the isotope ratio of isoprene prior to reaction, the products were depleted in ^{13}C by 2.2–4.6%. This observed fractionation agrees, within the error of measurements, with predictions from a reaction scheme that used KIEs specific for the reactions of different isoprene isotopomers.

The isotope ratio of total carbon in suspended particulate matter formed by the OH-radical initiated oxidation of toluene in the gas phase has been measured [18,81]. The results show substantial ^{13}C depletion in the particulate phase relative to the reactant. This can be explained by the KIE of the initial reaction step, i.e. for reaction of toluene with the OH-radical. Based on mass balance calculations, it was concluded that overall, for these experiments no significant isotope fractionation between gas phase and particle phase occurred. However, the measurements did not include CSIA of either particle or gas phase OTC and therefore, these studies provide no information on possible isotope effects for individual products of the atmospheric oxidation of toluene. A study of the reaction products of β -pinene ozonolysis showed that the isotope ratio for total carbon in the particle phase was only slightly higher (0.5%) than that of the β -pinene used in the experiments, independent of the extent of precursor processing. In this work, CSIA for two of the components of the particle phase was conducted and it was found that the two individual components had both isotope ratios that differed from that of total particle phase carbon. Fig. 4 shows the change of the carbon isotope ratio of the reactant, β -pinene, and nopinone, an important product of β -pinene ozonolysis as function of precursor processing. Overall, the observations show reasonable agreement with model predictions based on the KIE for β -pinene ozonolysis. Nevertheless, there is a small difference between prediction and observation, which is currently not understood.

5. Isotope ratios of OTC source emissions and atmospheric VOC

The available literature on isotopic composition of OTC in the gas and particle phase is summarized in parts 5.1 and 5.2, respectively. We first discuss current understanding of isotopic composition from different source types at emission, followed by ambient observations. As stated before, most of the available data focusses on $\delta^{13}\text{C}$ with less information available for stable H, N, and O isotopes.

5.1. Gas phase observations

Emissions. An overview of the carbon isotope ratios for a wide range of VOC is shown in Fig. 5. The carbon isotope ratios for different VOC cover a wide range, but for several groups of VOC and for some of the most important sources, some simple principles can be seen. For many NMHC, isotope ratios of emissions from combustion type sources, such as internal combustion engines or biomass burning, are close to that of the parent material. Ethane, propane, benzene and toluene emissions have carbon isotope ratios that seldom differ by more than two per mill from the bulk fuel. For more reactive NMHC, the difference seems to be larger. In some cases, the emissions are several permil heavier than the parent material. The most striking difference is seen for ethyne, which is typically enriched by 15–20‰ compared to the fuel. This enrichment in ^{13}C has been tentatively explained as reservoir effect, i.e. as ^{13}C enrichment due to partial degradation of NMHC in the combustion zone following formation.

Carbon isotope ratios of VOC in industrial emissions as well as many industrially produced VOC cover a wide range. For some HVOC, carbon isotope ratios often differ by more than 5‰ between manufacturers [82]. This is partly due to differences in industrial processes. Moreover, the use of raw materials with very different carbon isotope ratios, such as natural gas or crude oil, has a significant impact.

Carbon isotope ratios of isoprene emitted from vegetation is typically depleted by about 2‰ compared to leaf carbon [82,83]. This might be associated with an isotopic discrimination during the rate-limiting step in the isoprene synthesis from recently assimilated photosynthate [84]. However, engagement of an alternative carbon source due to stress can significantly change the carbon isotope ratio of VOC emissions from vegetation. For example, isotope ratios for isoprene and some OVOC emitted from damaged plants, were reported to differ by more than 10‰ from those of intact plants [26].

The carbon isotope ratios of methyl halide emissions cover an extremely wide range of nearly 100‰. Some of this variability can be ascribed to differences between specific source types such as production by higher plants and biomass burning. However, even within one source category, isotope ratios of emissions can vary substantially. For example a range of about 20‰ for carbon isotope ratios of methyl chloride emitted from different species of higher plant was reported [85].

The number of measurements of hydrogen isotope ratios for VOC emissions is much smaller than for carbon isotope ratios. The ranges of δD values shown in the lower part of Fig. 6 therefore may not be representative for the different types of sources. Nevertheless, the results from different studies show reasonable consistency, although the range covered by the observations is substantial. Benzene in exhaust from gasoline engines mostly has δD values in the range of –40‰ to –140‰. The only study of δD for NMHC in exhaust from Diesel engines [42] reports substantially heavier values around 0‰, which may provide the possibility to differentiate between exhaust from Diesel and gasoline engines. Combining δD with $\delta^{13}\text{C}$ will increase the possibility to distinguish between different VOC sources [43], but the currently very limited

information on δD measurements for VOC emissions is insufficient to draw generally valid conclusions at this stage.

Atmospheric observations. The number of carbon isotope ratio measurements for atmospheric NMHC is substantial (Fig. 6). For many NMHC, there is a reasonable understanding of the factors that determine their carbon isotope ratios in the atmosphere. The similarity in the carbon isotope ratio for many important sources of NMHC severely limits the possibility to use $\delta^{13}\text{C}$ measurements of atmospheric NMHC for source apportionment studies, or to constrain atmospheric NMHC budgets. However, it was realized that this allows to use the change in carbon isotope ratio resulting from atmospheric reactions of NMHC to gain information on the photochemical history of NMHC [12].

As long as the change in isotope ratio due to VOC sources with different isotope ratios is small compared to the change resulting from atmospheric reactions, the difference in isotope ratio between sources ($\delta_{\text{R}}^{13}\text{C}$) and VOC that have been subject to atmospheric reactions ($\delta_{\text{R}}^{13}\text{C}$) can be expressed by a simple equation: $\delta_{\text{R}}^{13}\text{C} = \delta_{\text{R}}^{13}\text{C} + k_{\text{OH}}\varepsilon_{\text{OH}}[\text{OH}]_{\text{av}}t$. Here, k_{OH} is the rate constant of the VOC oxidation reaction by OH-radicals, ε_{OH} is the kinetic isotope effect of this reaction and $[\text{OH}]_{\text{av}}$ is the average OH-radical concentration for the time t between VOC emission and observation. It has become customary to use the term ‘photochemical age’ for $[\text{OH}]_{\text{av}}t$. Strictly speaking, the photochemical age is $\int [\text{OH}]dt$, but for simplicity, the average OH-radical concentration $[\text{OH}]_{\text{av}} = \int [\text{OH}](dt/t)$ is used. It has been shown that even in the case of mixing of air masses with very different photochemical ages, this is a valid approximation for the photochemical age of the studied VOC [13]. In principle, this approach can be used for all types of atmospheric reactions and different isotopes. Yet, most of the currently available studies employ carbon isotope ratio measurements to investigate VOC processing by OH-radicals. Using this concept, photochemical history and origin of several light alkanes, benzene and toluene have been investigated on regional and hemispheric scales [13,24,25]. There are also a few studies using global numerical model simulations for the interpretation of $\delta^{13}\text{C}$ values of atmospheric NMHC [25,97]. It is important to realize that, depending on the reactivity of the individual NMHC, different NMHC represent the photochemical history of the studied air mass for different time scales.

A potential source of uncertainty in the use of isotope ratios to determine the photochemical age of VOC is the unknown isotope ratio variability of VOC emissions. Therefore, it has been suggested to use a combination of hydrogen and carbon isotope ratio measurements to simultaneously investigate the impact of processing and emissions [59]. The basis of this approach is the substantial difference in KIE between hydrogen abstraction reactions and addition for reactions of VOC with the OH-radical. Carbon KIEs for reactions of unsaturated VOC are substantially larger than for abstraction reactions, while hydrogen KIEs for addition are small compared to KIEs for abstraction reactions [59]. Consequently, it can be expected that atmospheric processing will result in larger changes in carbon isotope ratios for unsaturated VOC than for saturated VOC, while for hydrogen, isotope ratio changes will be larger for saturated VOC. However, to our knowledge, there is still no published study on systematic simultaneous measurements of carbon and hydrogen isotope ratios of atmospheric VOC.

The carbon isotope ratios of several HVOC, including some chlorofluorocarbons (CFC), have been investigated primarily with the intention to gain new insight into their atmospheric budgets [28,47,94,98]. Many HVOC, such as methyl chloride and CFCs, have long atmospheric residence times, which results in atmospheric distributions with only small spatial and temporal variability in the troposphere. Moreover, CFC emissions have been drastically reduced during the last decade as consequence of the Montreal Protocol and its amendments. It is therefore expected that in the troposphere CFCs and other HVOC of low reactivity will exhibit

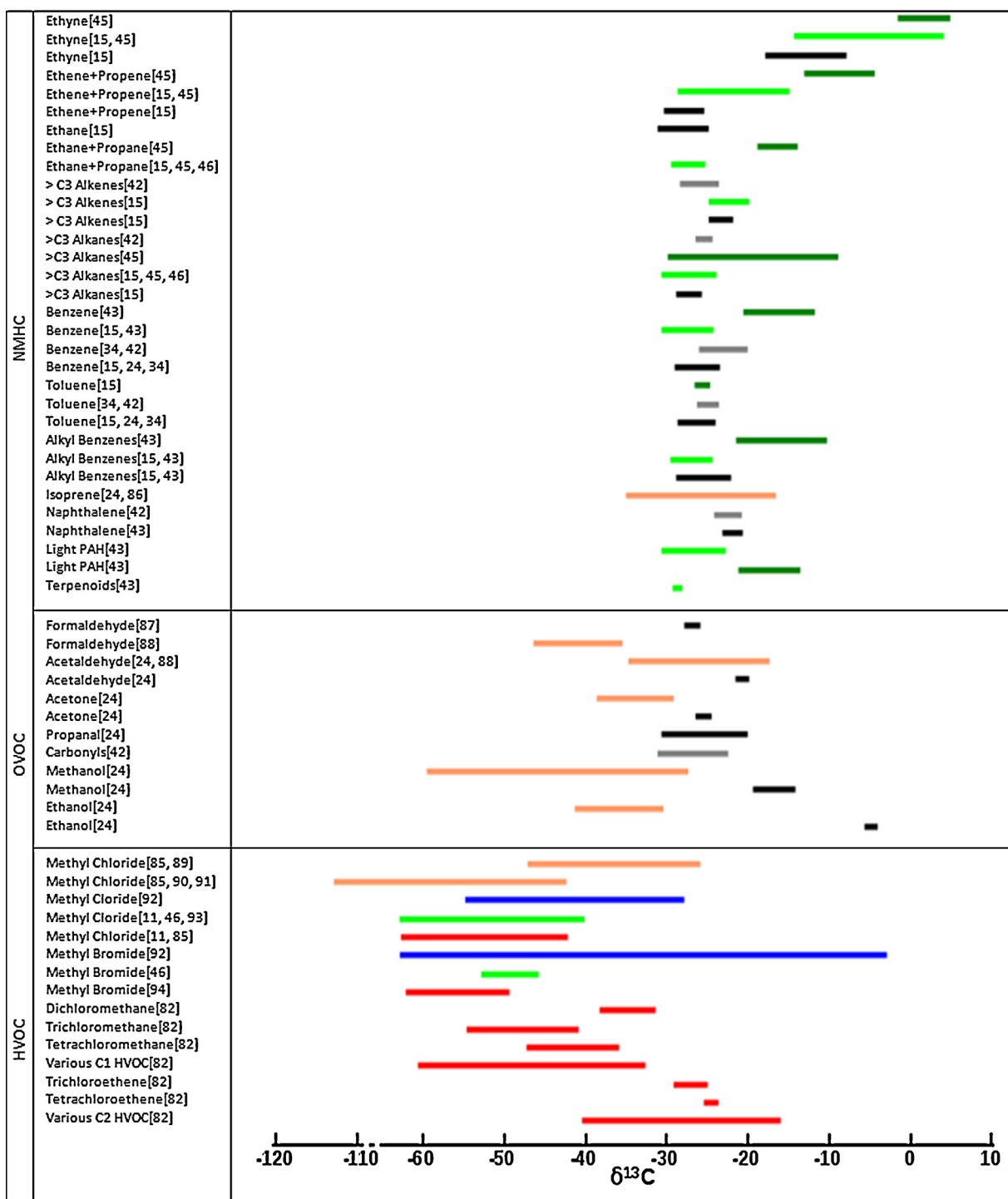


Fig. 5. Summary of $\delta^{13}\text{C}$ measurements of non-methane hydrocarbon (NMHC), oxygenated VOC (OVOC), and halogenated VOC (HVOC) from different source types. Maximum observed $\delta^{13}\text{C}$ ranges are color coded for emissions types: C3 (light green) and C4 (dark green) biomass burning, traffic and engine/car emissions (black), stack emissions (gray), biogenic emissions (light red), salt marsh (blue), and industrial production (dark red). See refs. [86,88–93].

little spatial variability in isotope ratios. In this case it is possible to derive representative averages from a limited number of measurements [47]. Indeed, measurements of the carbon isotope ratios of atmospheric CFC12 (CF_2Cl_2), CFC11 (CFCl_3), CFC113 ($\text{C}_2\text{F}_3\text{Cl}_3$) and methyl chloride by several research groups [11,30,47,95,99] provide reasonably consistent and representative averages. However, the large range for carbon isotope ratios of CFC and methyl chloride emissions currently limits the value of carbon isotope ratio measurements to constrain their atmospheric budget. The

long term trend in carbon isotope ratios of atmospheric CFC12 was determined from measurements in firn air samples [100]. Based on these measurements, the authors conclude that during the last 50 years, the $\delta^{13}\text{C}$ value of atmospheric CFC12 changed drastically. The authors explain this by a change in the carbon isotope ratio of CFC12 emissions.

There are only very few δD measurements for atmospheric VOC. The δD values of benzene and toluene were measured at three roadside locations in Japan [44]. The authors report that for both

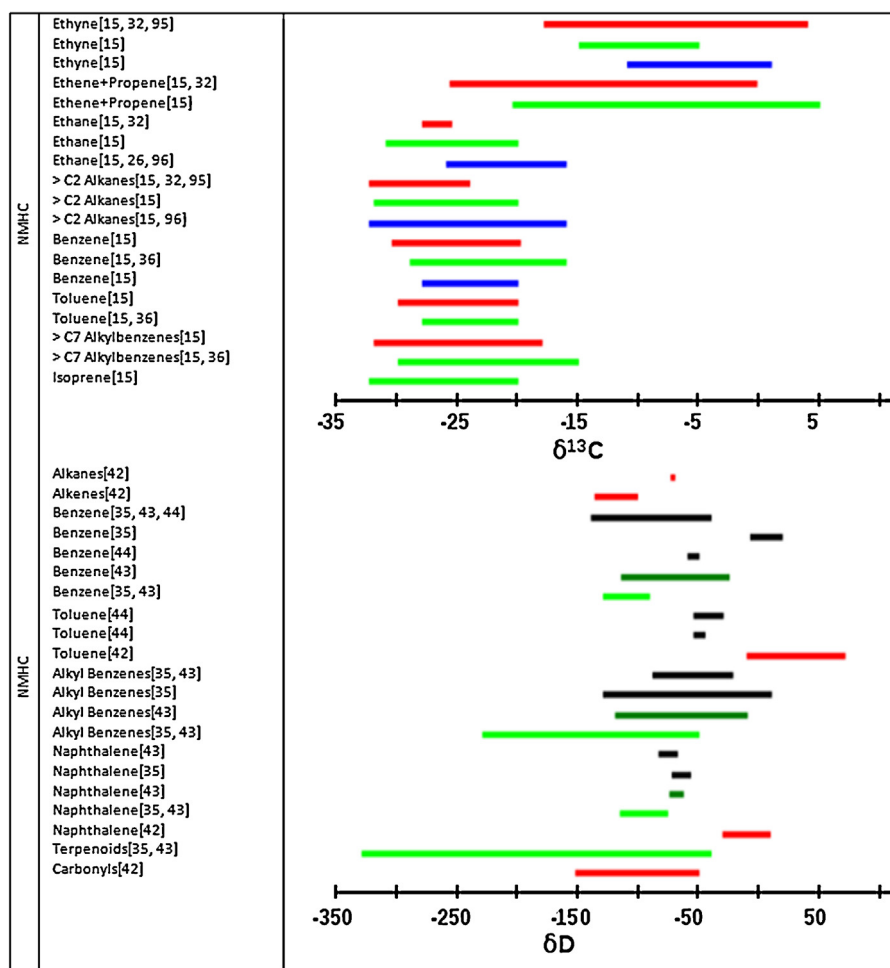


Fig. 6. Observed $\delta^{13}\text{C}$ (upper panel) and δD (lower panel) of VOC, presented for the full range of ambient measurements. $\delta^{13}\text{C}$ values are depicted color coded for different environments (urban (red), rural (green) and remote (blue)). The bar colors for δD measurements differentiate major sources of the sampled NMHC: C3 (light green) and C4 (dark green) biomass burning, engine/car emissions (black) and industrial production (dark red). See ref. [96].

compounds the measured δD values covered a range of about 100%. The difference in isotope ratio between different samples exceeded the estimated uncertainty of the measurements. However there was no systematic difference between the three sampling sites and the reason for the substantial variability of the measured δD values could not be identified.

Also δD and $\delta^{13}\text{C}$ of atmospheric formaldehyde was measured at an urban location (Seattle, U.S.) [87]. A strong negative correlation between δD and the concentration of formaldehyde was observed. In contrast, no correlation was observed between $\delta^{13}\text{C}$ and the concentration. Due to technical reasons, the δD measurements were made during a different time period than the $\delta^{13}\text{C}$ measurements. The $\delta^{13}\text{C}$ covered only a period of one month and therefore, direct comparison of the δD and $\delta^{13}\text{C}$ measurements was not possible. Nevertheless, these results demonstrate the potential of combined δD and $\delta^{13}\text{C}$ for studies of the atmospheric chemistry of VOC.

For some VOC sources, the net impact on the atmospheric VOC budget is the result of a combination of emission and deposition. In this case, the net emission rate will depend on the atmospheric VOC concentration. An interesting example is the existence of ‘compensation points’ for emission of some OVOC from vegetation, although the same fundamental principles apply to all net sources or sinks that result from a combination of deposition and emission processes. In these cases, contributions to atmospheric budgets are often based on the combined effects of emission and deposition in the form of a net emissions or deposition rate. However, the

impact of bidirectional exchange on the isotope ratio will depend on the KIE for the deposition process, ambient VOC concentration and their isotope ratio, as well as on the isotope ratio of the emission. Consequently, emission and deposition processes have to be considered separately in order to correctly determine the impact of bidirectional exchange on ambient isotope ratios. While this complicates the interpretation of ambient isotope ratios, it also opens the possibility of using isotope ratio measurements to separate the net effect of a combination between emission and deposition fluxes into individual contributions.

5.2. Particle phase observations

Particle phase observations can be grouped into *bulk measurements*, investigating total carbon (TC), organic carbon (OC), or subgroups such as the water soluble (WSOC) and water insoluble (WINSOC) organic carbon fraction, and *compound specific measurements*, investigating individual tracer and marker molecules of primary and secondary origin. In the following we review the particle phase observations, starting with bulk measurements and continuing with observations of primary and secondary compounds, respectively.

An overview of observations of $\delta^{13}\text{C}$ in ambient aerosol is presented in Fig. 7. The most common applications of organic aerosol isotopic analyses explore the *bulk measurement* of total carbon (TC), or fractions of the particulate matter such as elemental and organic



* only with odd C number

Fig. 7. Observed $\delta^{13}\text{C}$ values for ambient aerosol sampled in different environments. Values are presented to report the full range of observations for different compound classes. For reference typical values of TC $\delta^{13}\text{C}$ of source aerosol originating from combustion of different fuels are shown as vertical bars for C3 [119] and C4 [119] plant material (green), fossil fuels [103,119,137] (gray) and dung cakes [137] (brown). Bulk measurements such as total carbon (TC), water soluble organic carbon (WSOC), water insoluble organic carbon (WINSOC), total elemental and organic carbon (TE and TOC, respectively) are given as black bars covering the full range of values reported in the literature. Compound specific measurements of primary emitted organic species are shown in blue (odd N-alkanes) and green (low and high molecular weight (LMW and HMW, respectively), fatty acids), whereas compound specific measurements of secondary products are reported in red. See refs. [120,123,127,130,132,134].

carbon (EC and OC, respectively) and water soluble and insoluble organic carbon (WSOC and WINSOC, respectively). This technique has been successfully employed to better understand the contributions of marine and continental sources at remote oceanic sites [101,102], to differentiate fossil fuel combustion types in big cities [103,104], or the C3, C4 and CAM plant origin of primary organic aerosol (e.g. [105,106]). To enhance the understanding of carbon cycling between different pools, from the plant- to atmosphere scales, reference materials on $\delta^{13}\text{C}$ of bulk tissues or chemical compounds extracted from plants were developed [57,107–109] and references therein]. Accordingly, $\delta^{13}\text{C}$ values are deployed for source apportionment, using a two-component mixing equation with isotopic end-member values from the literature [110]. Additionally, TC isotopic measurements investigate seasonal patterns of $\delta^{13}\text{C}$ in organic material to give insights in processes depending for instance on temperature [111,112]. As seen in Fig. 7, for ambient aerosol TC $\delta^{13}\text{C}$ values are found to be in the C3 and fossil fuel source ranges, reflecting their global dominance as a source of primary and secondary aerosol.

Further, Fig. 7 shows that the WSOC fraction of organic aerosol is often found to be enriched in ^{13}C compared to the WINSOC fraction [53,113]. This enrichment could be due to isotopic fractionation throughout the partitioning of semi-volatile organics between gas and particle phase [53] or due to chemical losses of WSOC [36]. Depending on measurement location, $\delta^{13}\text{C}$ of WSOC is found to have a seasonal dependence, e.g. due to seasonality of biogenic sources [114].

Compound specific isotopic analyses (CSIA) of a single or a set of marker compounds by combining chromatography and IRMS are used to investigate sources and long-range atmospheric transport of aerosols. To be considered as marker molecules, the compounds have to fulfil a number of requirements. They need to be chemically stable during atmospheric transport, with both concentration and isotopic composition unaffected by atmospheric oxidation. Individual marker sources should be limited, confined to defined anthropogenic or biological activities and primary only, i.e. not chemically formed in atmospheric reactions. Fig. 7 includes the most prominent biogenic primary marker molecules (N-alkanes, low and high molecular weight fatty acids).

N-Alkanes from higher plants typically have long carbon-chains (C_{25} – C_{35}) with a strong predominance of odd-carbon-number homologues and their carbon isotopic signature has long been used for source apportionment and investigations of aerosol transport in the atmosphere [138–140]. N-Alkane isotopic measurements often reveal $\delta^{13}\text{C}$ values in the range of C3 plant sources, since the alkanes separated from parent plant material are depleted by up to 11‰ compared to the bulk tissue [107]. Thus, long range transport of aerosol from C3 plants is verified with n-alkane isotopic measurements e.g. [110,128]. Seasonal variations in n-alkane isotopic composition can be attributed to seasonal variability of C3 and C4 contributions to aerosol collected far from primary source areas e.g. [110].

High molecular weight (HMW) *fatty acids* are also good tracer for leaf wax contribution to aerosol. As seen from Fig. 7, low molecular weight (LMW) fatty acids consistently show higher $\delta^{13}\text{C}$ values compared to the HMW molecules, suggesting their common sources and transport pathways [126,131]. Bimodal fatty acid distributions with maxima at C_{16} and C_{26} , with lower $\delta^{13}\text{C}$ values for C_{26} acid, indicating its C3 terrestrial plant source, were reported for semi-urban aerosol collected in Hokkaido [52], Japan, as well as for aerosol sampled in Northern Japan [116].

Due to the impact of biomass burning on the global aerosol burden [141], the polycyclic aromatic hydrocarbons (PAH) and monosaccharide derivatives from the breakdown of cellulose (such as levoglucosan and its isomers) represent valuable organic markers. Due to its atmospheric stability *levoglucosan* is hitherto

the most used molecular tracer for biomass burning processes. It is also emitted in large quantities and combustion of biofuels is its only identified source. Stable carbon isotope ratio analysis of levoglucosan has so far been performed for source aerosol from C3 plant combustion only [50]. It was found that carbon isotope fractionation during the combustion, defined as $\Delta = \delta^{13}\text{C}_{\text{holocellulose}} - \delta^{13}\text{C}_{\text{levoglucosan}}$ was on average -1.89% , making $\delta^{13}\text{C}$ measurements of levoglucosan in ambient aerosol a promising tool for the source and atmospheric stability characterization of levoglucosan. To the best of our knowledge, no such measurements have been published to date.

PAH are formed during both incomplete combustion of fossil fuels and pyrolysis of organic materials. The isotopic composition of PAH in ambient aerosol varies from -12.9 to -32.5% [142–145] with the main source identified to be fossil fuel burning for which $\delta^{13}\text{C}$ varies with the fuel type [146]. A review of fossil fuel burning aerosol related PAH was recently presented [51]. Overall, it is found that while the isotopic composition of the parent plant material is preserved in the PAH generated from lignin during burning [147], ambient observations of smoke haze indicate that PAH mainly originated from automobile exhaust, even during episodes with strong fire events [143].

LMW dicarboxylic acids (DCA) can arise from primary sources (e.g. incomplete combustion of fossil fuels and biomass burning), but their main source is formation in the atmosphere. Therefore DCA are commonly used as tracers for SOA. LMW diacids can further be oxidized in the aqueous phase by OH radicals or NO_3 . Therefore, contrary to the biomarkers, the isotopic composition of these reactive organic compounds undergoes changes due to the KIE of their reactions, thus giving information on the extent of their atmospheric processing. Depending on measurement location, $\delta^{13}\text{C}$ of DCA indicates either local secondary production [129] or transport of aged aerosol [117,118], being not affected by local photochemical processes. Increasing $\delta^{13}\text{C}$ values in oxalic acid and other dicarboxylic acids from mid-latitudes toward the equator imply aerosol aging [136], as does the overall higher $\delta^{13}\text{C}$ of C2 DCA compared to higher DCA (see Fig. 7). For a full understanding of regional and size distribution dependence of the DCA isotopic composition [121], laboratory kinetic data of isotope effects are needed. Such information is currently not available. The $\delta^{13}\text{C}$ values of glyoxal and low molecular ketoacids (ωC_2) are close to those of the oxalic acid (Fig. 7). This indicates a close link among these compounds in their photochemistry [117]. Overall, a wide range of variability in the isotopic composition of DCA can be seen in Fig. 7. This emphasizes the combined role of these compounds as products, but also as precursors in atmospheric chemistry [121].

The stable carbon isotopic composition of *2-methyltetrols*, marker compounds of the photooxidation of isoprene, was determined in ambient aerosols from the Changbai boreal mountains and the subtropical region of Dinghu [133]. The measured carbon isotope ratios were in the range of -24 to -29% . The authors suggest that the isotope ratio of the methyltetrols can be used “as an indicator of proportions of C3 to C4 plants in vegetation”. However, the only known KIE in the reaction sequence resulting in formation of 2-methyltetrols is the initial step, the reaction of isoprene with OH-radicals or ozone [59,64]. Furthermore, the isotope ratio of isoprene reaction products will depend on the extent of precursor processing. In the absence of such information it is difficult to draw firm conclusions about the carbon isotope ratio of isoprene emissions.

Stable hydrogen and nitrogen isotopic investigations are used complementarily to the stable carbon isotope measurements. δD of n-alkanes in bulk plant materials were measured [57,108,148], offering references to interpreting ambient aerosol measurements. Contrary to stable carbon isotopic composition, δD values represent no diagnostic discriminator for C3, C4 and CAM plants

but correspond to the isotopic differences of water inside living organisms. δD studies of n-alkanes can therefore be employed in investigations of source regions, as proxy of temperature and relative humidity. Combined $\delta^{13}C$ and δD measurements of individual n-alkanes in aerosol from urban and remote areas have recently been performed [115]. Good negative correlation between δD and carbon preference index (CPI) of the isolated long-chain n-alkanes allows eliminating fossil fuel contribution from the samples, using a simple mass balance approach.

$\delta^{15}N$ of ambient aerosol are to the best of our knowledge performed for total nitrogen (TN) only, i.e. including both inorganic and organic nitrogen. Comprehensive studies, including ambient as well as source $\delta^{15}N$ and $\delta^{13}C$ values of bulk plant material [124,125,149] or e.g. cow-dung [122,150], together with NH_4 and NO_3 measurements, can indicate the major aerosol sources such as e.g. continental versus marine N-sources [135,137]. Nitrogen isotopes furthermore serve as process tracer helping to constrain the origin of primary and secondary N-production in aerosol [151].

Finally, sulfur stable isotopes can give information on dimethyl sulfide (DMS) fluxes in remote environments. Since sulfate and sulfuric acid aerosols are important contributors to the global radiation budget, understanding the role of DMS as source of atmospheric sulfate is essential. Methanesulfonic acid (MSA) is considered to be a specific organic marker for aerosol of biogenic marine origin, since it is formed only by DMS oxidation. Hitherto, $\delta^{34}S$ was measured either for total sulfur (MSA and SO_4) [152] or compound specifically for MSA alone [153] in ambient aerosol. The latter method might be employed to investigate whether the isotope fractionation is selective for the competing DMS oxidation pathways, leading either to MSA or to SO_2 .

6. Conclusions

There is a significant number of studies that demonstrate the value of stable isotope ratio measurement for investigating the atmospheric chemistry of OTC. It seems save to conclude that isotope ratio measurement is no longer an emerging approach but a proven tool to study atmospheric chemistry and budgets of OTC. Source discrimination and determination of photochemical age are possible by isotopic composition measurements of individual OTC in gas or particle phase. Nevertheless, there are currently several limitations that hinder the use of the full potential of this approach. Part of current limitations originate from the lack of basic information, such as detailed studies of emission sources or KIE for reactions of atmospheric relevance, information that is essential for meaningful interpretation of atmospheric measurements of OTC isotope ratios. The methodology to make these measurements exists and it seems safe to predict that, either using existing instrumentation or new developments, the available pool of information will keep growing. As far as atmospheric observations are concerned, there are significant challenges, many of them resulting from the necessity to conduct accurate measurement of isotope ratios at very low concentration in samples of complex composition. Here method development to increase sensitivity, selectivity and accuracy will be very valuable.

Moreover, most of the data available to date is restricted to the measurement of stable carbon isotopic composition. While source signatures of $\delta^{13}C$ differ significantly for some of the oxygenated and halogenated gas phase VOC, large overlap exists for alkanes and alkenes. Here, the use of dual or multiple isotope analysis will provide additional source constraints, but the approach of studying multiple heteroatom isotopic composition has not yet been exploited in atmospheric studies. Prerequisite for the applicability of such an approach is the availability of sensitive and accurate measurement techniques. As measurements of H, N, and O isotopic composition require larger sample amounts and are less precise

than $\delta^{13}C$ measurements [23], efforts are needed for improvements of these measurements for atmospheric OTC.

Any change in the isotopic composition due to e.g. derivatization must be well quantified. Therefore, methods should be developed basing on well characterized standards and internal standards, tracking potential isotopic fractionation throughout the whole sample treatment sequence. They should be used to enhance comparability of observations from different laboratories and analytical procedures. The use of standards to verify measurement procedures is often hindered by the availability of compound specific standards with known isotopic composition and therefore relies on reference gases which in practice characterize the IRMS part of e.g. $\delta^{13}C$ measurements of OTC only. Procedures to use internal standards which track the whole sequence of atmospheric observation from sampling to sample handling through chromatographic separation and IRMS are needed for full method evaluation and would strongly enhance comparability of results between individual research groups. This is particularly true for semi-volatile species, where change in phase partitioning during sampling can result in isotopic fractionation, thus deteriorating the results.

While general concepts for the use of KIE in interpretation of ambient OTC isotope composition [12] have been established for more than a decade now, the available data is still restricted to $\delta^{13}C$ and few δD observations in a relatively small set of gas phase reactions (see Fig. 3 for a summary). Potential effects of temperature on KIE are even less well characterized [63] and no study is available to date that determines KIE for condensed phase reactions, which could play a role in chemical aging of particle phase OTC.

As detailed here, at the current state, atmospheric gas or particle phase OTC are sampled and analyzed for isotopic composition offline. This routine is due to the fact that current IRMS instrumentation is not field deployable. As sampling and sample storage may introduce isotopic fractionation, in situ analysis of OTC isotope ratios would not only minimize the risk of artifacts but also greatly enhance data coverage. This could be achieved by further development of GC-IRMS or GC-qMS into field deployable instrumentation. For small molecules, also optical methods such as FTIR, tunable diode laser spectroscopy or cavity ring down [154] look promising, although significant improvement of sensitivity will be needed before these methods can be applied to isotopic composition measurements of atmospheric OTC.

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