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 δ^{13}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 hydrochlorofluoracarbons 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 $1500\,\mathrm{Tg\,yr^{-1}}$ and $2200\,\mathrm{Tg\,yr^{-1}}$. 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 compounds 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.

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

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 Pedee Belemnite (VPDB) with $\left(^{13}C/^{12}C\right)_{VPDB} = 0.0112372$ [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}):

$$KIE = \frac{k_{12}}{k_{13}} \tag{2}$$