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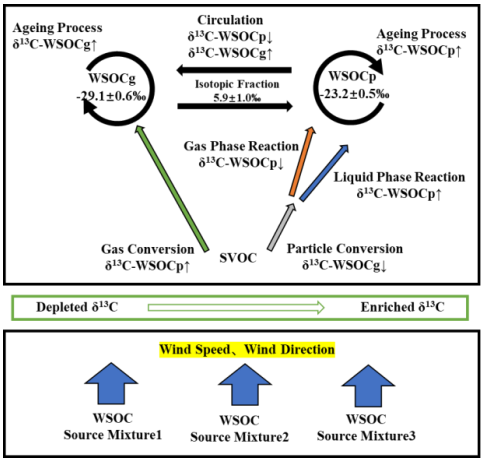
High-resolution observation of stable carbon isotope ratios of water-soluble organic carbon in particle/gas phases at an urban site in China: Using an improved isotope ratio mass spectrometry method

Hao-Ran Yu, Yan-Lin Zhang*, Fang Cao, Xiao-Ying Yang, Tian Xie, Yu-Xian Zhang, Yongwen Xue

[1] School of Applied Meteorology, Nanjing University of Information Science & Technology, Nanjing 210044, China.

[2] Atmospheric Environment Center, Joint Laboratory for International Cooperation on Climate and Environmental Change, Ministry of Education (ILCEC), Nanjing University of Information Science & Technology, Nanjing 210044, China.

TOC:



Key points:

1. Obvious fractionation exists between δ^{13}C-WSOCp and δ^{13}C-WSOCg, and there is obvious diurnal variation of it.
2. Mutual conversion between WSOCp and WSOCg only happens during daytime, but radiation intensity has no effect on the formation mechanism and gas-particle distribution mechanism of WSOC.
3. Gas-particle distribution mechanism of WSOC was restricted by meteorological conditions, precursor gaseous pollutants, gaseous oxidants and acid gases, and is accompanied by the formation of secondary inorganic ion component

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Abstract: A high time resolution synchronous sampling method along with determination of stable carbon isotopes of gaseous water-soluble organic carbon (WSOCg) and particulate water-soluble organic carbon (WSOCp) was realized in this research through equipment modification and method improvement. It was found that WSOCg has significant higher concentration than WSOCp and a more depleted $\delta^{13}C$. Both concentrations of WSOCp and WSOCg have the seasonal variation characteristics of high in winter (WSOCp=15.7±3.9μg/m^3; WSOCg=42.4±6.0μg/m^3) and low in summer (WSOCp=5.9±1.8μg/m^3; WSOCg=25.2±5.2μg/m^3), with greater increase in WSOCp (167%) than that in WSOCg (68%). During wintertime, WSOCp and WSOCg had similar daily variation characteristics of concentration, and opposite daily variation characteristics of $\delta^{13}C$. WSOCp had a bimodal distribution with obvious low value at sunrise and sunset, while $\delta^{13}C$-WSOCp had a unimodal distribution with low in daytime (-24.6±1.1‰) and high in nighttime (-22.3±1.7‰). WSOCg and $\delta^{13}C$-WSOCg had same distribution with high in daytime and (49.3±8.8μg/m^3; -27.9±1.1‰) low in nighttime (38.3±4.6μg/m^3; -29.9±0.4‰). Combining the $\delta^{13}C$ variation characteristics with the synchronous observation results of meteorological conditions, gaseous precursor pollutants, gaseous oxidants, gaseous acids and fine particle components, the restriction factors of WSOC gas-particle distribution mechanism were discussed. The presence of radiation rather than its intensity decided whether generations process of WSOCp and WSOCg are divided, for $\delta^{13}C$-WSOC of two phases showed significant correlation only during daytime. Meteorological conditions, gaseous precursor pollutants, gaseous oxidants and gaseous acids restrict the gas particle distribution of WSOC by affecting the aging process of WSOCp and WSOCg, gas-particle conversion ratio of semi-volatile organic compounds (SVOC) and the gas phase and liquid phase generation ratio of WSOCp. At the same time, the gas-particle distribution process of WSOC is strongly related to the formation of secondary inorganic ions (nitrate, sulfate, ammonium), and the gas-particle distribution between gaseous nitrous acid and nitrite.

Keywords: gas phase, particle phase, WSOC, $\delta^{13}C$.

1. Introduction

Carbonaceous aerosols were considered to be one of the largest sources of uncertainty in the estimation of global radiative forcing in climate change research (Bond, et al., 2013; Pöschl, 2005)，and water soluble organic carbon is an important component of carbonaceous aerosols, which has an important impact on haze formation, human health and the earth's radiation balance. Generally,

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carbonaceous aerosols include organic carbon (OC), elemental carbon (EC) and carbonate carbon (CC) aerosols. For the content of CC is generally low (<5%) and its properties are relatively stable, research of atmospheric environment and climate mainly focuses on EC and OC, which can account for 20-50% of the mass concentration of $PM_{2.5}$(Pöschl, 2005). According to the water solubility of OC, it can be divided into water insoluble organic carbon (WIOC) and water-soluble organic carbon (WSOC). Most of WSOC comes from biomass burning or secondary organic aerosol (SOA)(Kondo, et al., 2007; Weber, et al., 2007), mainly contains dicarboxylic acids, ketoacids, dicarbonyl compounds, long-chain fatty acids and short-chain monocarboxylic acids, which can contribute 20-80% of OC mass concentration. However, there exist quite different distribution characteristics of WSOC in different regions(Fu, et al., 2013; Ho, et al., 2006; Miyazaki, et al., 2006; Wang, et al., 2012).

The formation of WSOC is closely related to gas-particle distribution, emission source and meteorological conditions. The synchronous study on particle phase of WSOC (WSOCp) and gas phase of WSOC (WSOCg) is helpful to understand the sources and atmospheric process of SOA. Though WSOCp was considered to characterize SOA to some extent when the direct contribution of biomass combustion can be neglected(Kondo, et al., 2007; Weber, et al., 2007)，more and more evidences showed an important contribution of WSOCg to the generation of SOA.。Similar to WSOCp, WSOCg can be generated from secondary conversion of VOCs, in addition to the direct emission such as biomass burning and fossil fuel combustion(Carlton, et al., 2009; Liu, et al., 2012; Liu, et al., 2012; Meng, et al., 2014). There is evidence that VOCs emitted from natural or man-made sources can be oxidized to WSOCg in the atmosphere (Carlton and Turpin, 2013; Sareen, et al., 2017), and liquid phase reaction of WSOCg absorbed by cloud water or aerosol liquid water is one of the important ways to formation of SOA(Liu, et al., 2012). In addition, a large part of the intermediate products of isoprene oxidation, which was considered to be the most important precursor of SOA, can constitute WSOCg, including glyoxal, methylglyoxal, and isoprene epoxydiol, and some low molecular organic acids (such as formic acid and acetic acid) (Carlton, et al., 2009; El-Sayed, et al., 2015). However, there is still great uncertainty in assessing the contribution of natural and man-made sources to WSOCg under the background of compound atmospheric pollution. Only qualitative or semi quantitative calculation can be carried out by means of characteristic molecular markers, while the results based on model simulation are limited by the

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understanding of atmospheric mechanism and lack of direct observation evidence for verification.

Previous researches had studied on gas-particle distribution mechanism of WSOC by synchronously measuring the concentration of WSOCp and WSOCg. The research in Atlanta reported that the WSOCg in summer ranged from 1.1 to 73.1 μgC m^{-3}, average 13.7μgC m^{-3}, which was obviously higher than WSOCp (3.3±1.8μgC m^{-3}), but had a certain linear correlation with WSOCp (Hennigan, et al., 2009)。Later，research in Atlanta and Los Angeles found that WSOCp and WSOCg had similar diurnal variation rules, and both reached the highest value after noon (about 14:00), .indicating important contribution of secondary reaction(Zhang, et al., 2012). It was also found that difference of precursors may lead to the change of WSOC in the gas-particle distribution relationship. The variation of WSOCp in Atlanta was controlled by the aerosol liquid water content (ALWC) under the influence of humidity, which was similar to WSOCp in Chongming island, China(Lv, et al., 2022). While variation of WSOCp in Los Angeles was independent of ALWC, but depended on OC concentration(Zhang, et al., 2012). Similarly, variation of WSOCp in Prague was found to depend on TC in gas phase. There may be obvious regional differences in the gas-particle distribution relationship of WSOC.

Stable carbon isotope ratio ($^{13}C/^{12}C$, $\delta^{13}C$) can provide important information about the sources and atmospheric chemical conversion processes of carbonaceous aerosols. $\delta^{13}C$ was generally used to distinguish sources of carbonaceous aerosols, such as C3 and C4 plant, vehicle exhaust, coal combustion and other fossil sources(Cao, et al., 2011). However, $\delta^{13}C$ has a mass dependent isotope fractionation phenomenon, leading an isotope variation apart from effects of sources. The secondary reaction of VOCs to generate SOA is an important source of WSOCp(Kondo, et al., 2007; Weber, et al., 2007), and aerosols formed by VOCs usually have a more depleted $\delta^{13}C$ than the precursor(Anderson, et al., 2004; Rudolph, et al., 2003; Rudolph, et al., 2000). For example, isotope fractionation in the process of biosynthesis of isoprene will lead to $\delta^{13}C$ of isoprene 2.6 ± 0.9 ‰ smaller than it in blade(Rudolph, et al., 2003). The main scavenging pathway of VOCs is its reaction with OH radical and ozone, and these atmospheric oxidants tend to react with VOCs depleted $\delta^{13}C$ (reverse dynamic isotope effect), resulting in the $\delta^{13}C$ enrichment of residual VOCs in the atmosphere and $\delta^{13}C$ dilution of particles as oxidation products(Anderson, et al., 2004; Rudolph, et al., 2003; Rudolph, et al., 2000). Some studies have also shown that $\delta^{13}C$ will be enriched in particles during ageing process, such as process in which binary acid reacts with OH and is removed in the

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form of CO_2/CO(Aggarwal and Kawamura, 2008; Noziere, et al., 2015; Pavuluri, et al., 2011; Wang, et al., 2012; Zhang, et al., 2016). Measurement based on high time resolution observation of δ^{13}C-WSOCp and δ^{13}C-WSOCg will provide a new perspective for deep understanding of the whole life cycle of WSOC.

2. Data and methods

2.1 Sampling and chemical analysis

The two phases WSOC samples were collected from 4 to 14 December of 2021 in Nanjing, a megacity in eastern China. The sampling site is located at the agrometeorological station of Nanjing University of Information Science and Technology, which is close to a busy traffic road and surrounded by a large number of industrial factories. The WSOC mass concentration was measured with the total organic carbon analyzer (TOC-L, Shimadzu, Japan), analyzed along with peak area signal of isotope ratio mass spectrometer (MAT253, Thermo Fisher Scientific, USA). Six anions (F^-, Cl^-, NO_2^-, NO_3^-, $SO_4^{2-}$and PO_4^{3-}), five cations (Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+}) and three organic acids (formic, acetic, and oxalic acids) were measured using the ion chromatography system (IC-5000, Thermo Fisher Scientific, USA). The $PM_{2.5}$ and pollution gas concentration were observed at Pukou environmental supervising station, and the meteorological data was observed at Pukou meteorological station. The radiation data are from the shared data of the comprehensive meteorological observation base of Nanjing University of Information Science and Technology. During 3 June and 13 July of 2021, 202 samples were collected with ions and WSOC concentration analyzed, which was used as summer data compared with winter mass concentration.

A wet annular denuder (WAD) combined with scrub and impactor aerosol collector (SCI) (IGAC, Machineshop, Taiwan, China) was used for water-soluble organic carbon collecting. .Based on the principle of gas diffusion, gas phase of WSOC was absorbed and washed away by the absorption liquid flowing through the pipe wall of WAD. The steam generated by the SCI will capture the particle phase of WSOC by collision and condensation after that, and the sample will be collected by inertial impact in liquid form. A very sharp cut cyclone (VSCC) was set in the entrance of to filter particles above 2.5μm. WSOCp and WSOCg samples were collected in glass tubes by an automatic rotating device at the end of system. The system can collect 20mL WSOCp and 20mL

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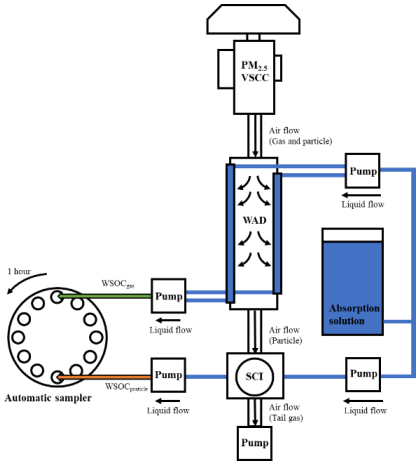
143 WSOCg samples from 1 m^3 of air every hour. The system pipeline should be flushed with ultrapure
144 water for one week before each sampling to reduce blank pollution, and the glass tubes were
145 prebaked at 450°C for 6 h before use. Blank pollution of WSOC accounted 8% of average WSOCp
146 and 3% of average WSOCg. To analyze filter-based WSOCp, $PM_{2.5}$ aerosol samples were also
147 collected onto quartz fiber filters which were prebaked at 450 °C for 6 h using an automatic sampler
148 (DHA-80, Digital, Switzerland). Sampling flow rate was 500L/min and the time resolution was 1 h.
149 Daily average of filter-based WSOCp accounted for 81% of WSOCp determined by IGAC system.
150 It was similar to a percentage of 89% in a study using IGAC system at Chongming island(Anderson,
151 et al., 2008). It may accounted to the speciation of the sampled organic gases which resulted in the
152 variation in denuder efficiency(Anderson, et al., 2008). However, the lower WSOCp sampling
153 efficiency of denuder compared with filter is still hard to explain, for evaporation loss of OC,
154 especially volatile and semi volatile carbonaceous components, was proved to happen on filter
155 surfaces(Lewtas, et al., 2001; Yang, et al., 2021). It is considered that the denuder had passive
156 sampling capability of WSOC, but it's hard to estimate the artifacts accurately for there was a
157 variation of passive sampling along with pollution level(Jingyue, et al., 2010).



158
159 Fig 1. High resolution WSOCp and WSOCg synchronous sampling device
160
161 2.2 Stable carbon isotope analysis
162 δ^{13}C-WSOC values were analyzed with a GasbenchII-IRMS system. Due to the low content of
163 WSOC in liquid samples, an improved method was used for determination of δ^{13}C in this study,

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mainly included pretreatment improvement and instrument transformation. Subsequent data analysis used person correlation analysis.

2.2.1 Sample pretreatment and isotope determination

The wet oxidation method was used to pretreat the samples in order to convert WSOC to CO_2。It took 4mL filtered liquid sample (0.22μm, Hydrophobic PTFE needle filter), along with 1mL acidifier (100μL 85% phosphoric acid, soluble in 100mL Milli-Q water), standing for 1h in order to remove WSIC (HCO_3^-, CO_3^{2-}). Otherwise, WSIC may cause a isotope fractionation of about 0.2 ‰(Suto and Kawashima, 2018). Oxidizer was prepared by 1g potassium persulfate ($K_2S_2O_8$, 99.99%), 50μL of phosphoric acid (H_3PO_4, 85%) and 100mL of Milli-Q water. It took 0.5mL of oxidizer injected into a 12mL pre-purged sealed headspace bottle (100mL/min high purity helium purging for 1 min). 2mL liquid sample was then injected into headspace bottle, and heated in sand bath with 100℃ for 1h. It took 6h to wait for complete condensation of water vapor after sand bath to avoid leakage of headspace bottle or damage of IRMS.

CO_2 blank in headspace bottle mainly came from three parts, OC of oxidizer/acidifier(Fisseha, et al., 2006), CO_2 dissolved in Milli-Q water and residual air CO_2 during purging. During the CO_2 blank test, the signal response of the mass spectrometer to samples was controlled to be 80 area/μgC. Compared with helium purging under liquid level after sample injection, a method of helium purging before sample injection could effectively eliminate the impact of residual CO2 in the air (<2area). In addition, CO_2 blank signal would increase around 10area (about 0.1μgC) with each 50mg increase of $K_2S_2O_8$. And CO_2 blank signal would increase around 20area (about 0.25μgC) with each 1mL increase of liquid in headspace bottle. In contrast, CO_2 blank is more affected by liquid content. And this part of CO_2 blank couldn't be controlled by He purging or pre-heating. By controlling the sample volume, reducing the oxidant concentration and injection volume, the total CO_2 blank signal finally reached around 30area (about 0.3μgC), approximately 19% of the average carbon content of WSOC sample.

The Gasbench-IRMS system and determination method were improved in this method. The system used high-purity helium as carrier gas. Sample gas was pushed through the water trap (magnesium perchlorate) and VOC trap in the preconcentration unit (Precon) by helium at a pressure of 1.7bar. After 260s of freeze enrichment and impurity removal in liquid nitrogen trap, helium at a pressure of 0.6bar was switched by rotating of six-way valve in Precon, pushing sample gas into gas

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chromatographic column (Polra PLOT Q) to separate N_2O and CO_2. Back purge valve of front pipeline was open at the same time to purge the sample injection pipeline. Finally, sample gas entered IRMS for $\delta^{13}C$ determination after water removal through a Nafion permeation tube. It took a total of 24min in this method, and the determination accuracy can reach 0.25 ‰ above 1μgC, can reach 0.53 ‰ above 0.5μgC.

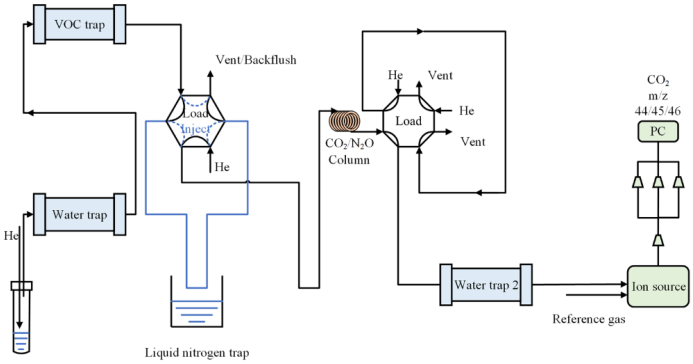

Fig 2. Stable carbon isotope ratio determination system

3. Results and discussion

3.1 Improvement of determination method

Determination limit was improved to less than 5μgC in this study(Zhang, et al., 2019). However, determination values have obvious peak area independence in this range of carbon content (Fig. 3a). Based on the consideration of drug solubility in water, three working standards were used in this study in order to establish the standard curve between true value and determination value (Fig. 3b): potassium hydrogen phthalate (KHP) and two kinds of sucrose (Suc-1 and Suc-2) with different $\delta^{13}C$. The carbon isotope composition of these three standards is analyzed by combustion method, using an elemental analyzer combined with an isotope ratio mass spectrometer (EA-IRMS, Thermo Fisher Scientific, USA), as follows: -12.08‰ (Suc-1), -24.83‰ (Suc-2), and -30.62‰ (KHP). This range of $\delta^{13}C$ values is able to cover the majority of the $\delta^{13}C$-WSOC values in ambient air samples. Standards were resolved in Milli-Q water (resistivity 18.2MΩ) to make standard solutions of a carbon content of 0.5, 1, 2 and 4 μg in 2mL standard solution to test the procedures during the pretreatment. What's more, it was found in this study that over-heated oxidant would cause severe dilution of $\delta^{13}C$ in standard samples.

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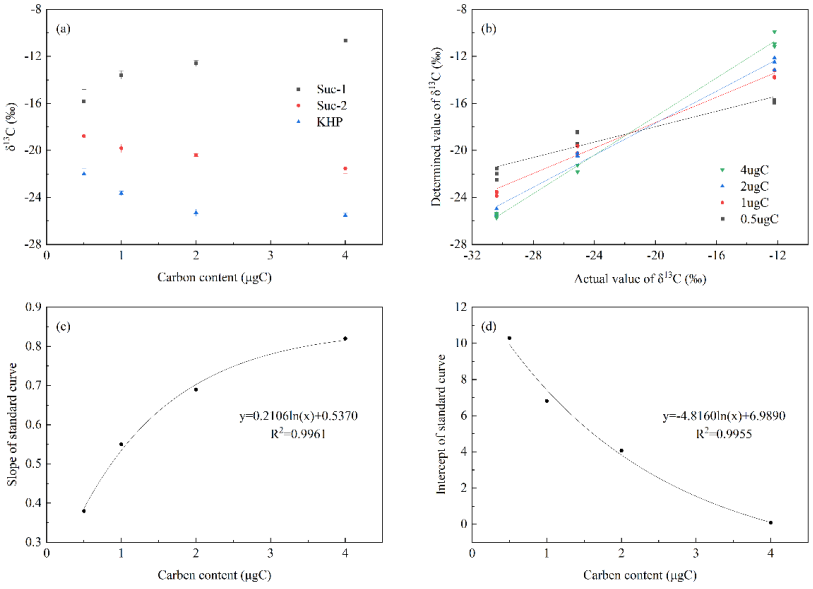

Fig 3. Determination value of three isotopic working standard with different carbon contents. (a) Peak area dependent effect of $\delta^{13}C$; (b) Standard curve with different carbon content; (c) Slope correction curve of standard curve; (d) Intercept correction curve of standard curve.

3.2 Component and concentration variation

Table 1 Concentration distribution of different components

μg/m^3	WSOC	WSII	$PM_{2.5}$	Formate	Acetate	Oxalate
Particle phase	15.7±3.9	29.1±13.6	57.0±26.9	0.16±0.07	0.30±0.20	0.18±0.03
Gas phase	42.4±6.0	25.1±10.9		0.54±0.50	5.66±3.23	0.16±0.03

During study period, WSOCp was in the range of 8.7~35.8 μg C m^{-3} and had an average concentration of 15.7±3.9 μg C m^{-3}. WSOCp accounted for 27.5% of the mass concentration of $PM_{2.5}$, and there was a significant correlation between them ($p<0.01$). The range of WSOCg concentrations observed was 25.6~61.2 μg C m^{-3}, and the mean concentration was 42.4±6.0 μg C m^{-3}. Overall, there is a very significant level of positive correlation between WSOCp and WSOCg ($p<0.01$), which indicates a common source of two phases of WSOC. WSOCp and WSOCg were both positively correlated with CO, $PM_{2.5}$ and PM_{10} ($p<0.01$), indicating a common CO emission source of WSOCp and WSOCg and the significant contribution of WSOCg to sever haze

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pollution. It seems concentration of WSOCg was not affected by meteorological condition in winter, but relative humidity could enhance generation of WSOCp.

WSOCp and WSOCg were obvious higher in wintertime. During summertime, WSOCp was in the range of 1.7~12.1 μg C m^{-3} and had an average concentration of 5.9±1.8 μg C m^{-3}. The range of WSOCg concentrations observed was 16.4~40.0 μg C m^{-3}, and the mean concentration was 25.2±5.2 μg C m^{-3}. Enhancement of WSOCp (166%) was stronger than WSOCg (68%), indicating a more favorable environment for gas phase to particle phase transformation in wintertime.

Diurnal profiles of WSOCp and WSOCg were similar, indicating importance of photochemical reaction in WSOC formation (Fig4a, Fig4b). Both WSOCp and WSOCg reached daily maximum concentration at early noon (at 10:00 LT), and reached relatively low concentrations at early morning (about 6:00 LT) and early evening (about 18:00 LT). Differently, there were obvious valley concentration of WSOCp appeared at sunrise and sunset (at 07:00 LT and 17:00 LT), indicating different generation process of WSOCp in daytime and night time. Compared with WSOCp (55%), WSOCg had a relatively lower enhancement (28%) after sunrise. It suggests a substantial regional background and a relatively long lifetime of WSOCg.

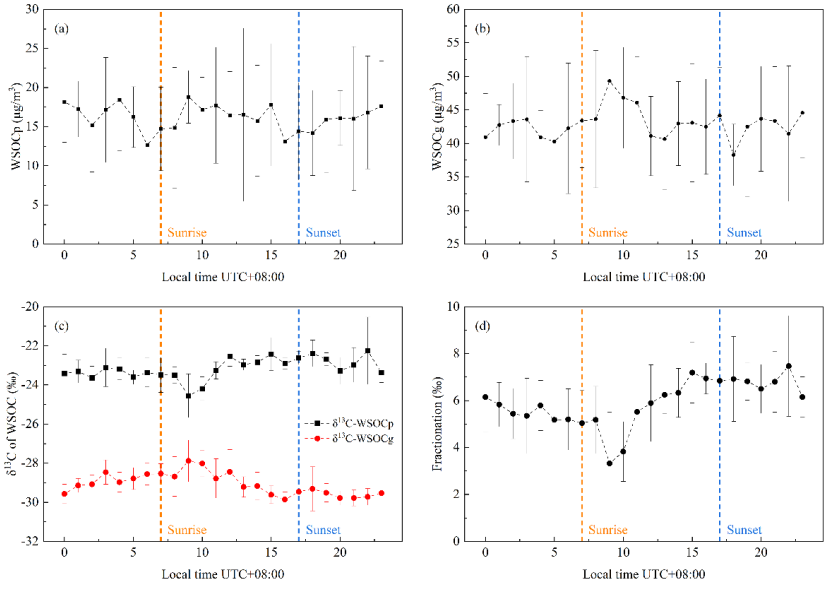

Fig. 4 Diurnal variation distribution (a) Concentration of WSOCp; (b) Concentration of WSOCg;

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(c) $\delta^{13}C$ of WSOCp and WSOCg; (d) $\delta^{13}C$ fractionation between WSOCp and WSOCg.

Different from similar concentrations of water-soluble inorganic ions (WSII) in two phases, WSOCg was apparently higher than WSOCp, and components of WSOC in different phase may also differed greatly. As a typical component of WSOC, organic acids mainly existed in gas phase. Acetic acid, formic acid and oxalic acid were the main organic acids in WSOC, and the fraction ratios in the particle phase were 0.05, 0.23 and 0.53 respectively.

3.3 Stable carbon isotopic variation characteristic

WSOCp had a more enriched $\delta^{13}C$ compared with WSOCg. During study period, $\delta^{13}C$-WSOCp was in the range of -22.5~-28.0 ‰ and had an average $\delta^{13}C$ of -25.9±0.7 ‰, $\delta^{13}C$-WSOCg was in the range of -24.3~-31.5 ‰ and had an average $\delta^{13}C$ of -29.9±0.9 ‰. Both $\delta^{13}C$-WSOCp and $\delta^{13}C$-WSOCg had an obvious diurnal variation characteristic. $\delta^{13}C$-WSOCp was high in night time and low in day time, and $\delta^{13}C$-WSOCg was on the contrary. Difference between $\delta^{13}C$-WSOCp and $\delta^{13}C$-WSOCg reached minimum at around 09:00 LT, and reached maximum at about 23:00 LT (Fig4c).

Difference between $\delta^{13}C$-WSOCp and $\delta^{13}C$-WSOCg, which was considered as isotope fractionation between two phases of WSOC, had negative correlation with concentration of CO、$PM_{2.5}$、PM_{10}、WSOCg and relative humidity (RH) above significant level ($p<0.05$), had positive correlation with O_3 on an extremely significant level in a daily view. However, only O_3, WSOCg, $PM_{2.5}$, PM_{10} had extremely significant correlation with $\delta^{13}C$-WSOCp, $\delta^{13}C$-WSOCg and fractionation at the same time ($p<0.01$). For there was extremely significant positive correlation between fractionation and WSOCg, $PM_{2.5}$ and PM_{10}, main source of WSOC and its emission intensity may have an obvious diurnal change (Such as liquid fossil-fuel, $\delta^{13}C$ of which is about -25.5±1.3‰(August, et al., 2015)).

After distinguishing daytime and nighttime according to radiation intensity, it was found that decrease of temperature and O_3, along with increase of WSOCg and RH, promoted decreasing of fractionation on an extremely significant level during daytime, and increase of O_3, $PM_{2.5}$ and PM_{10} promoted increase of fractionation on an extremely significant level during nighttime ($p<0.01$). Though there was no correlation between fractionation and radiation, there was not only a negative correlation on an extremely significant level ($p<0.01$), but also a highly fitting linear response

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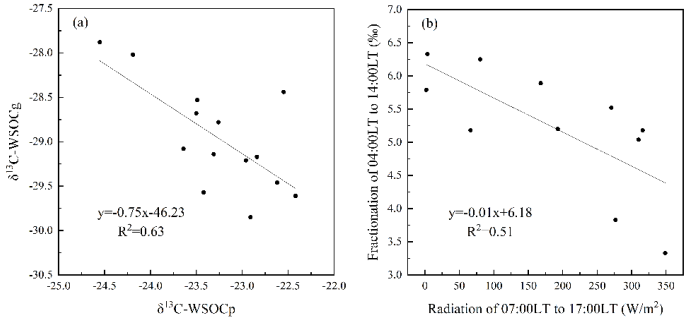
281 relationship (R^2=0.63) between δ^{13}C-WSOCp and δ^{13}C-WSOCg in an environment with non-zero
282 radiation (Fig5a). It indicated that the mutual conversion between WSOCp and WSOCg may only
283 exists during daytime, and the generations of WSOCp and WSOCg were two independent processes.
284 We also found it was interesting that fractionation had a significant negative correlation with the
285 solar radiation after 3 hours ($p<0.05$), along with a highly fitting linear response relationship
286 (R^2=0.51), which was hard to explain (Fig5b).



287
288 Fig. 5 Linear response relationship during daytime (a) δ^{13}C-WSOCp and δ^{13}C-WSOCg; (b)
289 Fractionation (04:00LT to 14:00LT) and Radiation (07:00LT to 17:00LT).
290
291 Enrichment of δ^{13}C-WSOCg had an extremely significant correlation with the increase of
292 WSOCp and WSOCg at the same time ($p<0.01$). However, dilution of δ^{13}C-WSOCp only had a
293 significant correlation with the increase of WSOCg ($p<0.05$), with no correlation with WSOCp. It
294 was believed that increase of WSOCp and WSOCg was attributed to changes in emission intensity.
295 WSOCg is more affected by the direct emission source, and WSOCp more from the conversion of
296 gaseous substances rather than direct emission source.
297 3.3 Effects of gaseous pollutants
298 Isotopic fraction of δ^{13}C between gas phase and particle phase of WSOCp and WSOCg was
299 considered mainly to mainly come from five parts: isotope fractionation due to gas-particle
300 distribution of SVOC(Vodicka, et al., 2022); isotope fractionation due to equilibrium exchange of
301 WSOCp and WSOCg(Gensch, et al., 2014); isotope changes caused by source proportion changes
302 and emission intensity changes of WSOCp and WSOCg(Saehee, et al., 2020); enrichment of δ^{13}C
303 caused by retention and aging of WSOCp and WSOCg; isotope fractionation due to proportion

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change of gas phase reaction and liquid phase reaction in generation process of WSOCp. According to the principle of isotope mass conservation showed as formula (F1), with a certain mass of SVOC, more gas phase conversion will result in enrichment of δ^{13}C-WSOCp, and more particle phase conversion will result in dilution of δ^{13}C-WSOCg。The conversion of WSOCp and the dissolution of WSOCg on the aerosol surface may result in consistent δ^{13}C of WSOCp and WSOCg due to isotope exchange. Changes in the sources of WSOCp and WSOCg will directly cause δ^{13}C-WSOCp and δ^{13}C-WSOCg to approach the δ^{13}C of main source(Cao, et al., 2011), and concentration changes of WSOCp and WSOCg only happens when emission intensity changes. It had been proved that oxidants in atmosphere tend to react with VOCs which have more depleted δ^{13}C (Anderson, et al., 2004; Rudolph, et al., 2003; Rudolph, et al., 2000), leading to a more enriched δ^{13}C in residual VOCs. Aged OC in aerosol was also proved to have more enriched δ^{13}C(Aggarwal and Kawamura, 2008; Pavuluri, et al., 2011; Wang, et al., 2012; Zhang, et al., 2016). Therefore, it's believed that aging of WSOC leads to more enriched δ^{13}C-WSOCp and δ^{13}C-WSOCg. While there is a more enriched δ^{13}C in residual VOCs due to reverse kinetic isotope effect of oxidants(Noziere, et al., 2015), SOA generated by gas phase reaction will have more enriched δ^{13}C, which means δ^{13}C of SOA will be depleted when proportion of liquid phase reaction increases. Similarly, it was believed increased proportion of gas phase reaction leaded to dilution of δ^{13}C-WSOCp, increased proportion of gas phase reaction leaded to enrichment of δ^{13}C-WSOCp.

$$\frac{\mathrm{WSOC_p} \times \delta^{13}\mathrm{C}(\mathrm{WSOC_p}) + \mathrm{WSOC_g} \times \delta^{13}\mathrm{C}(\mathrm{WSOC_g})}{\mathrm{WSOC_p} + \mathrm{WSOC_g}} = \mathrm{SVOC} \times \delta^{13}\mathrm{C}(\mathrm{SVOC}) \quad \text{(F1)}$$

In which WSOCp and WSOCg are the parts converted from SVOC.

Increase of CO leaded to enrichment of δ^{13}C-WSOCg on an extremely significant level ($p<0.01$). Though there was also extremely significant positive correlation between concentration of CO and WSOCp, WSOCg ($p<0.01$), along with significant positive correlation between concentration of CO and fp-WSOC ($p<0.05$), it was difficult for CO to affect conversion between WSOCp and WSOCg by participating in the atmospheric chemical reaction. For higher concentration of CO indicated a stronger primary emission source(August, et al., 2015), it was believed that emission of WSOC enhanced in an environment with high concentration of CO, leading generation and retention of plenty of WSOCg, along with aging of those WSOCg. However, there was no effect on gas-particle distribution mechanism of WSOC.

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Increase of NH_3 leaded to dilution of δ^{13}C-WSOCp, enrichment of δ^{13}C-WSOCg and increase of WSOCg on an extremely significant level ($p<0.01$). For there was research found increase of ALWC along with decrease of pH of aerosol in environment of high concentration of NH_3(Shaojun, et al., 2022), which may be conducive to aerosol release WSOCg. Dilution of WSOCp may came from mutual conversion of WSOCp and WSOCg, while enrichment of δ^{13}C-WSOCg may came from aging of WSOCg which was generated in an environment of high concentration of NH_3 considering increasing concentration of WSOCg. There was also possibility of increasing emission intensity of specific source, which leaded to δ^{13}C-WSOCp and δ^{13}C-WSOCg tended to be consistent. However, it was hard to explain why there was no significant effect on WSOCp. Considering both δ^{13}C-WSOCp and δ^{13}C-WSOCg closed to -26‰ at the same time when fractionation decreased, which is similar to characteristic δ^{13}C value of liquid fossil-fuel(August, et al., 2015), it was believed that liquid fossil-fuel was a common source during a period of high concentration of NH_3.

With no correlation with concentration of neither WSOCp nor WSOCg, increase of NO_2 leaded to dilution of δ^{13}C-WSOCp and δ^{13}C-WSOCg at the same time on an extremely significant level ($p<0.01$). For there is dilution of δ^{13}C-WSOCp along with enrichment of δ^{13}C-WSOCg at the same time, there was little possibility of dilution of δ^{13}C-WSOCp caused by mutual conversion of WSOCp and WSOCg. Considering evidence for gas phase reaction of organic nitrates(Alexander, et al., 2019), it was believed that SVOC may be more converted to particle phase, and the gas phase formation reaction of SOA was strengthened under high concentration of NO_2.

Increase of O_3 leaded to enrichment of δ^{13}C-WSOCp and dilution of δ^{13}C-WSOCg on an extremely significant level ($p<0.01$). Similar with NO_2, neither WSOCp nor WSOCg had correlation with concentration of O_3, which means none variation of emission intensity of WSOC source when δ^{13}C changed. It was believed that SVOC conversed more to WSOCp under high concentration of O_3, leading to of dilution of δ^{13}C-WSOCg. The aging of WSOCp was promoted at the same time, leading to enrichment of δ^{13}C-WSOCp. Dilution of δ^{13}C-WSOCg caused by conversion from SVOC to WSOCp exceeded enrichment of δ^{13}C-WSOCg caused by aging of WSOCg, leading to a more dilute δ^{13}C-WSOCg, indicating that O_3 tends to react with SVOC rather than WSOCg.

It seems different gaseous acids had different effects on WSOC. Increase of HONO leaded to dilution of δ^{13}C-WSOCp and enrichment of δ^{13}C-WSOCg over a significant level ($p<0.05$). For there was also extremely significant positive correlation between HONO and WSOCp, WSOCg

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(p<0.01), emission intensity of WSOC sources may increase under high concentration of HONO, along with mutual conversion of WSOCp and WSOCg. Considering that HONO participates in formation of SOA as an oxidant(Chi, et al., 2022), there was also possibility of enhanced gas phase generation of WSOC leaded to dilution of δ^{13}C-WSOCp. Increase of HCl leaded to enrichment of δ^{13}C-WSOCg and increase of WSOCg on a significant level (p<0.05), with no correlation with δ^{13}C-WSOCp. The presence of HCl may inhibit the transformation from WSOCg to WSOCp, promoting the retention and aging of WSOCg. Differs from other acids, gaseous oxalic acid leaded to dilution of δ^{13}C-WSOCg on a significant level (p<0.05) without affecting concentration of WSOCp and WSOCg, which may be caused by the increase in proportion of SVOC conversion to WSOCp.

3.4 Effects of component of $PM_{2.5}$ and gas-particle distribution

Increase of $PM_{2.5}$ and PM_{10} leaded to enrichment of δ^{13}C-WSOCg on an extremely significant level (p<0.01). There was also extremely significant positive correlation between $PM_{2.5}$, PM_{10} and WSOCp, WSOCg. For there was no correlation between $PM_{2.5}$, PM_{10} and δ^{13}C-WSOCp, it was believed that emission intensity of WSOC sources increased with none change of main source under high concentration of $PM_{2.5}$ and PM_{10}. Aging of WSOCg and concentration increase of particle matters had consistent atmospheric environmental conditions, and aging of WSOCg may make a considerable contribution to formation of haze.

Different components of $PM_{2.5}$ had different responses to the concentration and isotopes of WSOCp and WSOCg. Consistent with $PM_{2.5}$ and PM_{10}, SO_4^{2-}, NO_3^- and NH_4^+ (SNA) all had extremely positive correlation with enhancement of δ^{13}C-WSOCg, along with increase of WSOCp and WSOCg (p<0.01). Aging of WSOCg may cause generation of haze by participating in formation of SNA. Apart from extremely positive correlation with WSOCp and WSOCg, increase of SO_4^{2-} leaded to enrichment of δ^{13}C-WSOCp on a significant level (p<0.05). For sulfate is largely formed in liquid phases(Gehui, et al., 2018; Gehui, et al., 2016), it was believed that liquid phase generation reaction of WSOCp enhanced during haze period with high concentration of SO_4^{2-}. Increase of NO_2^- leaded to dilution of δ^{13}C-WSOCp on an extremely significant level (p<0.01), indicating a possible enhancement in gas phase generation reaction of WSOCp. However, formation of NO_2^- in atmosphere is still uncleared.

Generally, fp=WSOCp/(WSOCp+WSOCg) represented gas-particle ratio of WSOC(Hennigan, et al., 2009). fp of ions was used to represent gas-particle ratio of ions in this research. It was found

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that though increase of fp of SNA promoted increase of WSOCp and WSOCg in the same time on a significant level ($p<0.05$), increase of fp-NH_4^+ only related to enrichment of δ^{13}C-WSOCp and increase of fp-NO_3^- and fp-SO_4^{2-} only related to enrichment of δ^{13}C-WSOCg. Organic nitrate and organic sulfate generated by aged WSOCg may play an important role in gas-particle conversion of nitrate and sulfate. However, it was hard to distinguish contribution by aging of WSOCp, gas conversion of SVOC and liquid phase formation of WSOCp in gas-particle conversion of ammonium, for both of them can lead to enrichment of δ^{13}C-WSOCp. Increase of fp-NO_2^- leaded to enrichment of δ^{13}C-WSOCp and dilution of δ^{13}C-WSOCg on an extremely significant level ($p<0.01$). Particle conversion of SVOC, liquid phase generation of WSOCp and aging of WSOCp may enhanced in rapid gas-particle conversion of NO_2^-. However, this was in contradiction with δ^{13}C-WSOCp depleted when concentration of NO_2^- increased. NO_2^- may have other relatively important formation pathways apart from gas-particle conversion from HONO, such as heterogeneous absorption of NO_2 by acetate in WSOCp to generate NO_2^-(Wen-Xiu, et al., 2022). Increase of fp-acetate leaded to increase of WSOCp on an extremely significant level ($p<0.01$), with none correlation with δ^{13}C-WSOC. Acetate may be the main component of WSOCg which converses to particle. Increase of fp-oxalate leaded to enrichment of δ^{13}C-WSOCg on a significant level ($p<0.05$), with none correlation with concentration of WSOC. Oxalate may be an important component of WSOCg which is easier to aging.

3.5 Effects of meteorological conditions

Increase of wind speed promoted enrichment of δ^{13}C-WSOCp and δ^{13}C-WSOCg on an extremely significant level ($p<0.01$), with no effects on isotope fractionation and concentration of WSOC in two phases. However, change of wind direction could affect fp-WSOC and δ^{13}C-WSOCg on an extremely significant level ($p<0.01$). It was believed that there was a source around sampling site with depleted δ^{13}C. WSOC transmitted under high wind speed environment mixed with local pollutants, leading to a different source composition. However, gas-particle distribution mechanism of WSOC and emission intensity of pollution sources unchanged. For accidental effects of wind direction was filtered by mean daily analysis, it's believed there existed a strong source of WSOC in the northwest wind direction.

Among the other meteorological elements, the increase of temperature promoted enrichment of δ^{13}C-WSOCp at a significant level ($p<0.05$). Increase of atmospheric pressure, RH and radiation

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intensity promoted the enrichment of δ^{13}C-WSOCg above a significant level ($p<0.05$). The increase of relative humidity, air pressure and radiation may promote the aging of WSOCg. Though conversion of WSOCp to WSOCg can also lead to an enriched δ^{13}C-WSOCg, a significant positive correlation between RH and WSOCp ($p<0.05$) indicated a high possibility that intensity of specific emission source changed in environment with high RH. There was none significant correlation between temperature and concentration of WSOC, indicating that the change of temperature may has no effect on emission intensity. Increase of temperature may be caused enrichment of δ^{13}C-WSOCp by promoting more conversion of SVOC to WSOCg and accelerating the aging of WSOCp

4. Conclusion

In this study, we developed a high time resolution method for determining the δ^{13}C values of WSOCp and WSOCg by combination of wet oxidation pretreatment and IRMS. With improvement of oxidation method and determination method, δ^{13}C value of liquid sample with a carbon content between 0.5 to 5μg can be determined with an accuracy of 0.6 ‰. Using this method, the δ^{13}C value of WSOCp and WSOCg in winter of 2021 at an urban site of Nanjing were determined, which were -25.9±0.7 ‰ and -29.9±0.9 ‰ respectively. Approaching δ^{13}C of WSOCp and WSOCg indicted a common source during heavy haze period, which may be liquid fossil fuel.

The fractionation between δ^{13}C-WSOCp and δ^{13}C-WSOCg had a significant diurnal variation of low in the day and high in the night, reaching the lowest at early noon. The existence of sunlight determined whether the formation of WSOCp and WSOCg was an independent chemical process, but there was no correlation between isotope signal and radiation intensity. The fractionation was restricted by WSOCg, RH, O_3 and temperature during daytime, and was restricted by O_3, $PM_{2.5}$ and PM_{10} during nighttime. Rise of WSOCg and RH were negative factor for isotope fractionation, and rise of temperature, O_3, $PM_{2.5}$ and PM_{10} were positive factor for isotope fractionation.

Gas-particle distribution mechanism of WSOC was restricted by meteorological conditions, precursor gaseous pollutants, gaseous oxidants and acid gases, which can lead to isotope dilution and enrichment by affecting gas-particle distribution of SVOC, gas-liquid phase reaction proportion of WSOCp, aging process of WSOCp and WSOCg and gas-particle exchange of WSOC. Gas-particle distribution of SVOC was restricted by NO_2, O_3, gaseous oxalic acid and temperature; Gas-liquid phase reaction proportion of WSOCp was restricted by HONO and NO_2; Aging process of

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WSOCp was restricted by O_3 and temperature; Aging process of WSOCg was restricted by CO, NH_3, HCl, RH, pressure and radiation; Gas-particle exchange of WSOC was restricted by NH_3, HCl and HONO.

In the components of $PM_{2.5}$, generation of SNA had significant correlation with gas-particle distribution of WSOC. The formation of SNA and WSOCp was accompanied by the aging of WSOCg and the enhancement of liquid phase reaction of WSOCp. Generation of haze may be related to retention and aging of WSOCg. Reaction between HONO and NO_2^- may also have some unknown effects on generation of WSOC through gas phase reaction.

Author Contribution

Hao-Ran Yu and Yan-Lin Zhang designed the experiments; Hao-Ran Yu adapted the instruments, carried out isotope test; Fang Cao, Xiao-Ying Yang, Tian Xie and Yu-Xian Zhang organized the sampling, Yongwen Xue carried out TOC test. Hao-Ran Yu prepared the manuscript with contributions from all co-authors.

Competing Interests

The authors declare that they have no conflict of interest.

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