Response to reviewers' comments

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Anonymous Referee #1:

This study developed a new method and system to determine stable carbon isotope in both the water-soluble organic carbon in the gaseous and particle phases. The novelty of this study lies in the method and its potential application. They also found the difference in WSOC mass concentration and the isotope composition between the day and night samples. Although the explanation of the influencing factors for the differences remains unresolved, I strongly recommend it for a quick publication after they can address the following specific comments.

Dear reviewer:

Thank you very much for your comments and advises on our paper! They have been encouraging and constructive. We have learnt quite a lot from it.
After carefully studying the comments and advises, we have made corresponding changes to our paper.

1.Line 26-27: the sentence was not clear.
The authors should use the isotope expression more carefully. For examples: lower, higher, depleted or enriched. For example, to say that "one sample is enriched in 15N relative to another because of ..." is proper usage. Phrases such as "a sample has an enriched d15N value" are misuses of terminology.

Author's response:

Thanks for the reviewer's comments. Sentence in line 26-27 is modified to "It was found that WSOCg has significant higher concentration than WSOCp, and is depleted in $\delta^{13}C$ relative to WSOCp.".

2.Line 38-40: rewording is necessary

Author's response:

Thanks for the reviewer's comments. Description in line 38-40 is modified to "Generations of WSOCp and WSOCg during nighttime are two independent processes, and the presence of radiation decides conversion between WSOCp and WSOCg, for $\delta^{13}C$-WSOC of two phases showed significant correlation only during daytime.".

3.Line 149: details are needed here,
Was the method for 13C in WSOC improved or optimized compared to the previous method. If so, the details should be given or highlighted.

Author's response:

Thanks for the reviewer's comments. Details in line 149 is suppled as "WSOCp was sampled by filters at the same time to compare the sampling efficiency of IGAC system. The daily average of WSOCp sampled by filters was 24.1μg/m^3, while WSOCp determined by the IGAC system sampled at the same time was 29.7μg/m^3.". And the detailed data is added to Supplement

Information Table S9.

Table S9 Comparison of WSOCp sampled by filter and by IGAC system

Time	IGAC WSOCp (μg/m3)	Filter WSOCp (μg/m3)
2021/12/10 1:00	31.75	15.99
2021/12/11 2:00	26.57	17.45
2021/12/12 3:00	21.23	19.04
2021/12/13 4:00	20.84	22.32
2021/12/14 5:00	26.96	19.38
2021/12/15 6:00	29.40	20.35
2021/12/16 7:00	28.34	21.32
2021/12/17 8:00	27.17	19.14
2021/12/18 9:00	25.65	21.89
2021/12/19 10:00	33.37	21.30
2021/12/20 11:00	32.63	16.38
2021/12/21 12:00	32.25	27.41
2021/12/22 13:00	31.11	47.91
2021/12/23 14:00	31.49	35.49
2021/12/24 15:00	31.87	23.08
2021/12/25 16:00	26.76	18.91
2021/12/26 17:00	30.68	29.84
2021/12/27 18:00	31.76	24.55
2021/12/28 19:00	34.64	20.36
2021/12/29 20:00	37.51	22.18
2021/12/30 21:00	39.22	37.75

For the details of this method. It’s an improved method for $\delta^{13}C$ in WSOC compared to the previous method both in instrument transformation and correction method improvement. Details are given in chapter 3.1 Improvement of determination method, as “Compared with previous determination method (Zhang, et al., 2019), the determination limit was improved to less than 5μgC in this study. The headspace bottle is pre purged before sample injection and liquid content of sample injection is unified as 2mL to reduce the influence of carbon dioxide dissolved in water. The composition of oxidizer is changed to reduce the influence of carbon blank in oxidizer.”

4.The influences of the metrological condition and chemical composition should be reordered. the mechanism for the WSOCg-WSOCp distribution was not well explained and further discussion is needed.

Author’s response:

Thanks for the reviewer’s comments. The influences of the meteorological condition and chemical composition is reordered. Discussion now is reordered as 3.3 Stable carbon isotopic variation characteristic, 3.4 The influence of meteorological condition, 3.5 The influence of gaseous pollutants, and 3.6 The indication by chemical composition of particle matters. The influence of radiation which used to be discussed in chapter 3.3 Stable carbon isotopic variation characteristic is moved to chapter 3.4 The influence of meteorological condition.

The mechanism for the WSOCg-WSOCp distribution is rediscussed in chapter 3.3, chapter 3.4, chapter 3.4, chapter 3.5, and chapter 3.6.

In chapter 3.3, five processes of WSOCg-WSOCp distribution generating isotopic fraction of δ^{13}C between the gas phase and particle phase of WSOC were discussed, including "isotope fractionation due to the gas-particle distribution of SVOC (Vodicka, et al., 2022); isotope fractionation due to equilibrium exchange of WSOCp and WSOCg (Gensch, et al., 2014); isotope changes caused by source composition changes and emission intensity changes of WSOCp and WSOCg (Saehee, et al., 2020); enrichment of δ13C caused by retention and aging of WSOCp and WSOCg; isotope fractionation due to proportion change of gas phase reaction and liquid phase reaction in the generation process of WSOCp."

In chapter 3.4, influences of wind speed, radiation intensity, temperature and RH were rediscussed separately. It is concluded as "The liquid phase reaction of WSOCg to WSOCp may be dominant in the daytime, and the oxidative aging of WSOCp may be dominant at night. The existence of sunlight rather than its intensity determined whether the formation of WSOCp and WSOCg were independent chemical processes. Temperature and radiation may accelerate the aging process of WSOCp."

In chapter 3.5, influences of CO, NH_3, O_3, NO_2 and gaseous acids were rediscussed. It is concluded that CO has influence on sources of WSOC while no influence on WSOCg-WSOCp distribution. NH_3 has both influence on sources of WSOC and WSOCg-WSOCp distribution. O_3, NO_2 and gaseous acids has influence on WSOCg-WSOCp distribution while no influence on sources of WSOC. It is concluded as "O_3 and NO_2 promote the conversion to particle phase and the aging process of WSOCp, NH_3 promotes the retention and aging process of gas phase."

In chapter 3.6, we rediscussed the generation processes of different components in particle matters, and the relationship between them and WSOCg-WSOCp distribution processes. It is concluded as "the emission intensity of WSOC sources increased while the source composition remains stable under a high concentration of particle matters." and "conversion of WSOCg to WSOCp may be along with SNA generation process."

Based on the discussions, conclusion is rewrite as "In this study, we developed an improved high-time resolution method for determining the δ^{13}C values of WSOCp and WSOCg by a combination of wet oxidation pretreatment and IRMS. With the improvement of the oxidation method and determination method, the δ^{13}C value of the 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 the winter of 2021 at an urban site in Nanjing were determined, which were -25.9 ± 0.7 ‰ and -29.9 ± 0.9 ‰ respectively. Approaching δ^{13}C of WSOCp and WSOCg indicated a common source during the 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 change of fractionation mainly come from gas-particle distribution of SVOC, equilibrium exchange of WSOCp and WSOCg, source composition and emission intensity changes of WSOCp and WSOCg, retention and aging of WSOCp and WSOCg, proportion change of gas phase reaction and liquid phase reaction in the generation process of WSOCp.

The liquid phase reaction of WSOCg to WSOCp may be dominant in the daytime, and the oxidative aging of WSOCp may be dominant at night. The existence of sunlight rather than its intensity determined whether the formation of WSOCp and WSOCg were independent chemical processes. Temperature and radiation may accelerate the aging process of WSOCp. O_3 and NO_2 promote the conversion to particle phase and the aging process of WSOCp, NH_3 promotes the retention and aging process of gas phase. Indicated by response of chemical composition in particle matters, conversion of WSOCg to WSOCp may be along with SNA generation process."

Thank you very much for the excellent and professional revision of our paper!