PAPER

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Sampling and determination of antimony isotopes in airborne particles: an assessment of membrane filter materials†

Chao Zhang,[abd] Guangyi Sun,*[a] Xinyu Li,[ac] Yunjie Wu,[ab] Heng Yao,[a] Jen-How Huang[a] and Xinbin Feng 🄳 *[a]

Isotopic compositions of antimony (Sb) in airborne particles could reveal the sources and geochemical processes of Sb. Today, the precise analysis of the Sb isotopic ratio in airborne particles is still challenging due to technical difficulties in the sampling and pretreatment processes. In this study, traditional methods of sampling and pretreatment of Sb in airborne particles were optimized to meet the isotope measurement requirements. Suitable digestion methods were suggested for various membrane filters (MF) of different materials and brands, and the Sb blank values in these membrane filters were compared. The results showed that the Whatman brand quartz microfiber MF had the lowest Sb blank value (1.13 ng cm^{-2}), and could meet the needs of continuous large flow sampling, making it the most ideal MF for sampling Sb in airborne particles for the subsequent measurement of Sb isotope ratios. Synthetic samples of the MF spiked with certified reference materials (CRMs) were digested and tested. Nearly identical ε^{123}Sb values were observed among CRMs, (MF + CRMs), and (MF + CRMs) subtracting the content proportion of MF, which indicated that the isotope fractionation occurred during the pretreatment was negligible, and that the Sb isotopic composition of airborne particulate matter was basically not affected by the Whatman brand quartz microfiber MF. This method has been successfully applied to total suspended particles and fine particulate matter (PM$_{2.5}$) collected in Guiyang in southwest China.

1. Introduction

The wide usage of antimony (Sb) containing products in industry and daily life can release Sb into the atmosphere.[1–3] Besides human activities, Sb can also be emitted into the atmosphere through natural processes.[4] Antimony has a strong affinity to airborne particulate matter[5] and can be significantly enriched on the surfaces of fine airborne particles.[6] Antimony in the air can damage human health through inhalation and can damage sensitive ecosystems through atmospheric deposition.[7–10] Antimony attached to airborne particles has a long settling time (hours to weeks) in the air.[11] It can be transported regionally or even globally and therefore is considered as a global pollutant.[12–15] It has thus been listed as

[a]State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550081, China. E-mail: sunguangyi@mail.gyig.ac.cn; fengxinbin@vip.skleg.cn
[b]School of Earth Sciences, China University of Geosciences, Wuhan, 430074, China
[c]University of Chinese Academy of Sciences, Beijing 100049, China
[d]Institute of Soil and Water Resources and Environmental Science, College of Environmental and Resource Sciences, Zhejiang University, Hangzhou 310058, China
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one of the priority pollutants by the United States Environmental Protection Agency[16] and the European Union.[17]

Antimony in airborne particulate matter has been proved to be an important source of Sb exposure for urban residents[18] and is of particular concern because, once inhaled, both Sb and its vectors might have adverse effects on human beings.[19–21] Therefore, it is necessary to investigate the sources and geochemical pathways of Sb in airborne particulate matter. Currently, the means of source tracing of Sb in airborne particulate matter mainly include microanalysis,[22] chemical mass balance,[23] hierarchical cluster analysis,[24] enrichment factors,[25] principal component analysis,[26] chemical speciation analysis,[27] and positive matrix factorization model.[28] However, these methods require a large amount of samples, and are affected by analysis interference and environmental factors, so the results of source tracing are not accurate.

As a new technology that has developed rapidly in recent years and has high stability and high precision, non-traditional stable isotope technology has shown unique advantages and potentials for tracing the sources and processes of metals in airborne particulate matter.[29–31] The diversity of Sb sources in airborne particulate matter[32] and the differences of their isotopic compositions[33,34] make it possible to trace Sb in airborne particulate matter using isotope technology. However,

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most previous studies have focused on the analysis of Sb isotope ratios in rock,[35–39] soil,[40] sediment,[35] water,[36,41] glass,[42–44] fly ash,[40] and hydrothermal sulfide samples.[35] Limited by the blank interference of sampling medium, low content of actual samples, isotope fractionation in the process of purification, and other technical challenges, there is still a lack of data on the collecting, pretreatment, and measurement of Sb isotopes in airborne particulate samples.

To fill this gap, we conducted this study to (1) select a suitable membrane filter for the sampling and measurement of Sb isotopes in airborne particulate samples by comparing the digestion method and blanks and (2) test the feasibility of the candidate membrane filter for Sb isotope study by comparing the isotopic signals with and without the spiking of certified reference materials (CRMs). Finally, the proposed method was implemented in total suspended particles (TSP) and PM$_{2.5}$ samples collected in Guiyang in southwest China, and the sources of Sb were preliminarily revealed.

2. Experimental methods

2.1. Materials, reagents, and standards

All critical sample preparation and laboratory experiments were conducted in a class 1000 clean room facility at the State Key Laboratory of Environmental Geochemistry (SKLEG) of the Institute of Geochemistry, Chinese Academy of Sciences (IGCAS). Two NaBH$_4$ solutions (0.5% w/v and 2% w/v) were used for the online reduction of Sb for quantification and isotope analysis, respectively.[34] The NIST SRM 3108 cadmium standard solution (NIST®, USA) was used for mass bias correction and the NIST SRM 3102a Sb standard solution (NIST®, USA) was used as the isotope standard. Antimony solutions from Sigma-Aldrich (Merck, Germany; lot: BCBT7006), Alfa Aesar (USA; lot: 1227270 B), and Spex CertiPrep (USA; lot: CL 10-49SBY) were utilized as the secondary standard solutions for isotopic analysis. Five CRMs comprising soil (NIST 2711a and GBW07405), stream sediment (GBW07312), urban particulate matter (NIST 1648a), and municipal waste incineration fly ash (BCR-176R) were taken for the method development and validation. NIST 2711a and NIST 1648a were bought from the National Institute of Standards and Technology (NIST®, USA); BCR-176R was obtained from the Institute for Reference Materials and Measurements (IRMM, Belgium); and GBW07405 and GBW07312 were purchased from the National Center for Standard Materials (Beijing, China).

Six membrane filters, namely, a polycarbonate (PC) membrane filter (Jinteng, China), a mixed cellulose ester (MCE) membrane filter (MF-Millipore, Germany), a cellulose acetate (CA) membrane filter (Jinteng, China), a quartz microfiber (QM) membrane filter (Whatman, UK; PALL, USA), a glass microfiber (GM) membrane filter, and a polytetrafluoroethylene (PTFE) membrane filter (Ahlstrom-Munksjö, Sweden), were used for method development. To obtain airborne particles, a total volume of 1440 m^3 and 144 m^3 of air over 24 h was collected on membrane filters using a high-flow-rate air sampler and a medium-flow-rate air sampler (Qingdao Laoying Environmental Technology Co., Ltd, China) at flow rates of 1 m^3 min^{-1}

and 0.1 m^3 min^{-1}, respectively. The air sampler was placed at a height of 2 m above the ground according to a Chinese standard[46] (the height from the ground shall not be less than 1.5 m) on an urban street with frequent traffic in Guiyang in southwest China. The passing vehicles include cars, buses, and trucks, and the cars predominate. The major fuel for passing vehicles is gasoline.

2.2. Sample digestion

All types of membrane filters were digested using a two-step high-temperature, high-pressure closed-vessel acid digestion process,[34] but with distinct pretreatment processes before the two-step acid digestion process. The pretreatments of the MCE, CA, and PC membrane filters were as follows: the membrane filter was placed into a Teflon vessel, and then 2–3 mL concentrated HNO$_3$ was added. The QM and GM membrane filters were then pretreated with a 4 mL mixture of 50% (v/v) HF and 20% (v/v) HNO$_3$. Hydrofluoric acid was used to treat the siliceous composition. Adding concentrated HF to the Teflon vessel containing the membrane filter would induce a violent chemical reaction, while using diluted HF to pretreat the membrane filter would require a huge amount of HF. Therefore, 50% (v/v) HF was recommended to digest the QM and GM membrane filters. The function of 20% (v/v) HNO$_3$ was to oxidize Sb during dissolution to prevent its loss.

The PTFE membrane filter could not be completely digested; therefore, washing was performed. A PTFE membrane filter (<200 mg) was placed in a Teflon vessel (excessively large samples may cause an explosion risk), and a mixture of 3 mL concentrated HNO$_3$ and 1 mL concentrated HF was added. The Teflon vessel was then placed in the oven at 185 °C for 48 h. Thereafter, the Teflon vessel was removed from the oven. The lid of the Teflon vessel was removed, and the membrane filter became wrinkled. The membrane filter was then clamped out using a clean tweezer and washed with 2 mL concentrated HNO$_3$. The washing solution was then placed in a Teflon vessel for the subsequent treatment.

For QM membrane filters loaded with airborne particles, a quarter area was sheared and placed in a Teflon vessel, to which 4 mL mixture of concentrated HF (50% v/v) and HNO$_3$ (20% v/v) was added. The Teflon vessel was placed on the hot plate at 90 °C with an open lid until the solution completely evaporated. During this process, the vessel was shaken every 5 min to ensure that all the membrane filters sank into the solution. Next, a mixture of 3 mL concentrated HNO$_3$ and 1 mL concentrated HF was added to the Teflon vessel, then covered with a lid and placed in an oven at 185 °C for 48 h. After heating, the Teflon vessel was removed from the oven. After cooling, 1 mL of H$_2$O$_2$ was added and placed on a hot plate at 100 °C for 1 h and then at 90 °C until the sample was completely digested. Subsequently, 3 mL of concentrated HNO$_3$ was added to the Teflon vessel, which was then placed in the oven at 185 °C for 24 h. Thereafter, the Teflon vessel was placed on a hot plate at 90 °C until the sample was completely digested. Next, 3 mL of 40% HNO$_3$ was added to the Teflon vessel. The solution in the Teflon vessel was transferred to a tube after the sample was

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completely dissolved. Finally, 1 mL of 40% HNO_3 was added to rinse the Teflon vessel, and the rinsing solution was transferred to the tube.

2.3. Sb concentration and isotopic measurements

The atomic fluorescence spectroscopy (AFS) model 8520 (Beijing Haiguang Instrument Co., Ltd, China) was used to measure Sb concentrations.

The sample purification (to separate Sb from the matrix), impact of interference elements, and potential isotopic fractionation during the purification and measurement process have been investigated in our preliminary study.[34] Antimony isotope ratios were determined using hydride generation-multicollector inductively coupled plasma mass spectrometry (HG-MC-ICP-MS, Nu Plasma II, Nu Instruments Ltd, UK) at the Institute of Geochemistry, Chinese Academy of Sciences (Guiyang, China). The analytical procedures and instrument parameters used in this study are detailed in our previous study.[34] The sample or standard solution was introduced using the HG system.

The Sb isotope composition was reported in epsilon notation (ε), which is expressed as:

$$\varepsilon^{123}\text{Sb}\left(\%oo\right) = \left(\frac{\left(^{123}\text{Sb}/^{121}\text{Sb}\right)_{\text{sample}}}{\left(^{123}\text{Sb}/^{121}\text{Sb}\right)_{\text{standard}}} - 1\right) \times 10\,000$$

where the $\left(^{123}\text{Sb}/^{121}\text{Sb}\right)_{\text{sample}}$ is the isotope ratio measured for the sample, and the $\left(^{123}\text{Sb}/^{121}\text{Sb}\right)_{\text{standard}}$ is the mean isotope ratio of the Sb standard solution NIST SRM 3102a. Hereinafter, it is referred to as the "matching standard" (MS) measured before and after each sample.

2.4. Quality control

All operations involving contact with the membrane filter use nonmetallic tweezers after cleaning with ultrapure water. Milli-Q (MQ) water (18.2 MΩ, Millipore, Bedford) was used to prepare all the aqueous solutions. Ultrapure HCl, HNO_3, and HF from Sinopharm Chemical Reagent (China) were double-distilled with a DST-1000 acid purification system (Savillex, USA) prior to use. All PFA beakers, centrifuge tubes, and pipette tips were first cleaned with MQ water, then with 50% (v/v) HCl, 20% (v/v) HCl, and 10% (v/v) HNO_3 separately, and finally rinsed thoroughly with MQ water before being used.[34,45] The recoveries of Sb from NIST 2711a, GBW07405, GBW07312, NIST 1648a, and BCR-176R averaged 97%, 98%, 98%, 96%, and 90%, respectively (Table S7†). The amounts of CRMs added to the membrane filters for the validation experiment are shown in Table S8.† Parallel and blank samples were added during sample processing to test the quality of the experiment. The Sb concentrations in all blank samples are all below the detection limit (0.05 ng g^{-1}). The long-term external reproducibility of the NIST SRM 3102a standard with the applied procedure was estimated conservatively to be better than 0.40ε.[34] Therefore, if the isotope ratio between samples is $\leq 0.40\varepsilon$, it is considered that there is no significant difference in isotopic composition between samples. The standard deviation of Sb isotope ratios of CRMs and (MF +

CRMs) range from 0.06ε to 0.30ε and 0.02ε to 0.35ε (Table S7†), showing good repeatability ($n = 2$–8).

3. Results and discussion

3.1. Selection of membrane filters and sampling times

The blank values of Sb in different types of membrane filters were obtained using the aforementioned digestion methods (Fig. 1). The blank values of Sb in the PC, MCE, and CA membrane filters were all below the detection limit (0.05 ng g^{-1}). Although these membrane filters contain low Sb, they are not suitable for $PM_{2.5}$ sampling owing to their high-flow resistance and compactness (pore size of 0.45 μm). The actual air flow rate could not meet the standard (0.1 m^3 min^{-1}) for $PM_{2.5}$ collection when using these membrane filters. Nevertheless, these membrane filters can be used for the collection of TSP samples in the air and particulate matter samples in water. The blank values of Sb in the GM and PTFE membrane filters were 503.71 ng cm^{-2} and 40.54 ng cm^{-2}, respectively (Table S2†), which were much higher than those in the QM membrane filters (Fig. 1). The QM membrane filter advantages over the others due to its optimal pore size and high digestibility. It has also been proven to be ideal for $PM_{2.5}$ sampling.[30,47–49] In comparison, namely, PTFE filter is characterized by high blank value and hard to be digested, and PC, MCE, CA filters are not suitable for $PM_{2.5}$ sampling owing to their high-flow resistance and compactness (pore size of 0.45 μm). Therefore, the QM membrane filter was the best medium for collecting Sb from airborne particulate matter. The mean blank value of Sb was 1.85 ng cm^{-2} in the PALL QM membrane filter and 1.12 ng cm^{-2} in the Whatman QM membrane filter (Fig. 1 and Table S2†). Accordingly, the Whatman QM membrane filter would be a better choice for Sb collection from airborne particulate matter. The blank monitoring of the Sb total mass in the Whatman QM membrane filters of each production batch was
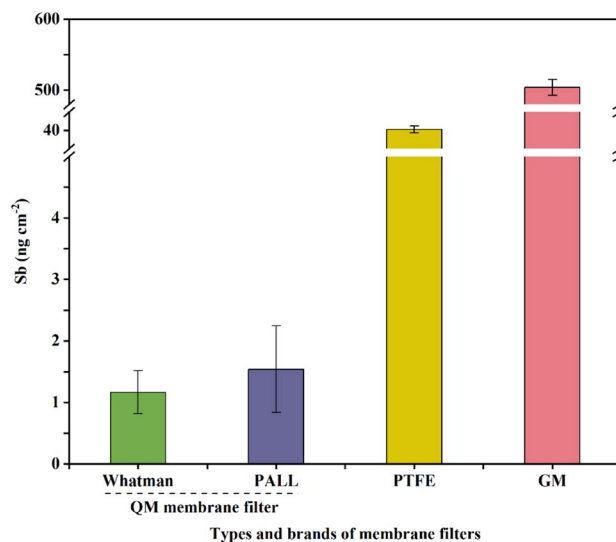

Fig. 1 Blank values of antimony (Sb) in the membrane filters of different types and brands.
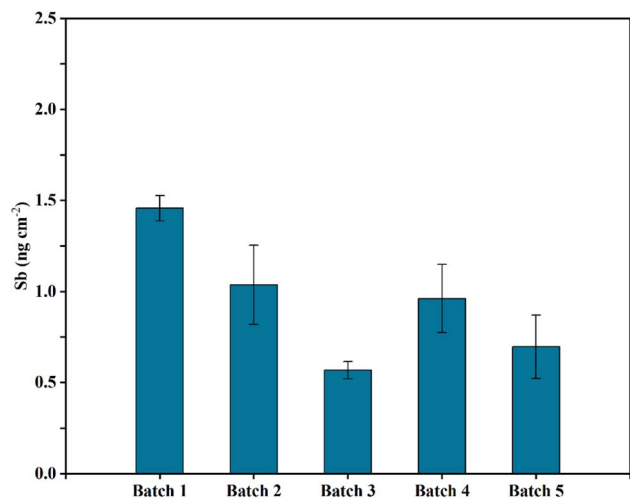
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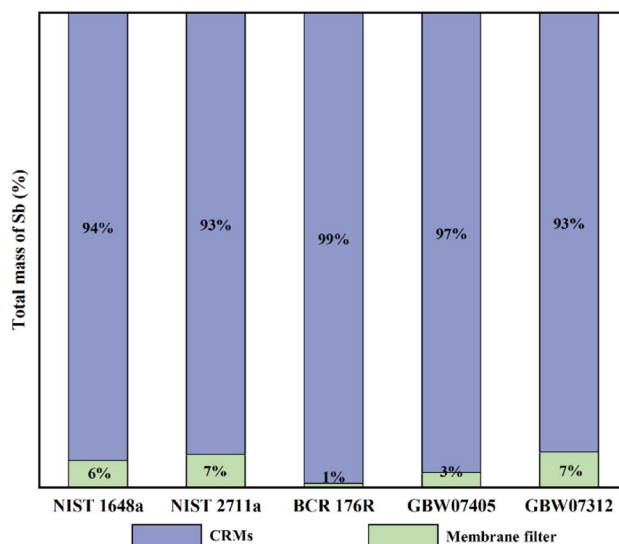Fig. 2   Blank values of antimony (Sb) in Whatman QM membrane filters of different production batches.

Fig. 3   The proportion of total antimony (Sb) in the blank membrane filters and certified reference materials (CRMs) in (MF + CRMs). The masses of the CRMs are given in the ESI; see Table S8.†

performed to check the stability and reproducibility (Fig. 2). Although the blank values of Sb in different production batches of Whatman brand QM membrane filters varied (0.50–1.59 ng cm^{-2}), the Sb concentrations in the constituent substances of the membrane filters from the same production batch should be identical (Table S5†).

The airborne particulate matter to be digested is a mixture of membrane filters and airborne particulate matter. The proportion of Sb in airborne particulate matter in mixed samples could be increased by prolonging the sampling time to eliminate the interference of membrane filters on the isotopic composition of airborne particulate matter. Jiang et al.[32] reviewed the published Sb contents in airborne particulate matter and reported that the contents of Sb in PM$_{2.5}$ in urban, suburban, and background areas were in the range of 0–11, 0–10, and 0–4 ng m^{-3}, respectively. The flow rate of the air sampler in the market was 60 m^3 h^{-1} (PM$_{2.5}$). Therefore, the optimal sampling time of Sb in PM$_{2.5}$ in urban, suburban, and background areas could be estimated. When the sampling time was longer than 17.8 h in urban areas, 19.6 h in suburban areas, and 48.9 h in background areas, the ratio of the Sb content in Whatman QM membrane filters (the highest was 821.5 ng) to that in PM$_{2.5}$ would be ≤7%. Under this condition, the membrane filters basically did not interfere with the isotopic compositions of the collected samples (Fig. 3). This result is only a preliminary estimate based on the reported data and is only applicable to the study area where the Sb concentration in PM$_{2.5}$ is unknown.

3.2.   Isotope validation using the standard addition method

The standard addition method was used to evaluate the effect of Whatman QM membrane filters on the isotopic compositions of the samples, in terms of recovery efficiencies, effects of different membrane filter sizes, effects of different production batches and parts of the membrane filters. The proportion of the total Sb mass in the added CRMs out of those of CRMs plus membrane filters was controlled to be more than 90% (Fig. 3).

The Sb recovery efficiency for the CRMs and (MF + CRMs)$_{MF}$ $_{subtraction}$ ranged from 90% to 112% (Table S7†). The Whatman QM membrane filters of different sizes had different Sb isotopic signatures, and the one with a size of Ø = 90 mm showed a heavier Sb isotope value of 1.91 ± 0.37ε (2SD, n = 9). The Sb isotopic compositions of Whatman QM membrane filters (203 mm × 254 mm) from different production batches tested at different time periods were basically identical, with a value of 0.94 ± 0.43ε (2SD, n = 8) (Table 1), which also verifies the long-term precision and reliability of the isotope analysis method used in this study. Moreover, the isotopic compositions of different parts of the same Whatman QM membrane filter could be considered the same, indicating even distribution of isotopic composition of the filter (Fig. 4).

The isotopic compositions of the CRMs, (MF + CRMs), and MF were analyzed. The proportion of membrane filters in the isotopic compositions of (MF + CRMs) was subtracted through the content proportion (Fig. 5). The ε^{123}Sb values of (MF + NIST 1648a)$_{MF}$ $_{subtraction}$, (MF + NIST 2711a)$_{MF\ subtraction}$, (MF + BCR176R) $_{MF}$ $_{subtraction}$, (MF + GBW07405) $_{MF\ subtraction}$, and (MF + GBW07312) $_{MF\ subtraction}$ were 2.59 ± 0.29ε (SD, n = 6), 1.73 ± 0.21ε (SD, n = 6), 0.41 ± 0.09ε (SD, n = 2), 2.47 ± 0.36ε (SD, n = 3), and 3.25 ± 0.02ε

Table 1   Antimony stable isotope ratios (ε^{123}Sb, ε) of the blank Whatman QM membrane filters tested in different time periods

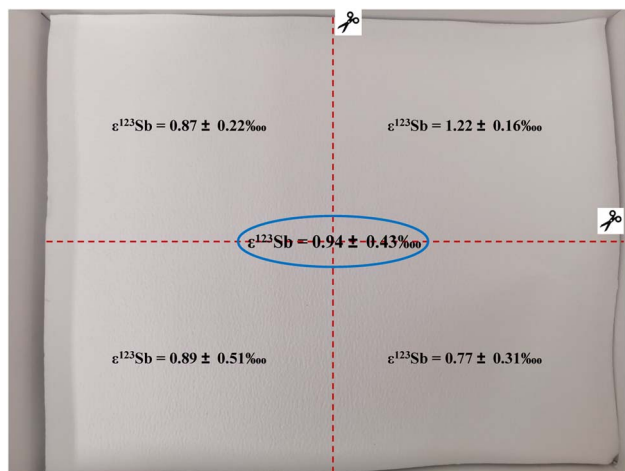| Date	203 mm × 254 mm			Ø = 90 mm		
2020.11.13	n = 3	Average	0.98			
		2SD	0.48			
2020.11.14	n = 2	Average	0.77			
		2SD	0.31			
2021.02.04	n = 3	Average	1.00	n = 9	Average	1.91
		2SD	0.49		2SD	0.37

Fig. 4 Spatial distribution of the antimony (Sb) stable isotope ratios over an entire Whatman QM membrane filter.

Table 2 Concentrations and stable isotope ratios of antimony in TSP and PM$_{2.5}$ samples collected in Guiyang

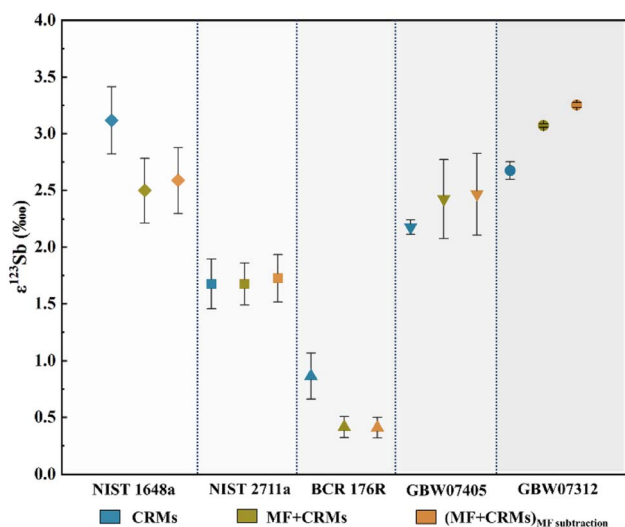| Sample type	Sampling duration (h)	Total Sb collected (µg)	Sb concentration (ng m^{-3})	ε^{123} Sb (ε)	SD
TSP					
1	72	12.89	3.86	1.90	0.02
2	96	24.31	5.80	1.99	0.07
3	95.5	13.97	3.21	2.34	0.02
PM$_{2.5}$					
1	72	8.01	2.43	2.16	0.02
2	96	13.45	3.20	2.23	0.07
3	95.5	8.02	1.84	2.57	0.02

Fig. 5 Antimony (Sb) stable isotope ratios of the certified reference materials (CRMs), CRMs + MF, and (MF + CRMs)$_{MF\ subtraction}$. NIST SRM 1648a and NIST SRM 2711a are standard solutions. BCR176R, GBW07405, and GBW07312 are three solid reference materials.

(SD, $n = 3$), respectively, which were favorably comparable to those of corresponding CRMs and (MF + CRMs), indicating that the blank values of the Whatman QM membrane filters basically did not affect the Sb isotopic compositions of the airborne particulate matter samples when the content proportion of the samples in the (samples + membrane filters) was ≥93%. Certainly, the correction of the membrane filter isotopic perturbation is recommended at all times.

3.3. Application to TSP and PM$_{2.5}$ samples

To verify the feasibility of the method proposed in Section 2.2 and to trace the sources of Sb in fine particles in Guiyang, TSP and PM$_{2.5}$ samples on a selected street in this city were collected

on the Whatman QM membrane filters and then pretreated using the method described above for Sb isotope measurement. The results showed that the mean concentrations of Sb in TSP and PM$_{2.5}$ were 4.29 ± 1.35 and 2.49 ± 0.68 ng m^{-3} (Table 2), respectively. These numbers were remarkably lower than most of the previously reported values in urban environments worldwide.[32] This may be due to the fact that most of the reported cases were old, and strict emission reduction policies had not been implemented at that time. Taking China as an example, the Air Pollution Prevention and Control Action Plan (2013–2017) and the Three Year Action Plan to Win the Battle for a Blue Sky (2018–2020) had been implemented in the past decade. In addition, most reports have focused on atmospheric Sb in typical industrial cities.

Comparing with the literature reported Sb isotopic compositions of the CRMs (Fig. 6),[34,40] the isotopic compositions of Sb in TSP (2.08 ± 0.23ε) and PM$_{2.5}$ (2.32 ± 0.22ε) samples are similar to those of the soil reference material (GSS-5; 2.12 ± 0.10ε). GSS-5 was collected from a copper polymetallic mine area in China, which indicates that mining or smelting activities may be one of the sources of Sb in airborne particles in the study area. SGR-1b is an oil shale powdered reference material collected from Mahogany zone in America. The ε^{123}Sb value of SGR-1b (0.29 ± 0.31ε) is significantly lower than that of all soil reference materials, TSP and PM$_{2.5}$ samples, which may be related to isotopic fractionation in the process of oxidative weathering of shales. Similar conclusions have been confirmed in the study of Se isotopes.[50] It is necessary to conduct further actual sample analysis to deeply reveal the isotopic fractionation behavior of Sb in the process of weathering of shales. It was reported that the main anthropogenic atmospheric emission of Sb in Guizhou province was coal combustion.[1] Therefore, the heavier isotope value of the coal fly ash reference material (NIST 1633c) compared with the airborne particles in this study indicates other sources of airborne particles-Sb in the study area. The ε^{123}Sb value of human urine reference material (ClinChek urines level II; 3.04 ± 0.20ε) is heavier than that of airborne particles and human blood reference material (Seronorm whole blood level II; 2.24 ± 0.10ε). It has been reported that the inhalation of airborne particles constitutes a source of Sb in

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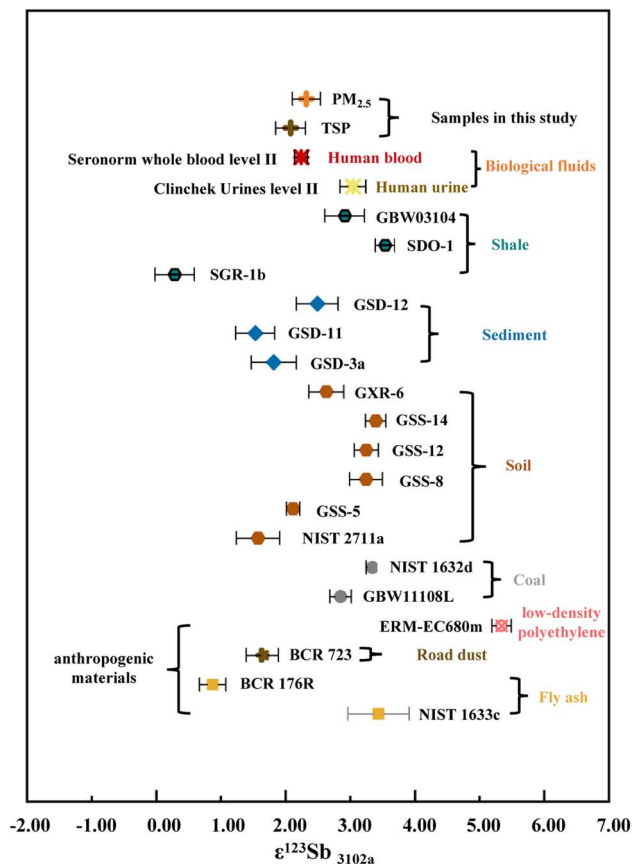
Fig. 6 Antimony (Sb) stable isotope ratios of the TSP and PM$_{2.5}$ samples collected in Guiyang in this study and the results of different CRMs reported in Sun et al.[34] and Ferrari et al.[40]

4. Conclusions

In this study, a pretreatment method for Sb in airborne particulate matter for high-precision Sb isotopic analysis was developed for the first time. Owing to its lower Sb blank values and feasibility of long-term sampling, the Whatman QM membrane filter was recommended as the sampling medium for airborne particulate matter for Sb isotopic analysis. The long-term isotopic analysis of Sb from different production batches yielded identical results, confirming the reproducibility and precision of the measured isotopic ratios. The isotopic compositions of CRMs, (MF + CRMs), and (MF + CRMs)$_{MF\ subtraction}$ showed no significant differences, indicating that the Whatman QM membrane filter had almost no effect on the isotopic ratio of airborne particulate matter when its proportion in the (MF + CRMs) was ≤7%. The feasibility of this method was further verified with Sb isotopic measurements of TSP and PM$_{2.5}$ samples in Guiyang. In conclusion, this study has successfully delivered one of the indispensable tools needed for better understanding the sources and geochemical behaviors of Sb in airborne particulate matter.

Author contributions

All authors listed contributed to the study conception and literature writing. Conceptualization: Guangyi Sun and Xinbin Feng; experiment design and operation: Guangyi Sun, Xinyu Li, Yunjie Wu, and Chao Zhang; data analysis: Guangyi Sun, Xinyu Li, Yunjie Wu, and Chao Zhang; draft writing: Chao Zhang; writing-review & editing: Guangyi Sun, Heng Yao, Jen-How Huang, and Xinbin Feng; supervision: Guangyi Sun and Xinbin Feng. All authors read and approved the final manuscript.

Conflicts of interest

There are no conflicts to declare.

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pregnant women and the general population in urban areas.[18] Therefore, Sb in airborne particles can be absorbed by human body through respiration and further distribute in blood *via* circulatory system.[51] Then, similar to Cd behavior in other studies,[52] Sb in the blood may be bound with metallothionein (MT) and the Sb–MT complexes are easily filtered through the glomeruli because of their small size before being re-absorbed by the proximal tubuli. According to the known theory that light Cd isotope is preferentially enriched on thiol groups,[53] it is speculated that thiol groups in MT may preferentially combine with light Sb isotope, and un-complexed Sb in the urine would be enriched in the heavy Sb isotope. This may explain the enrichment of heavier Sb in urine. In addition, according to a study of Zn isotopes,[54] the difference between the isotope compositions of blood and urine may be due to the fact that low molecular weight molecules-Sb with a preferential enrichment of the light Sb isotope is filtered by the glomerulus during urination, resulting in heavier Sb isotopic composition in urine. Further studies on the mechanisms of adsorption/desorption, redox, methylation and human physiology are needed to verify these hypotheses. Such finding also reveals the potential of Sb isotopes as tracers of human Sb exposure. Overall, the method we proposed in this study is feasible in practical applications.

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