

RESEARCH ARTICLE

# Evaluating sulfur-impurity removal and modern carbon contamination in different preparation methods for radiocarbon dating of soil samples by accelerator mass spectrometry

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## Abstract

Radiocarbon (<sup>14</sup>C) dating of soil samples by accelerator mass spectrometry (AMS) has been proven useful for studying carbon (C) cycling in terrestrial ecosystems. However, this application has two primary difficulties in sample preparation: inhibition of graphite formation due to sulfur (S)-containing impurities and contamination of samples with modern C (MC). Herein, we evaluated these effects using three sample preparation methods (silver foil, silver wire, and Sulfix) by conducting AMS-<sup>14</sup>C measurements of a <sup>14</sup>C-dead charred wood and S-rich soil samples. The preparation methods were all successful in graphite formation and AMS-<sup>14</sup>C measurement for soil samples with an organic S content <6.9 wt%. The methods showed different percent modern carbon (pMC) values from 0.16% to 0.64% for the <sup>14</sup>C-dead sample. The results also revealed that across different methods, MC contamination can be significantly reduced by applying two-step procedure (combustion and subsequent reaction to remove S-containing impurities) during sample preparation. The three methods had a negligible influence on determining the <sup>14</sup>C age for samples that were at least younger than 12,000 yr BP. As the <sup>14</sup>C ages of the soil samples are typically younger than 12,000 yr BP, any method explored in this study can be employed for <sup>14</sup>C dating with sufficient accuracy for application to C cycle studies.

## 1. Introduction

Global warming and its effects on the climate system is one of the greatest threats to all life on Earth. Therefore, there is an increasing interest in understanding the global carbon (C) cycle as global warming is tightly coupled with the global C cycle (Crowther et al. 2016; IPCC 2021). Soil plays a critical role in the global C cycle; it stores a huge amount of C as soil organic carbon (SOC) and produces a large emission flux of carbon dioxide (CO<sub>2</sub>), the primary greenhouse gas, from the soil to the atmosphere through SOC decomposition (IPCC 2021). Hence, an accurate assessment of the capability of soil to preserve SOC is essential to improve our ability to predict the future of Earth's climate.

Radiocarbon (<sup>14</sup>C) can be a powerful tool to quantitatively assess the SOC cycling rate in soils because it provides information on the timescale of C as it has been preserved in soils since its fixation and incorporation from the atmosphere (Schoor et al. 2016; Trumbore 2009). Briefly, the abundance of natural <sup>14</sup>C, cosmogenically produced at a moderately constant rate in the upper atmosphere, can be used to identify stable SOC pools that are old enough for significant radioactive decay (with a half-life of 5730 years) in soils.

Accelerator mass spectrometry (AMS) is the most widely used and extremely sensitive technique for  $^{14}\text{C}$  measurements. Recently, the demand for AMS- $^{14}\text{C}$  measurements of soil samples has been increasing due to the great benefit of  $^{14}\text{C}$  analysis in studying SOC cycling (Saito-Kokubu et al. 2023; Schuur et al. 2016). However, two critical difficulties occur in conducting AMS- $^{14}\text{C}$  measurements for soil samples with high reliability and accuracy, both of which are encountered during AMS sample preparation. Sample preparation primarily comprises the combustion of soil samples to generate  $\text{CO}_2$  and graphitization through the catalytic reduction of  $\text{CO}_2$ . The first challenge appears mainly in the combustion process. C-containing impurities associated with chemicals are introduced to the samples, contaminating the samples with modern ( $^{14}\text{C}$ -enriched) C (MC) (Mueller and Muzikar 2002; Schleicher et al. 1998; Vandeputte et al. 1998). The second difficulty appears in the graphitization process. Sulfur (S)-containing impurities (S oxides) generated from the soil samples during combustion are introduced to the samples, inhibiting formation of graphite, the typical target for AMS- $^{14}\text{C}$  measurement (Minami et al. 2011; Thomsen and Gulliksen 1992; Zazzo et al. 2013). The effect of S-containing impurities on graphite formation might be more critical for soil samples than other samples because S is present in organic matter in all soils (Schnug et al. 2017). Various methods, for example, using silver (Ag) wire and Sulfix reagent (a mixture of tricobalt tetra-oxide and Ag), have been attempted to remove S-containing impurities during sample preparation (Boutton et al. 1983; Hua et al. 2001; Koarashi et al. 2009; Nakajima et al. 2004; Zazzo et al. 2013). However, few studies have comprehensively examined the removal of S-containing impurities and MC contamination during sample preparation for different preparation methods.

Therefore, the present study aimed to evaluate the applicability of sample preparation methods to the  $^{14}\text{C}$  dating of soil samples with sufficient accuracy for C cycle studies. We conducted two investigations using three sample preparation methods for AMS. The first test is to evaluate the effects of the methods on S removal and  $^{14}\text{C}$  dating based on the graphitization conditions and AMS- $^{14}\text{C}$  measurements for S-rich soil samples. The second test is to quantify MC contamination from the methods based on the AMS- $^{14}\text{C}$  measurement of a  $^{14}\text{C}$ -dead charred wood sample.

## 2. Materials and methods

### 2.1. Sample preparation methods

This study considered three common methods for removing S-containing impurities during sample preparation: (1) Ag foil (Boutton et al. 1983; Koarashi et al. 2009), (2) Ag wire (Hua et al. 2001; Nakajima et al. 2004), and (3) Sulfix (Vandeputte et al. 1998; Nakajima et al. 2004; Zazzo et al. 2013; Beck et al. 2018). Details of the methods and preparation conditions are described below.

In the Ag foil method, a solid sample was flame-sealed in prebaked quartz tubes under vacuum, with approximately 1 g of copper oxide (CuO) wire and 0.5 g of reduced copper (Cu) wire. Ag foil (length 50 mm, width 5 mm, thickness 0.0045 mm, purity 99.99%, Shoko Co., Ltd.) was also added into the tubes to remove S-containing impurities. The samples in the sealed tubes were combusted at  $850^\circ\text{C}$  for 2 hr to generate  $\text{CO}_2$ . After that,  $\text{CO}_2$  in the generated gas was cryogenically purified and recovered using a vacuum line.

The Ag wire method is mostly the same as the Ag foil method. The only difference between the two methods was using an Ag wire (diameter 0.1 mm, length 10 mm, purity >99.5%, 5 pieces, FUJIFILM Wako Pure Chemical Corporation, Japan) instead of Ag foil.

The Sulfix method requires a two-step procedure (Nakajima et al. 2004; Vandeputte et al. 1998). First, similar to the other methods, a solid sample was flame-sealed in quartz tubes under vacuum, with approximately 1 g of CuO wire and a piece of platinum (Pt). The samples in the sealed tubes were combusted at  $850^\circ\text{C}$  for 2 hr, and the  $\text{CO}_2$  generated from the samples was cryogenically purified, as before. Second, the purified  $\text{CO}_2$  was transferred into prebaked Pyrex tubes where three grains of Sulfix reagent (diameter 0.8–2.4 mm, Kishida Chemical Co., Ltd., Japan) were placed, and the tubes were flame-sealed under vacuum. The tubes were baked at  $500^\circ\text{C}$  for 1 hr to react the S-containing impurities

**Table 1.** Preparation methods for removing sulfur-containing impurities

Method	Notation	Condition
Ag foil	Ag foil_UT	Untreated Ag foil
	Ag foil_PW	Ag foil washed with ultrapure water
	Ag foil_ET	Ag foil washed with ethanol
	Ag foil_AC	Ag foil washed with acetone
	Ag foil_500	Ag foil pre-baked at 500°C
	Ag foil_800	Ag foil pre-baked at 800°C
	Ag foil_TS500	Two-step preparation with Ag foil pre-baked at 500°C
Ag wire	Ag wire	
Sulfix	Sulfix_3	3 grains of Sulfix
	Sulfix_15	15 grains of Sulfix
	Sulfix_45	45 grains of Sulfix
	Sulfix_SS3	Single-step preparation with 3 grains of Sulfix

in the gas with Sulfix reagent, after which the CO<sub>2</sub> in the tubes was cryogenically purified and recovered using a vacuum line.

Table 1 summarizes the preparation methods investigated in this study. Regarding the Ag foil method, organic materials adhering to the surface of Ag foil can be a primary source of MC contamination in the AMS-<sup>14</sup>C measurement. Therefore, Ag foils subjected to various pretreatments to decontaminate the surface were used for comparison. The decontamination pretreatments for Ag foil include washing with ultrapure water, ethanol, and acetone and prebaking at 500°C and 800°C for 3 hr.

The Ag foil method has been commonly performed through the single-step procedure as described above. However, testing a two-step procedure in the Ag foil method still merits consideration especially in comparison with the Sulfix method under the same preparation condition. Therefore, the following two-step method was also examined in this study. A solid sample was combusted at 850°C for 2 hr in sealed quartz tubes under vacuum, with approximately 1 g of CuO wire and 0.5 g of Cu wire. The resulting CO<sub>2</sub> was cryogenically purified and transferred into prebaked Pyrex tubes where Ag foil (prebaked at 500°C for 3 hr) was placed. The tubes were baked at 500°C for 1 hr to react the S-containing impurities with Ag foil, and the CO<sub>2</sub> in the tubes was cryogenically purified again and recovered.

Regarding the Sulfix method, the effect of the amount of Sulfix on the AMS-<sup>14</sup>C measurements was also examined using different numbers (and thus, different amounts) of Sulfix grains (15 and 45 grains). Furthermore, the following single-step method was evaluated to investigate the effect of Sulfix on the AMS-<sup>14</sup>C measurement. Three Sulfix grains were flame-sealed in quartz tubes together with the Aso-3 sample, CuO, and Pt chip, and they were combusted simultaneously at 850°C for 2 hr. The CO<sub>2</sub> in the quartz tubes was then cryogenically purified and recovered, as before.

## 2.2. Graphitization and AMS-<sup>14</sup>C measurement

The purified CO<sub>2</sub> from the different preparation methods was converted into graphite by reducing it with hydrogen gas (H<sub>2</sub>) at 650°C in the presence of iron (Fe) powder (pre-reduced with H<sub>2</sub> at 450°C) as a catalyst (Kitagawa et al. 1993). The <sup>14</sup>C content of the sample was measured on the graphite target using AMS at the Tono Geoscience Center, Japan Atomic Energy Agency (JAEA-AMS-TONO-5MV and JAEA-AMS-TONO-300kV, Xu et al. 2000; Saito-Kokubu et al. 2023).

A subsample of the purified CO<sub>2</sub> was used to measure the stable C isotope ratio ( $\delta^{13}\text{C}$ ) with an isotope ratio mass spectrometer (IsoPrime100, Isoprime Ltd., UK), and the  $\delta^{13}\text{C}$  value (‰) was used to correct the mass-dependent isotopic fractionation effect on the <sup>14</sup>C result (Stuiver and Polach 1977). The <sup>14</sup>C results were reported as percent MC (pMC) with a blank correction. This study prepared the sample

processing blank using a quality control material, the International Atomic Energy Agency (IAEA)-C1 sample (carbonate with a recommended  $^{14}\text{C}$  activity value of 0.00 pMC; Rozanski et al. 1992; IAEA 2014). The blank correction was made by subtracting the  $^{14}\text{C}$  activity value of the blank sample from that of the measured sample. In the blank preparation,  $\text{CO}_2$  generation from the IAEA-C1 sample was achieved through the carbonate reaction with phosphoric acid without any combustion processes (i.e., without using any chemicals for combustion or sulfur oxide removal). Therefore, the  $^{14}\text{C}$  results reported here can be used to compare the  $^{14}\text{C}$ -contamination effects of the preparation methods, including contaminations from the chemicals used for combustion and S-impurity removal in the methods. The pMC values measured for the IAEA-C1 were  $0.13\% \pm 0.06\%$  (1std) and  $0.40\% \pm 0.01\%$  for JAEA-AMS-TONO-5MV and JAEA-AMS-TONO-300kV, respectively (Saito-Kokubu et al. 2019).

### ***2.3. Application of the preparation methods to soil samples***

The methods were applied to soil samples with different S contents to confirm whether they work well in removing S-containing impurities during sample preparation and forming graphite for AMS- $^{14}\text{C}$  measurements. This study used three soil samples (Soil-1, Soil-2, and Soil-3) collected in sulfur-rich hot spring areas (Takayu and Tsuchiyu) in Fukushima, Japan. The soil samples were dried, sieved with a 2-mm mesh, ground to a fine powder to homogenize the samples, and analyzed for organic C and S contents (as weight percent: wt%) using an elemental analyzer (vario PYRO cube, Elementar, Germany). The organic C contents were 6.1, 3.0, and 3.8 wt% for Soil-1, Soil-2, and Soil-3, respectively. The organic S contents were 6.9, 3.7, and 1.4 wt% for Soil-1, Soil-2, and Soil-3, respectively. In addition to the soil samples, sulfanilamide (an organic sulfur compound with a high S content of 18.6 wt%, Elementar, Germany) and a quality control material IAEA-C5 (subfossil wood, S content of 1.0 wt%) were also used to evaluate the methods.

The methods tested were the Ag foil (without any treatments for decontamination of foil surface), two-step Ag foil, and Sulfix (with 3 and 15 grains) methods. After preparing the different samples with different methods, AMS- $^{14}\text{C}$  measurements were conducted in the same manner as before. Then, the conditions of graphite formation, the graphitization yields (defined as the percentage of the C amount of formed graphite to the C amount of  $\text{CO}_2$  used for graphitization), and the AMS- $^{14}\text{C}$  measurement results were examined and compared.

### ***2.4. Evaluation of modern carbon contamination from the preparation methods***

The MC contamination introduced by these methods was evaluated based on the AMS- $^{14}\text{C}$  measurement of a charred wood sample (Aso-3). The Aso-3 sample was formed by the volcanic eruption of Mt. Aso more than 100,000 years ago and comprises dead carbon (i.e., it does not contain  $^{14}\text{C}$ ). The different preparation methods used approximately 3.5 mg of the Aso-3 sample as a solid sample.

## **3. Results and discussion**

### ***3.1. Applicability of the preparation methods to soil samples***

The soil samples that differ in organic S content were prepared with the Ag foil and Sulfix methods, and the results confirmed that all sample preparations ( $N = 18$ ) successfully generated graphite (Table 2). Moreover, the AMS- $^{14}\text{C}$  measurements were successful for all graphite targets, indicating that the preparation methods effectively removed S-containing impurities during sample preparation and can at least be used to prepare soil samples with an organic S content  $< 6.9$  wt%. As the total S contents in soils typically range from 0.01 wt% to 3.5 wt% (Schnug et al. 2017), the preparation methods can be applied to a broad range of soil samples collected from forests and even agricultural (i.e., fertilizer-adopted)

**Table 2.** Graphitization yields and accelerator mass spectrometry (AMS)- $^{14}\text{C}$  measurement results for different samples with different preparation methods

Method	Sample	C content (wt%)	S content (wt%)	Sample amount (mg)	Graphitization yield (%)	$\delta^{13}\text{C}$ (‰)	pMC (%)
Ag foil_UT	Soil-1	6.1	6.9	32.3	63.5	-25.0	95.7 ± 0.7 <sup>a</sup>
	Soil-2	3.0	3.7	63.7	86.5	-26.7	92.4 ± 0.7
	Soil-3	3.8	1.4	43.9	57.8	-29.2	100.0 ± 1.0
	Sulfanilamide	41.9	18.6	4.5	75.4	-27.1	0.88 ± 0.03
	IAEA-C5 <sup>c</sup>	49.0	1.0	4.9	46.7	-25.6	23.3 ± 0.2
Ag foil_TS500	Soil-1	6.1	6.9	32.6	84.9	ND <sup>d</sup>	95.1 ± 0.6
	Soil-2	3.0	3.7	60.0	83.0	ND	91.1 ± 0.7
	Soil-3	3.8	1.4	43.5	78.2	ND	98.5 ± 0.7
	Sulfanilamide	41.9	18.6	4.8	84.0	ND	0.08 ± 0.04
Sulfix_3	Soil-1	6.1	6.9	31.5 (0.5) <sup>b</sup>	46.2 (17.2) <sup>b</sup>	-24.9 (0.4) <sup>b</sup>	95.8 (2.1) <sup>b</sup>
	Soil-2	3.0	3.7	60.4 (0.1)	81.1 (4.2)	-26.5 (0.1)	92.6 (2.2)
	Soil-3	3.8	1.4	43.2 (0.0)	81.8 (8.9)	-29.8 (1.4)	98.9 (1.6)
Sulfix_15	Soil-1	6.1	6.9	31.1	86.3	-25.1	96.3 ± 0.7
	Soil-2	3.0	3.7	62.0	74.7	-26.9	92.4 ± 0.7
	Soil-3	3.8	1.4	43.9	71.1	-29.2	100.5 ± 0.7
	Sulfanilamide	41.9	18.6	4.8	89.6	-27.0	0.34 ± 0.02
	IAEA-C5 <sup>c</sup>	49.0	1.0	4.7	79.5	-25.6	23.3 ± 0.3

<sup>a</sup>Errors represent the counting errors in the AMS- $^{14}\text{C}$  measurement.<sup>b</sup>Mean and standard deviation (in parentheses) of three replicate samples ( $N=3$ ).<sup>c</sup>Subfossil wood sample provided as a quality control material by the IAEA (Rozanski et al. 1992; IAEA 2014).<sup>d</sup>ND: Not determined.

ecosystems developed on different parent materials globally. Furthermore, with these preparation methods, the graphitization and AMS- $^{14}\text{C}$  measurements were achieved for sulfanilamide, indicating that these preparation methods are potentially applicable to soil samples with an organic S content of up to 18 wt%.

The graphitization yield of the preparation methods was 32%–90% for the samples with different S contents, including soils, sulfanilamide, and subfossil wood. Although the graphitization yield was below 50% for some samples, no clear dependences of the graphitization yield on the sample type and preparation method were observed. However, lower graphitization yields for Soil-1 (with a high S content) in the Sulfix\_3 method may suggest an insufficient surface area of Ag reagent in the method to completely absorb S compounds, given that the estimated surface area of 3 grains of Sulfix reagent (approximately 0.06–0.3 cm<sup>2</sup>) was significantly smaller than those of 15 grains of Sulfix reagent (approximately 0.54–2.71 cm<sup>2</sup>) and Ag foil (2.5 cm<sup>2</sup>). Nakajima et al. (2004) reported a similar range of graphitization yield (29%–90%) for preparing elemental C (EC) in aerosol samples, with preparation methods using Ag wire, Sulfix reagent (15–30 mg, corresponding to the amount of 3 grains of Sulfix reagent in this study), and their combination. However, they further reported that graphite could not be obtained from three of the 11 EC samples, even though such preparation methods were employed to remove S-containing impurities. Moreover, Minami et al. (2011) reported that Sulfix treatment for CO<sub>2</sub> (with 30–40 mg of Sulfix reagent at 380°C for 1 hr) made it possible to form graphite from the samples (polyethersulfone) previously prevented from forming graphite with preparation methods using Ag wire and an *n*-pentane/liquid N<sub>2</sub> trap. Hence, the cause of the variability in graphitization yield is not yet fully understood and further work is needed for optimization of the methods.

The  $\delta^{13}\text{C}$  values obtained for the soil and sulfanilamide samples using the different preparation methods were consistent with each other (Table 2), and the values measured for the IAEA-C5 (subfossil wood sample) were in good agreement with the reference value (−25.5‰, with a standard deviation of 0.7‰; Rozanski et al. 1992; IAEA, 2014). The results support that the preparation methods have little influence on the  $\delta^{13}\text{C}$  determination.

Regarding the  $^{14}\text{C}$  measurements for soil and subfossil wood samples, no clear difference in the pMC value was observed between the preparation methods while considering the analytical uncertainty in the measurement and the standard deviation of the replicate samples (Table 2). However, with the  $^{14}\text{C}$  measurements for sulfanilamide, the pMC values were very low and differed between the preparation methods. The pMC value obtained for sulfanilamide was low in the order of Ag foil\_TS500 < Sulfix\_15 < Ag foil\_UT, which is consistent with the results of the MC contamination from the different preparation methods (see Section 3.2). Generally, the pMC values measured for IAEA-C5 were consistent with the reference value (23.05% ± 0.02%; Rozanski et al. 1992; IAEA, 2014).

The conventional  $^{14}\text{C}$  ages estimated for the different samples were compared between the Ag foil and Sulfix methods (Table 3). The results show that the methods give a similar  $^{14}\text{C}$  age for each of the three soil samples, indicating that for the studied soils with a  $^{14}\text{C}$  activity of approximately 90 pMC and higher, the preparation methods for the S-impurity removal do not play any role in the MC contamination. The  $^{14}\text{C}$  ages estimated for the IAEA-C5 (reference value: 11,790 ± 10 years BP) were 11,710 ± 70 years BP and 11,690 ± 90 years BP for the Ag foil and Sulfix methods, respectively, indicating that the preparation methods have a negligible impact on the determination of the  $^{14}\text{C}$  ages for samples at least younger than approximately 12,000 yr BP. However, the  $^{14}\text{C}$  age for sulfanilamide with the Ag foil method (~38,000 yr BP) was estimated to be significantly younger than those with the Sulfix method (~45,600 yr BP) and the two-step Ag foil method (~57,000 yr BP with a large uncertainty), probably due to MC contamination during sample preparation (see Section 3.2).

### **3.2. Modern carbon contamination from the different preparation methods**

For the different preparation methods for removing S-containing impurities, contamination by MC, which is introduced during sample preparation, was evaluated based on the AMS- $^{14}\text{C}$  analysis of the

**Table 3.** Conventional  $^{14}\text{C}$  ages estimated for different samples with different preparation methods

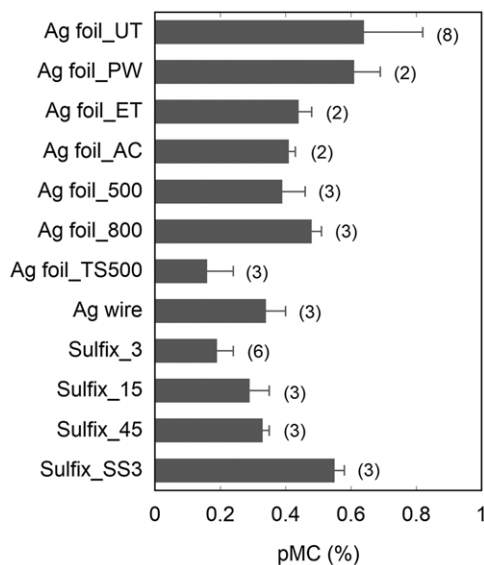
Sample	Conventional $^{14}\text{C}$ age (yr BP)			
	Ag foil_UT	Ag foil_TS500	Sulfix_3	Sulfix_15
Soil-1	350 ± 60 <sup>a</sup>	400 ± 50 <sup>a</sup>	340 (180) <sup>b</sup>	300 ± 60 <sup>a</sup>
Soil-2	640 ± 60	750 ± 60	620 (190)	640 ± 60
Soil-3	1 ± 80	120 ± 60	90 (130)	Modern
IAEA-C5 <sup>c</sup>	11,710 ± 70	— <sup>d</sup>	—	11,690 ± 90
Sulfanilamide	38,000 ± 200	57,000 ± 6,000	—	45,600 ± 400

<sup>a</sup>Errors represent the counting errors in the AMS- $^{14}\text{C}$  measurement.

<sup>b</sup>Mean and standard deviation (in parentheses) of three replicate samples ( $N = 3$ ).

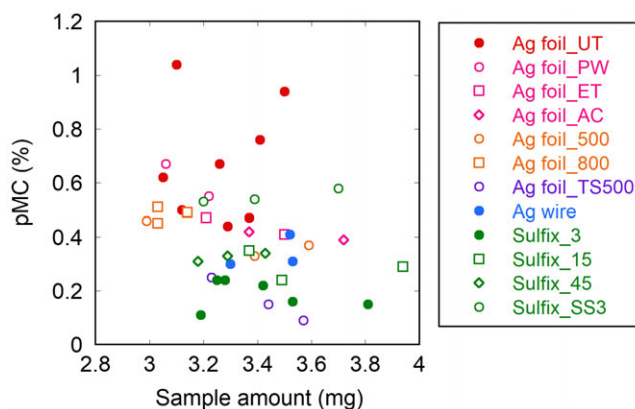
<sup>c</sup>Subfossil wood sample provided as a quality control material by the IAEA (Rozanski et al. 1992; IAEA 2014).

<sup>d</sup>Not available.

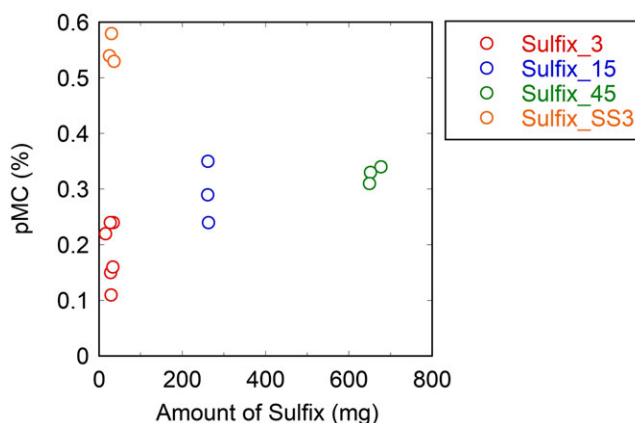


**Figure 1.** pMC values obtained for the Aso-3 sample with different preparation methods. The numbers in parentheses represent the numbers of replicate samples, and the error bars represent the standard deviation of the replicate samples. UT: Untreated Ag foil; PW: Ag foil washed with ultrapure water; Ag foil washed with ethanol; AC: Ag foil washed with acetone; 500: Ag foil pre-baked at 500°C; 800: Ag foil pre-baked at 800°C; 500TS: Two-step preparation with Ag foil pre-baked at 500°C; 3: 3 grains of Sulfix; 15: 15 grains of Sulfix; 45: 45 grains of Sulfix; SS3: Single-step preparation with 3 grains of Sulfix.

$^{14}\text{C}$ -dead (Aso-3) sample (Figure 1; see also Table S1 in the Appendix for numerical data for all measurements). These methods showed different pMC values from 0.16% to 0.64% with an average of 0.40%. As a general tendency, the pMC value was high when the sample was prepared with the Ag foil method and low when the sample was prepared with the Sulfix method. However, more importantly, the two-step Ag foil method (Ag foil\_TS500) showed the lowest pMC values and thus had the lowest levels of MC contamination among the methods investigated in the present study. This finding demonstrates that two-step procedure is the key to reducing MC contamination during sample preparation across different (Ag foil and Sulfix) methods. A weak negative correlation ( $r = -0.32$ ,  $p < 0.05$ ) was found between the pMC value and the amount of sample (Figure 2), but the figure also showed that this correlation was probably due to the methodological bias that overall, the amounts of sample used in the



**Figure 2.** pMC values obtained for different amounts of the Aso-3 sample with different preparation methods.



**Figure 3.** pMC values obtained for the Aso-3 sample with different amounts of Sulfix reagent in the Sulfix methods.

Ag foil methods were smaller than those in the Sulfix methods. Therefore, the results indicate that the level of MC contamination largely depends on the used method.

The pretreatments to decontaminate the Ag foil surface effectively reduced MC contamination in the Ag foil method (Figure 1), except when washing with ultrapure water (Ag foil\_PW). The pMC value for the Aso-3 sample decreased from 0.64% (for Ag foil\_UT) to 0.42% (for Ag foil\_ET and Ag foil\_AC) while washing the surface with organic solvents. Prebaking the Ag foil also decreased the pMC value to 0.44% (for Ag foil\_500 and Ag foil\_800). Hence, organic materials on the Ag foil surface are proposed to be a crucial source of MC contamination during sample preparation, and these pretreatment procedures help reduce contamination levels in the Ag foil method. Here, it should be emphasized again that even after the pretreatment for Ag foil, introducing the two-step procedure can further reduce MC contamination (Ag foil\_500 versus Ag foil\_TS500).

The Sulfix methods, except for the single-step Sulfix method (Sulfix\_SS3), had lower pMC values than the Ag foil methods with single-step procedure (Figure 1). The pMC value for the Aso-3 sample increased with the increasing amount of Sulfix reagent used (Figure 3), indicating that the Sulfix reagent itself can be the origin of MC contamination. This result is consistent with the study performed by Zazzo et al. (2013), who reported that the pMC values measured for the IAEA-C1 sample with Sulfix treatment



were higher (i.e., more contaminated with MC) than those without Sulfix treatment. Furthermore, the  $^{14}\text{C}$  age estimated with the Sulfix (~500 mg) treatment could be younger by 8000 yr than that without the Sulfix treatment for calcined bone samples of an expected  $^{14}\text{C}$  age of more than 32,000 yr BP.

Generally, the Sulfix method requires an additional sample preparation process because Sulfix treatment is applied to  $\text{CO}_2$  after purification and conducted at a reaction temperature lower than the sample combustion temperature (Minami et al. 2011; Nakajima et al. 2004). This study evaluated its potential applicability using a single-step procedure for the Sulfix method, where Sulfix treatment was applied to  $\text{CO}_2$  before purification at the combustion temperature. The single-step Sulfix method can form graphite (it was not for S-containing soil samples but for the charred wood sample) but represented a moderately high level of MC contamination (pMC value: 0.55%) compared with the general (i.e., two-step procedure) Sulfix methods (Figure 1). Thus, this result indicates that C-containing impurities were liberated from the Sulfix reagent at a high combustion temperature (850°C) and became a source of MC contamination during sample preparation. However, the contamination level was similar to that of the single-step Ag foil methods with decontamination pretreatments for Ag foil.

It was interesting to observe that the MC contamination from the Ag wire method was less than or comparable to that from the Ag foil methods (Figure 1), even though no pretreatment was applied to the Ag wire. The reason for the difference in the contamination level between the two is unclear; however, it might be due to the difference in the total surface area between Ag foil (2.5 cm<sup>2</sup>) and Ag wire (0.16 cm<sup>2</sup>) used in the methods. Another reason could be due to the difference in the storage conditions between the reagents: Ag wire was stored in a small gas-tight container until use, whereas Ag foil was stored in a desiccator.

### 3.3. Implications for $^{14}\text{C}$ dating to study carbon cycling in terrestrial ecosystems

The effect of MC contamination during sample preparation on the AMS- $^{14}\text{C}$  measurement can potentially be excluded by applying a straightforward blank correction when the contamination is assumed to be constant depending on the preparation method (i.e., preparing a blank sample in the same way as the target sample and subtracting the  $^{14}\text{C}$  activity value of the blank sample from that of the target sample) (Hua et al. 2004; Mueller and Muzikar 2002). This is because sample preparation (i.e., combustion of the sample, in particular) is a major source of MC contamination throughout the entire processes of AMS- $^{14}\text{C}$  measurement (Schleicher et al. 1998; Vandeputte et al. 1998; Vogel et al. 1987). However, the reliability and accuracy of the  $^{14}\text{C}$  dating still rely on minimizing the MC contamination during sample preparation, especially for small and old ( $^{14}\text{C}$ -depleted) samples (Rethemeyer et al. 2013; Sun et al. 2020; Vandeputte et al. 1998).

This study's results demonstrate that the two-step procedure is a useful way to reduce MC contamination during sample preparation for both the Ag foil and Sulfix methods. The  $^{14}\text{C}$  age of the soil (SOC) samples of primary interest in studying the interactions between the C cycle and climate change is typically younger than 12,000 yr BP (e.g., Balesdent et al. 2018; Koarashi et al. 2009; Luo et al. 2019; Shi et al. 2020). The two-step procedure in the preparation methods is time-consuming and labor-intensive compared with the single-step procedure. Therefore, we conclude that if the straightforward blank correction is conducted, any method examined in this study can be applied to  $^{14}\text{C}$  dating with sufficient accuracy to study SOC cycling in terrestrial ecosystems. This conclusion is consistent with the recent finding of Olsen et al. (2023), who showed that the effect of the Sulfix method on the  $^{14}\text{C}$  age is small and generally within the measurement uncertainties for cremated bone samples with an estimated  $^{14}\text{C}$  age of approximately 3000 yr BP. However, there has been an increasing demand for  $^{14}\text{C}$  dating of small samples, such as a minor fraction and specific compound of SOC, with the advancement of the research field of biogeochemical cycles (Koarashi et al. 2012; Kuzyakov et al. 2014; Nakanishi et al. 2012; Sun et al. 2020; Wijesinghe et al. 2020). For such small and old samples, it is recommended to use the two-step procedure for the preparation of AMS- $^{14}\text{C}$  measurements. It has also been documented that C-containing impurities associated with CuO and Fe powder, which are widely

used as oxidizing agent for organic materials and catalyst for graphitization, respectively, and are also used in the methods assessed in this study, are the primary contributors to MC contamination in AMS-<sup>14</sup>C measurements (Vandeputte et al. 1998). Therefore, continuous efforts for the overall blank assessment and reduction in the AMS-<sup>14</sup>C measurement are needed to improve the reliability and accuracy of <sup>14</sup>C dating and promote the application of <sup>14</sup>C dating to climate change science.

**Supplementary material.** To view supplementary material for this article, please visit <https://doi.org/10.1017/RDC.2024.137>

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