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RESEARCH PAPER

A Soil Water Extraction Method with Accelerated Solvent Extraction Technique for Stable Isotope Analysis

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Abstract: Soil water is one of the most important components in hydrological cycle. The stable isotopes (e.g., deuterium, ^{2}H, oxygen-18, ^{18}O) in soil water have been increasingly used as natural tracers in the ecological, environmental and hydrological research. In view of different techniques for extracting soil water, there are significant differences in the δD and $\delta^{18}O$ compositions. This paper presents a method for the accelerated solvent extraction (ASE) of soil water for stable isotope analyses by mass spectrometry. The optimum parameters of extracting soil water were as follows: dichloromethane as the extraction solvent, temperature of 100 ºC, pressure of 10.3 MPa, static time of 10 min. The samples were extracted three times, and with cycle values four, four and three, respectively. The extracted water was enriched in deuterium and oxygen-18 by 2.12‰–4.58‰ and –0.17‰–0.93‰, respectively, compared with the added water. The reproducibility of replicate extractions of soil water was around ±0.89‰ for δD and ±0.37‰ for $\delta^{18}O$.

Key Words: Soil water; Hydrogen isotope; Oxygen isotope; Accelerated solvent extraction

1 Introduction

Soil water is one of the most important components in hydrological cycle. The stable isotopes (e.g., deuterium, ^{2}H, oxygen-18 ^{18}O) in soil water have been increasingly used as natural tracers in the field of environmentology[1], geoscience[2–4], hydrology[5,6] and phytophysiology[7–9]. The main available extraction methods include vacuum distillation, azeotropic distillation, centrifugation and He-purging distillation[1,8–22]. Araguás-araguás *et al*[12] demonstrated that the vacuum distillation method could improve the result with an error of 3‰ for δD and 0.3‰ for $\delta^{18}O$, and the isotopic values in the extracted water were depleted by about 5‰–10‰ for δD and 0.3‰–0.5‰ for $\delta^{18}O$, compared with the added water. Liu *et al*[8] showed that almost no discrepancy of the δD and $\delta^{18}O$ between extracted water and added water was observed when extracting water from soil samples with high water content (15%–30%) by vacuum distillation method. Ingraham *et al*[18] proposed a kerosene azeotropic distillation method, and indicated a depletion of 3.0‰–4.7‰ in deuterium. A standard deviation of 2‰ for δD and 0.2‰ for $\delta^{18}O$ was achieved by Revesz *et al*[15] with Toluene azeotropic distillation method, and by this method the isotopic difference was 2.6‰ ± 0.6‰ (δD) and 0.56‰ ± 0.21‰ ($\delta^{18}O$) when extracting dry sand with low water content. Liu *et al*[8] observed a departure of 3.2‰ for δD and 0.25‰ for $\delta^{18}O$ between the extracted water and added water by using toluene azeotropic distillation method. The

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centrifugation method[14,17], based on the displacement of soil solution by centrifuging with an immiscible liquid, was only suitable for extracting water from soil samples with high water content, and the extracted water was enriched by around 3‰ compared with the added water in the case of water content larger than 10%[14]. Ignatev *et al*[19] developed a He-purging distillation method to remove water from the soil samples and obtained a standard deviation of 0.7‰ for δD and 0.08‰ for $\delta^{18}O$. An inter-laboratory comparison of the isotope values was performed by Walker *et al*[13]. The results showed significant differences in the isotopic composition of the extracted water (up to 30‰ for δD and 3.4‰ for $\delta^{18}O$) for samples with low water content. As mentioned above, different extracting methods have significant impacts on δD and $\delta^{18}O$ values, especially for the soil samples with low water content.

Accelerated solvent extraction (ASE) is a technique to extract the organic materials (pesticides, herbicides, PCBs, hydrocarbons) in natural environment under high temperature and pressure[23–25]. Its application in extracting water has not been found in previous literatures. Here, we developed a novel method for soil water extraction and isotopic analysis. The method includes ASE displacement, solid phase extraction (SPE) and IRMS determination. It can significantly improve the efficiency of sample preparation and isotopic analysis, especially for those samples with low water content.

2 Experimental

2.1 Instruments and reagents

Isotopic measurements were performed by MAT253 isotope ratio mass spectrometer and Flash EA HT 1112 element analyzer, which were connected by Conflo Ⅲ (Thermo Fisher Scientific, Germany). ASE 350 accelerated solvent extractor (Dionex, USA), KQ-500PB ultrasonic cleaner (ShuMei, China) and LXJ-ⅡB centrifugal machine (AnTing, China) were used for soil water extraction.

Teflon centrifuge tubes (50 mL) were purchased from Thermo Fisher (USA). The syringes (1 mL) were purchased from CNW Technologies (Germany). SPE extraction equipment (Supelco, USA) and activated carbon SPE column (CNW 100 g L^{-1}) were used to purify the extracted water. Dichloromethane of pesticide grade was purchased from Thermo Fisher (USA). The added water was deionized water with a known isotopic composition.

2.2 Extraction methods

2.2.1 Preparation of samples

The soil was oven dried at 105 ºC for 24 h and rehydrated with deionized water of known isotopes (δD_{add} = –57.8‰, $\delta^{18}O_{add}$ = –6.49‰) to form a homogeneous soil samples with a water content of 9.1%, 6.3% and 4.8%, respectively. The natural soil samples was collected in the garden with a water content of 14.9% (soils under trees), 12.6% (soil under grasses), 7.8% (soils without plants), respectively.

2.2.2 Ultrasonic centrifugation of soil samples

Aliquots of 40 g of samples prepared in Section 2.2.1 was added to 10 teflon centrifuge tubes, then dichloromethane was added into the tubes until it was 1 cm above the soil sample, then the mixture was ultrasonic vibrated for 10 min, centrifuged for 10 min at 4000 rpm, and frozen at –20 ºC. Under this situation, water was freeze but dichloromethane remained liquid. Then it was melted, and the water was removed by syringe from thawed sample. Centrifugation for 3 times was necessary to separate as much water as possible. The collected water was purified by SPE and stored at –20 ºC for isotopic analysis.

2.2.3 ASE extraction of soil samples

About 20 g of soil sample was placed in a 22-mL ASE stainless steel cell and then extracted for 10 min by dichloromethane at 100 ºC, under 10.3 MPa. The samples were extracted three times with cycle values of four, four and three, respectively. The collected water was treated according to the centrifugation method. The deuterium and oxygen isotope composition of purified water is represented by δD_{ase} and $\delta^{18}O_{ase}$.

2.3 Analysis of oxygen and hydrogen isotope ratios

The oxygen and hydrogen isotope ratios were measured by State Key Laboratory of Hydrology-Water Resources and Hydraulic Engineering at Hohai University in Nanjing, China. The pyrolysis temperature was set at 1380 ºC and column temperature was set at 90 ºC. The analytical error of IRMS was better than 2‰ for δD and 0.2‰ for $\delta^{18}O$. The data were relative to Vienna Standard Mean Ocean Water (V-SMOW):

$$\delta D\ (‰) = \left[\frac{(D/H)_{sample}}{(D/H)_{V\text{-}SMOW}} - 1\right] \times 10^3 \quad (1)$$

$$\delta^{18}O\ (‰) = \left[\frac{(^{18}O/^{16}O)_{sample}}{(^{18}O/^{16}O)_{V\text{-}SMOW}} - 1\right] \times 10^3 \quad (2)$$

3 Results and discussion

3.1 Isotopic effects of activated carbon purification on extracted water

The activated carbon SPE column was needed to adsorb organic materials mixed in the water because they could alter

CO_2 equilibration during IRMS measurements of $\delta^{18}O$. However, it may lose about 0.3 g waters during the process. The results indicated that almost no isotopic fractionation was found during the activated carbon purification process. The isotopic differences were only 0.1‰ for δD and 0.13‰ for $\delta^{18}O$ between the SPE treated water (δD_{spe} = –57.7‰, $\delta^{18}O_{spe}$ = –6.36‰) and the water without treatment (δD_{add} = –57.8‰, $\delta^{18}O_{add}$ = –6.49‰). They were within the analytical errors of IRMS.

3.2 Optimization of extraction conditions

3.2.1 Extraction temperature

Extraction temperature can greatly affect the water recovery during ASE extraction process. The water recovery rate at 100 ºC was from 55% to 60%, and the mean isotopic values were –54.1‰ for δD_{ase} and –6.00‰ for $\delta^{18}O_{ase}$. At 80 ºC, the water recovery was about 20% which was lower than that at 100 ºC, and the isotopic values showed a negative of 8‰ for δD_{ase} and 1‰ for $\delta^{18}O_{ase}$ than those at 100 ºC (Fig.1). The possible reason depletion occurred was incomplete extraction. Water with lighter isotopic composition was easier to be extracted than that with heavier one. To guarantee a complete extraction, an extraction temperature of 100 ºC was chosen for the soil samples.

3.2.2 Extraction time

Extraction time is a crucial parameter which can significantly influence the water recovery during the ASE extraction process. When extraction time was set as one and cycle time as four, the average recovery was 24%; when extraction time was set as two and cycle time as four, four, the average recovery was 45%; when extraction time was set as three and cycle time as four, four, three, the average recovery was 57%. Generally, as the extraction times increased, the recovery was improved and the enrichment factor of hydrogen and oxygen isotopes composition of the extracted water was increased. Under the selected conditions, the isotopic compositions were enriched by about 2.12‰–4.58‰ (δD) and –0.17‰–0.93‰ ($\delta^{18}O$) which were only slightly higher than the analytical errors of IRMS (Fig.2). Therefore, the times of extraction was set as three and the cycle times were set as four, four, three, respectively.

3.3 ASE extraction of soil samples with different water content

Under the optimized conditions, ASE extraction method was used to extract water from soil samples with different water contents (9.1%, 6.3% and 4.8% respectively), but the same isotopic compositions. As shown in Fig.3, the observed ranges of the $\Delta\delta D$ and $\Delta\delta^{18}O$ variations were no larger than 3.58‰ and 0.93‰ for δD and $\delta^{18}O$, respectively. The results indicated that ASE extraction method produced a higher isotopic precision for the soil samples with low water content.

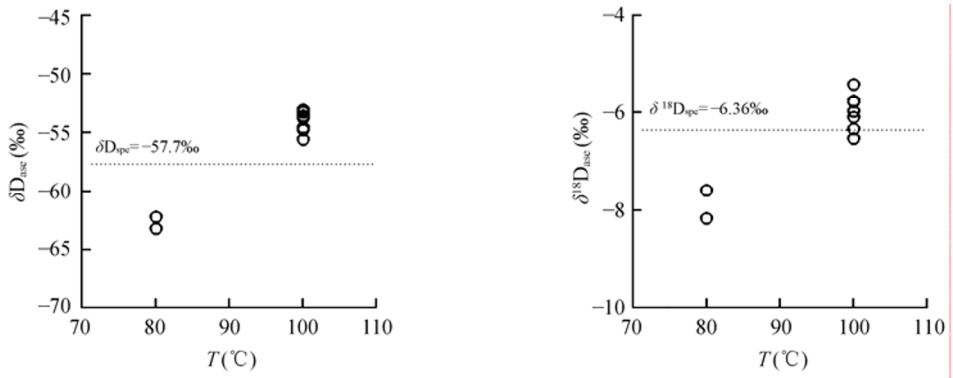

Fig.1 Isotope values of extracted water under different temperatures

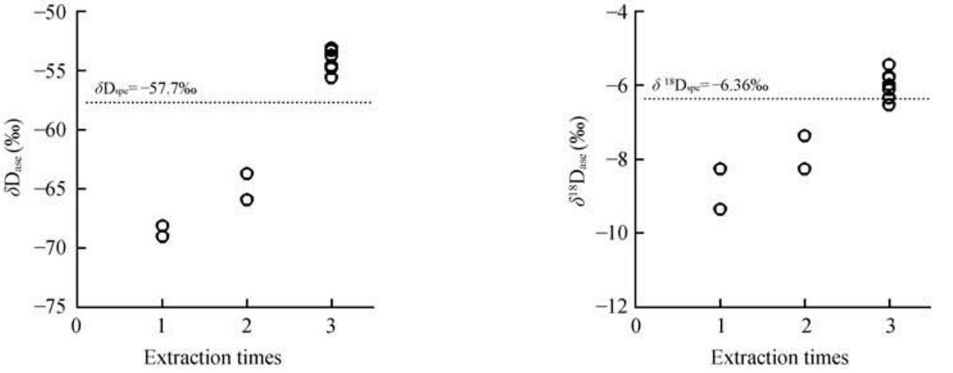

Fig.2 Isotope values of extracted water under different extracting times

The accuracy of conventional methods for the determination of water with low content in soil sample was low. The possible reason was the interaction between the added water and the mineral materials in the soil matrix[8,9,13,18,21]. The higher precision suggested that ASE extraction method could be used to extract the water with low content in soil sample[20, 21].

3.4 Comparison of ASE extraction method and ultrasonic centrifugation method

The ultrasonic centrifugation (USC) method was compared with ASE extraction method in this experiment. For the soil samples with a water content of 9.1%, extracted 1 g of water needed 57 g soil sample with USC; however, extracted 1 g of water needed only 18 g soil sample with AES. That is, it would take three times as much as soil sample amount for ultrasonic centrifugation to obtain the same amount of water than ASE extraction. As shown in Fig.4, the isotopic compositions of water extracted by ASE extraction method were enriched by 3.6‰ for δD and 0.36‰ for $\delta^{18}O$, but it was 1‰ for δD and 0.49‰ for $\delta^{18}O$ by USC. The reason caused the difference of enrichment maybe was the result of a combination of organic, mineral materials and bound water etc.[12,13]. The two methods yielded similar precision and accuracy. However, we observed that USC was unusable in extracting water from soil samples with low water content (6.3% and 4.8%). The ASE extraction method could be performed to extract water with low content in soil samples with higher accuracy.

3.5 Precision and accuracy

The standard deviation of ASE method was 0.89‰ for δD and 0.37‰ for $\delta^{18}O$ (n = 7). The results were comparable with the vacuum distillation (0.69‰–3‰ for δD, 0.14‰–0.4‰ for $\delta^{18}O$)[8–10,12] and azeotropic distillation (1.2‰–2‰ for δD, 0.2‰–0.3‰ for $\delta^{18}O$)[8,13–15] (Table 1).

When extracting soil samples with water content of 9.1%, the differences between extracted water and added water were from 2.12‰ to 4.58‰ for δD and from –0.17‰ to 0.93‰ for $\delta^{18}O$, which was similar to the results obtained by vacuum distillation (–5‰ to –10‰ for δD, –0.3‰ to –0.5‰ for $\delta^{18}O$)[8–10,12] and azeotropic distillation (2.0‰–3.2‰ for δD, 0.35‰–0.77‰ for $\delta^{18}O$)[11,17–19] (Table 1).

3.6 Extraction of natural samples

The two other different soil samples were selected to assess the applicability of ASE extraction method on soil waters of different isotopic compositions. The results are shown at study (b) and study (c) in Table 1. The extracted water from soil samples with isotopically heavy waters was enriched in both deuterium and oxygen by 1.2‰ and 0.9‰, respectively, when

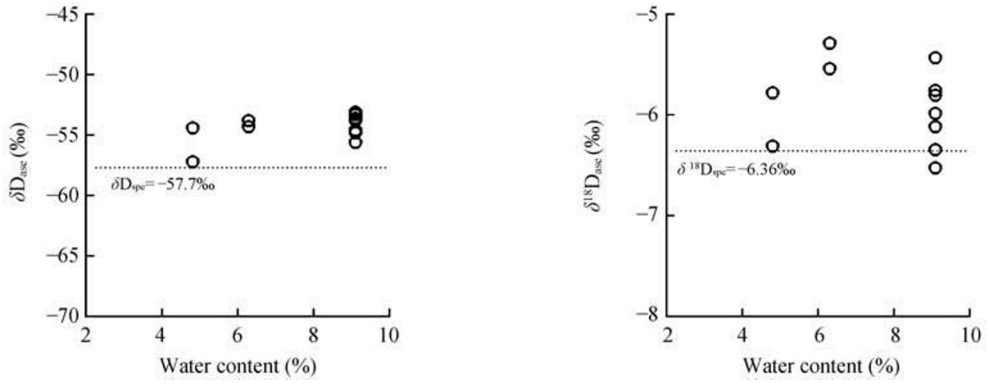

Fig.3 Isotope values of extracted water of soil samples with different water contents

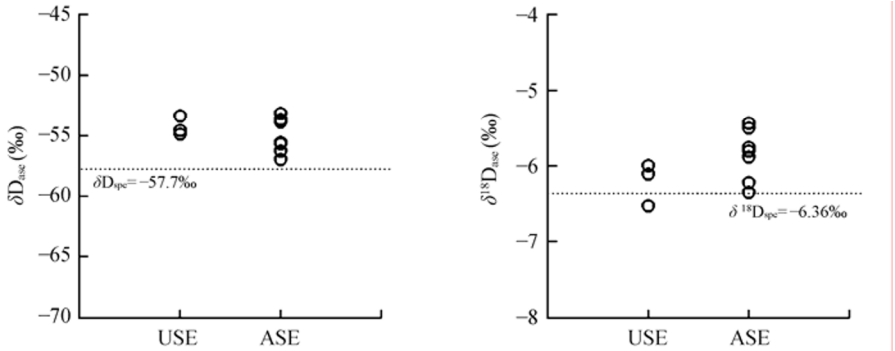

Fig.4 Isotope comparison of ASE and ultrasonic centrifugation extraction method

Table 1 Summary of other water extraction studies

Methods	Type	Water content (%)	Standard deviation		$\delta D-\delta D_{add}$	$\delta^{18}O-\delta^{18}O_{add}$	Reference
			δD	$\delta^{18}O$			
Azeotropic distillation	Sandy soil	> 3	2.0	0.2	2.0–3.2	0.35–0.77	[15]
Azeotropic distillation	Clayey sandy soil	5–25	1.2	0.3	—	—	[13]
Azeotropic distillation	Clayey soil	—	2	0.2	3.0–4.7	—	[14]
Azeotropic distillation	Clayey sandy soil	15–35	—	—	3.2	0.25	[8]
Vvacuum extraction	Clayey soil	34–42	3	0.3	–10– –5	0.3–0.5	[12]
Vacuum extraction	Clayey soil	—	0.69	0.15	—	—	[10]
Vacuum extraction	Sandy soil	—	3.0	0.4	—	—	[9]
Vacuum extraction	Clayey sandy soil	15–35	—	—	–0.02	0.16	[8]
He-purging	Soil	4–20	0.7	0.08	–1.1–1.3	–0.1–0.14	[19]
Direct equilibration	Soil	3–33	2	0.4	—	–1.55– –0.11	[22]
Direct equilibration	Geological media	8–27	1	0.3	—	0.4–0.6	[20]
Direct equilibration	Sandy soil	1–15	—	0.12	—	3	[21]
Centrifugation	Soil	> 10	—		0–3.0	—	[14]
ASE extraction	Soil	4.8–9.1	0.89	0.37	2.12–4.58	–0.17–0.93	This study (a)
ASE extraction	Soil	6.3	—	—	4.75	–0.03	This study(b)
ASE extraction	Soil	6.3	—	—	1.2	0.9	This study (c)

a, b and c showed the different isotopic ratio values in water. a, (δD_{spe} = –57.7‰, $\delta^{18}O_{spe}$ = –6.36‰); b, (δD_{spe} = –70.85‰, $\delta^{18}O_{spe}$ = –9.14‰); c, (δD_{spe} = –35.9‰, $\delta^{18}O_{spe}$ = –3.73‰).

compared with the added water. The enrichment was 4.75‰ and –0.03‰ for isotopically light water. Interestingly, the difference of isotopic compositions between extracted water and added water was inversely related to the isotopic value of added water. The explanation needed to be further researched.

The δD and $\delta^{18}O$ values were –33.2‰ and –3.88‰ for the soils under trees, –31.4‰ and –1.94‰ for the soils under grasses, –29.4‰ and –1.27‰ for the soils without plants covered, respectively. The evaporation was more severe for the soils without plants covered than the soils covered with plants. It was suggested that isotopically lighter water tended to be easily removed by evaporation, while the remained in the soil were with heavier isotopic values. Thus, the isotopic compositions of extracted water from the soil under a tree were more depleted[5,26,27].

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