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RESEARCH PAPER

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

ZHU Qing-Zeng[1,2], SUN Qing[3,*], SU Zhi-Guo[4], XIE Man-Man[3], SONG Jun-Yong[3], SHAN Ya-Bing[3], WANG Ning[3], CHU Guo-Qiang[1]

[1] Key Laboratory of Cenozoic Geology and Environment, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing 100029, China
[2] Graduate University of the Chinese Academy of Sciences, Beijing 100049, China
[3] National Research Center for Geoanalysis, Beijing 100037, China
[4] State Key Laboratory of Hydrology-Water Resources and Hydraulic Engineering, Hohai University, Nanjing 210098, China

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 δ^{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 δ^{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 δ^{18}O, and the isotopic values in the extracted water were depleted by about 5‰–10‰ for δD and 0.3‰–0.5‰ for δ^{18}O, compared with the added water. Liu *et al*[8] showed that almost no discrepancy of the δD and δ^{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 δ^{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‰ (δ^{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 δ^{18}O between the extracted water and added water by using toluene azeotropic distillation method. The

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* Corresponding author. Email: sunqing1616@yahoo.com
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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 δ^{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 δ^{18}O) for samples with low water content. As mentioned above, different extracting methods have significant impacts on δD and δ^{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 δ^{18}O. The data were relative to Vienna Standard Mean Ocean Water (V-SMOW):

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

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

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