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Tracing the Dynamic Changes of Element Profiles by Novel Soil Porewater Samplers with Ultralow Disturbance to Soil–Water Interface

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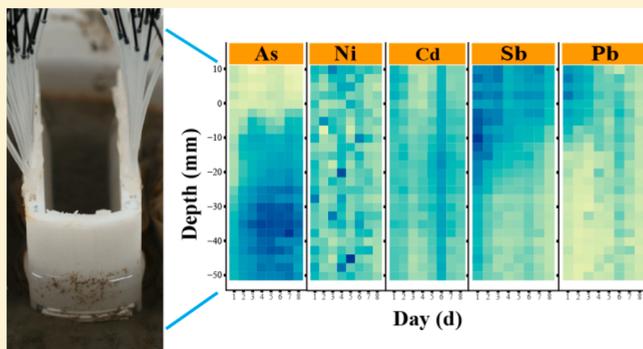
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Supporting Information

ABSTRACT: In flooded soils, soil–water interface (SWI) is the key zone controlling biogeochemical dynamics. Chemical species and concentrations vary greatly at micro- to cm-scales. Techniques able to track these changing element profiles both in space and over time with appropriate resolution are rare. Here, we report a patent-pending technique, the Integrated Porewater Injection (IPI) sampler, which is designed for soil porewater sampling with minimum disturbance to saturated soil environment. IPI sampler employs a single hollow fiber membrane tube to passively sample porewater surrounding the tube. When working, it can be integrated into the sample introduction system, thus the sample preparation procedure is dramatically simplified. In this study, IPI samplers were coupled to ICP-MS at data-only mode. The limits of detection of IPI-ICP-MS for Ni, As, Cd, Sb, and Pb were 0.12, 0.67, 0.027, 0.029, and 0.074 $\mu\text{g}\cdot\text{L}^{-1}$, respectively. Furthermore, 25 IPI samplers were assembled into an SWI profiler using 3D printing in a one-dimensional array. The SWI profiler is able to analyze element profiles at high spatial resolution (~ 2 mm) every ≥ 24 h. When deployed in arsenic-contaminated paddy soils, it depicted the distributions and dynamics of multiple elements at anoxic–oxic transition. The results show that the SWI profiler is a powerful and robust technique in monitoring dynamics of element profile in soil porewater at high spatial resolution. The method will greatly facilitate studies of elements behaviors in sediments of wetland, rivers, lakes, and oceans.



INTRODUCTION

Aquatic sediments play an important role as sinks for metals and metalloids.¹ The chemical speciation and mobility of elements are mainly controlled by the redox condition, pH, and organic matter content of the sediments.^{2–4} Under natural conditions, a redox transition occurs along the soil–water interface (SWI), and the biogeochemical characters vary at the mm scale in sediment.⁵ The element profile along SWI varies when the external environment changes (e.g., pH, seasonal wet–dry cycle, exogenous pollutants introduction, microbial degradation, and wetland plant roots activity).^{6–9} For example, arsenic (As) in soils is immobilized by mineral oxides adsorption under oxidizing conditions, but mobilized by the desorption of As from mineral oxides under reducing conditions.^{4,10} The redox changes along the SWI result in a distinct change of As

concentration in a saturated soil profile. As a gate controlling the mass exchange between the sediment and waterbody, it has always been of great interest to study the spatial as well as the temporal distribution of elements along the SWI at high-resolution. However, a deep understanding of the elemental behavior in the environment has been hindered to date by the techniques available to sample this zone.

Many techniques have been developed to study the behavior of elements along the SWI. Initially, slicing of frozen soil cores under anaerobic conditions was used.^{5,11,12} However, the soil

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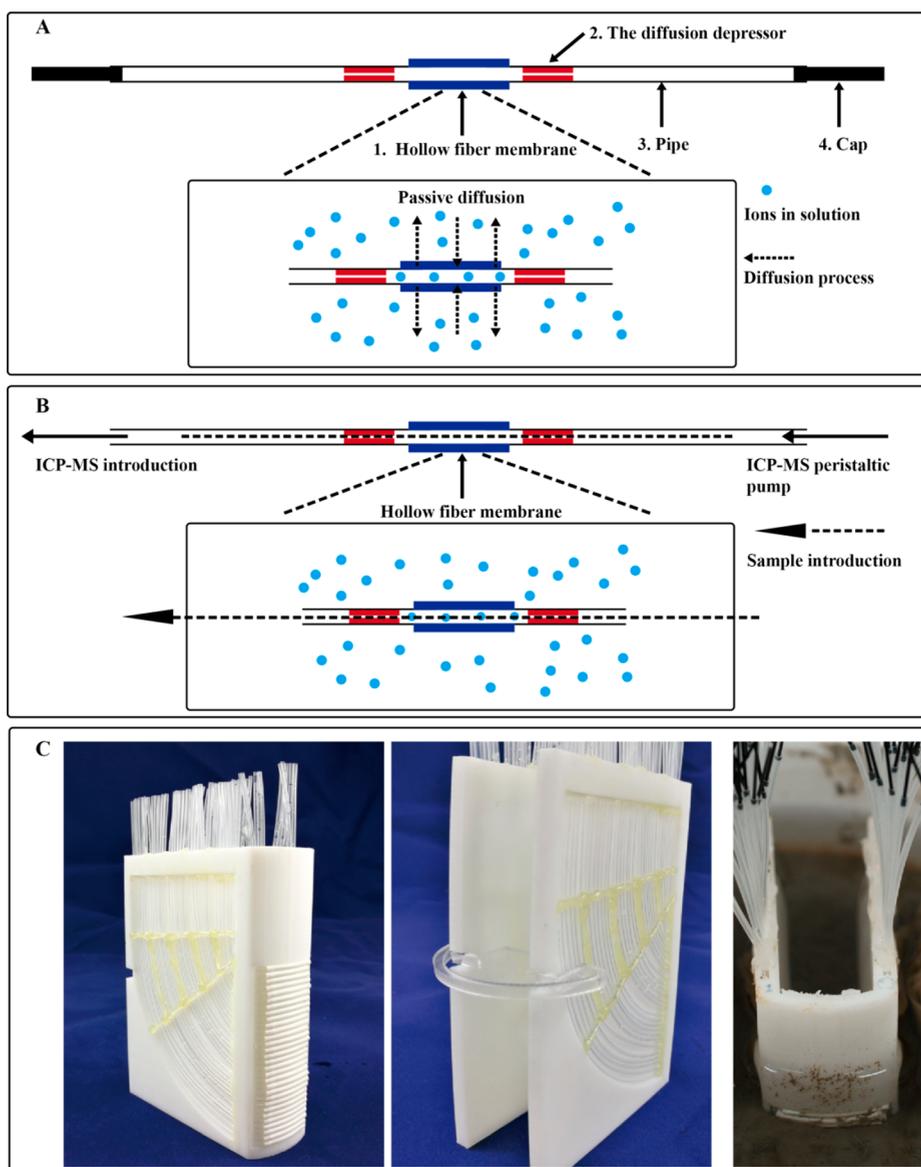


Figure 1. Schematic diagram of IPI sampler. (A) The loading stage of IPI sampler, element ions diffuse through the hollow fiber membrane; (B) the sample injection stage of IPI sampler, the solution inside the hollow fiber membrane is pumped into ICP-MS; and (C) photos of SWI profiler (from left to right, front, back and working in soil). Notes (A): 1. hollow fiber membrane; 2. the diffusion depressor; 3. pipe; and 4. cap.

slicing method is destructive, complex, and easily contaminated.¹³ More recent work has focused on nondestructive sampling methods. The rhizon sampler is a typical non-destructive method that is at low cost and easy to operate.^{14–18} When the samplers are placed horizontally along a profile, they can measure the vertical distribution of elements.¹⁵ However, the sampling zone of rhizon samplers is poorly defined and generally greater than 1 cm, its application in high-resolution SWI studies is limited.

Compared to rhizon samplers, peeper, diffusive equilibration in thin films (DET), and diffusive gradient in thin-films (DGT) are much powerful.^{4,19–25} Peeper and DET/DGT probes passively sample the solutes in porewater through diffusion/adsorption. When equilibrated, the liquid or gel is removed for element mapping analysis. The techniques have been used to map elements with high spatial resolution (μm to cm level). Although peeper and DET/DGT are powerful in mapping element profile, they can only be used once after deployment,

which limits the application of the technique in tracking temporal element change.⁴

In this study, a novel technique, called Integrated Porewater Injection (IPI) sampler, was developed to map spatial and temporal distribution of elements along the SWI. The IPI sampler uses a single hollow fiber membrane tube for passive sampling and active sample injection, thus the workload for sample preparation is minimized. We investigated the limit of detection (LOD), influences of carrier solution and humic acid (HA), and the characteristics of time-dependent diffusion across the sampling tube. We also reported the integration of an array of IPI samplers (SWI profiler) into a device that enables one-dimensional element profiling. The performance of SWI profiler was evaluated in field-collected paddy soils under a changing anoxic–oxic environment by pumping N_2 or air.

MATERIALS AND METHODS

Reagents and Materials. The chemicals used in this study were of analytical or electronic grade and supplied by Aladdin Chemical Reagent Co., Ltd. (Shanghai, China), unless stated otherwise. Calibration standards, including nickel (Ni), arsenic (As), cadmium (Cd), antimony (Sb), and lead (Pb), were purchased from Guobiao (Beijing) Testing & Certification Co., Ltd. (Beijing, China). Humic acid (HA) was provided by Alfa Aesar (catalog # 41747). All solutions were prepared with ultrapure water (18.2 M Ω cm, Millipore Corp., Bedford, U.S.A.) deoxygenated by purging with pure N₂ for more than 4 h. The sampling tube is made of a hollow fiber membrane tube (inner \times outer diameter = 1.0 \times 2.0 mm², polyvinylidene fluoride, Motimo Membrane Technology Co., Ltd., Tianjin, China). The membrane has a pore size of 0.05 μ m, and pore rate of 70–80%. All the materials were ultrasonic washed with 2% HNO₃ and 1% Decon solution for 15 min, respectively, and rinsed five times with ultrapure water. All the narrow tubes were oven-dried at 40 °C before use.

The soil samples used in the study were collected from paddy fields in Gan Zhou (GZ, 25°30'N, 114°36'E) and Qing Yuan (QY, 23°35'N, 113°20'E), China. The top 20 cm of soil was sampled. Soil samples were wet sieved through a 1 mm diameter sieve. The soil characteristics are shown in Table S1 of the Supporting Information (SI).

IPI Sampler Design and SWI Profiler Assembly. The structure of a typical IPI sampler is shown in Figure 1A (Tidu Inc. Suzhou, China). The IPI sampler contains four components: (1) the hollow fiber membrane tube (20 mm in length), with a volume of 16 μ L; (2) the diffusion depressor (0.3 \times 0.8 \times 5 mm³, inner \times outer diameter \times length, PTFE); (3) pipe (silica tube, 0.5 \times 1.5 \times 180 mm³, inner \times outer diameter \times length), with a volume of 35 μ L; (4) cap (carbon fiber, 0.8 \times 20 mm², diameter \times length). The hollow fiber membrane serves as a passive sampling tube during the sample collection (loading) stage. The diffusion depressor is designed to suppress the side diffusion of solutes from the hollow fiber membrane tube to the conduits through narrowing their connection. When connected to ICP-MS, the porewater sample in hollow fiber membrane tube is pumped out through the conduits. To avoid the negative influence of oxygen and dust in atmosphere, a carbon fiber cap is used to seal IPI sampler during sample loading stage. To extract soil porewater at different depth along SWI, SWI profiler was used. An SWI profiler is consisted of 25 IPI samplers, which are assembled side by side in a 3D printed holder (Figure 1C). The IPI sampler and SWI profiler were stored in carrier solution before use.

The Working Procedure of IPI Sampler. Once the IPI sampler is deployed into solution or saturated soil, the small molecules and ions diffuse into the hollow fiber membrane tube through the membrane (passive sampling stage, Figure 1A). When equilibrium state is reached, the solution inside the tubes is introduced into ICP-MS (NexION 350X, PerkinElmer, Inc., Shelton, CT U.S.A.) (active sample introduction stage, Figure 1B). When introducing the samples into ICP-MS, the caps were removed; the IPI sampler was integrated into the sampling system by replacing the sample loop in a six-way valve. The sample solution in an IPI sampler is pumped by ICP-MS peristaltic pump at the speed of 24 rpm. Twenty μ g·L⁻¹ rhodium in 4% HNO₃ was used as the internal standard. The ICP-MS conditions were as follows: STD mode; data only analysis; RF power 1600W; plasma gas flow rate 15 L·min⁻¹; auxiliary gas

flow 1.2 L·min⁻¹; nebulized gas flow 0.94 L·min⁻¹; the uptake flow rate is 0.5 mL·min⁻¹; and nickel sampling and skimmer cones were used.

Carrier Solution Test. The IPI samplers were deployed in the 10 μ g·L⁻¹ Ni, As, Cd, Sb, and Pb solution before test. Six kinds of matrix condition were tested: (i) ultrapure water in acidic condition (pH 1); (ii) ultrapure water in near-neutral condition (pH 6); (iii) 10 mM NaNO₃ in pH 1; (iv) 10 mM NaNO₃ in pH 6; (v) 10 mM NaCl in pH 1; and (vi) 10 mM NaCl in pH 6. The solution pH was adjusted by using NaOH or HNO₃.

The carrier effect of ultrapure water and 10 mM NaCl carrier solutions were also tested in near-neutral flooded soils. The IPI samplers were deployed at a depth of 2 cm in two flooded paddy soils (GZ and QY), respectively. After 24 h incubation, the sample was analyzed by directly introducing to ICP-MS.

Humic Acid Test. The humic acid (HA) was prepared according to the previous study.²⁶ The influence of HA on Ni, As, Cd, Sb, and Pb was investigated in pH 6 and 10 mM NaCl solutions (20 and 100 μ g·L⁻¹) during a period of 0–48 h. Three levels of HA were tested: (1) 0 mg·L⁻¹ HA; (2) 5 mg·L⁻¹ HA; (3) 20 mg·L⁻¹ HA.

Time-Dependent Response and Calibration Curve. The time-dependent response of IPI samplers was conducted in acidic and near-neutral conditions (pH 1 and 6; 10 μ g·L⁻¹ Ni, As, Cd, Sb, and Pb; 10 mM NaCl). The carrier solution was 10 mM NaCl. The solutions inside the samplers were measured after 0.5, 1, 3, and 6 h equilibrium time.

When developing the calibration curve a series of standard solutions, containing 1.0, 2.0, 5.0, 10, 20 μ g·L⁻¹ Ni, As, Cd, Sb, and Pb at pH 1 and 10 mM NaCl, were measured. The carrier solution was 10 mM NaCl. The ICP-MS measurements were conducted after 24 h of equilibrium time.

Comparison of IPI Sampler and Rhizon Sampler. Rhizon sampler and IPI sampler with the same hollow fiber membrane tube were compared in flooded soils. The samplers were fixed alternately on a clean acrylic plate with an interval of 1 cm in triplicate, and deployed horizontally at a depth of 2 cm in GZ and QY soils. After 24 h equilibration, the sample in IPI sampler was analyzed by ICP-MS. Then, 2 mL porewater was extracted by rhizon sampler and analyzed by ICP-MS.

Nondestructive Measurement of the Temporal Element Profile Change in SWI. An SWI profiler is made of 25 individual samplers with the assistance of a 3D printer. The SWI profiler is able to measure the elements distribution over a distance of 6 cm, with a resolution of \sim 2 mm. To detect the element profile, the SWI profilers were inserted into paddy soils which have been flooded for half a year, with 1 cm above SWI and 5 cm buried in paddy soils (Figure 1C). The porewater element concentrations were measured every day under different environmental disturbance: Day 0, SWI profiler installation; Day 1, no disturbance; Day 2–3, continuously N₂ bubbling in surface water; Day 4–6, continuously air bubbling in surface water; Day 7–8, continuously N₂ bubbling in surface water. Nitrogen gas was provided by a high pressure tank, air by an air pump. Three pipettes were deployed evenly at 1 cm above the SWI in the container, and the bubbling in surface water was via these pipettes.

Statistical Analysis. We used the statistical program R version 3.5.0 to analyze and plot the data. Standard deviation (SD) was used to show the variance. All raw data and the R scripts used to process and analyze the data can be found in the SI. A one-way ANOVA ($p < 0.05$, IBM SPSS statistics 22) was

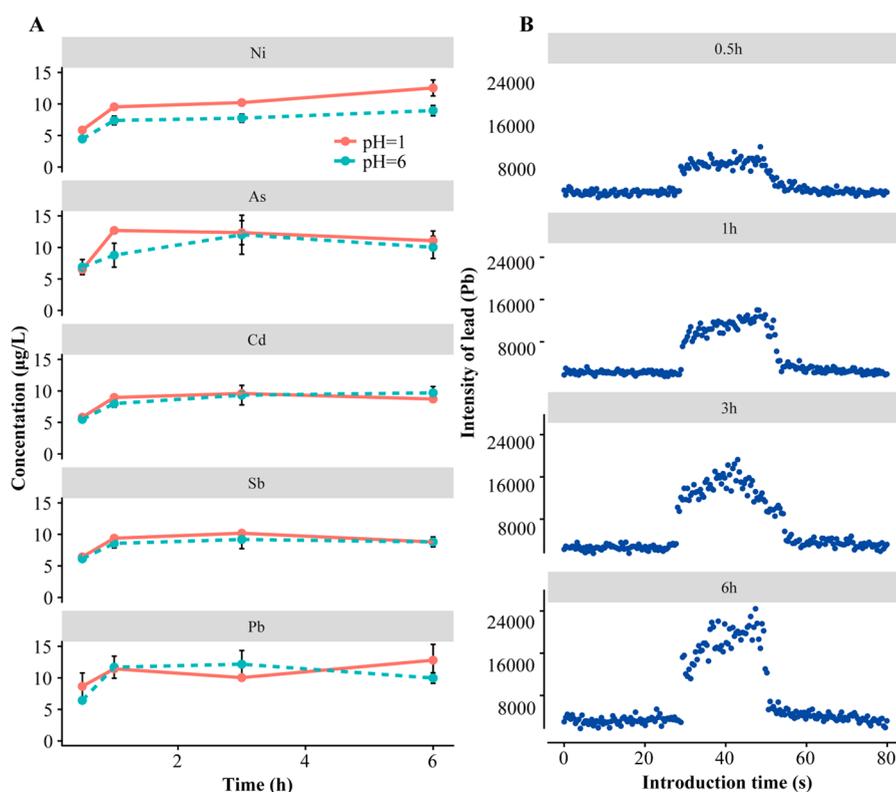


Figure 2. Dynamic equilibration process and peak area based calibration curve of different elements. (A) the dynamic equilibration process of $10 \mu\text{g}\cdot\text{L}^{-1}$ nickel (Ni), arsenic (As), cadmium (Cd), antimony (Sb), and lead (Pb) under acidic (pH 1, 10 mM NaCl) and near-neutral (pH 6, 10 mM NaCl) conditions; and (B) the peaks of Pb in different equilibration time under near-neutral conditions.

carried out to analyze the difference of IPI sampler and rhizon sampler for measuring elements.

RESULTS AND DISCUSSION

Effects of Carrier Solution. Carrier solution was used to expel the solution in the sampling tube. The composition of carrier solution may affect the diffusion processes of target ions across the membrane during passive sampling stage, and interfere the measurement during active sample injection stage. It is supposed that carrier solution may modify the characteristics of the membrane. Similarly, a certain ionic strength carrier solution is efficient in reducing the electrostatic interactions in DET/DGT.^{4,27,28} As for polyvinylidene fluoride membrane, a complexation effect may occur between metals, like Pb, and fluoride on the membrane.²⁹ If there is no significant interaction between target elements and membrane, then oxygen-free ultrapure water is the preferred carrier solution which has minimal interference to the sampling environment. In this study, three kinds of solutions, including ultrapure water, 10 mM NaNO_3 and 10 mM NaCl, were used to drive the sample solution inside the IPI samplers to ICP-MS.

The influences of carrier solution are summarized in Table S2. The results indicated that the pH condition did not significantly alter the response of the elements tested. Nickel, As, Cd, and Sb ions showed high permeability through the sampler membrane. High sensitivities of those elements were found when water, NaNO_3 , and NaCl solution were used as carrier solution in acidic and near-neutral conditions (Table S2). However, no Pb signal was observed under near-neutral conditions when using ultrapure water and 10 mM NaNO_3 . High sensitivities for Pb ions were observed under acidic conditions, or 10 mM NaCl as

the carrier solution under near-neutral conditions. It is speculated that the Pb ions were trapped by the fluoride on polyvinylidene fluoride membrane by forming fluoride-complexes.²⁹ Moreover, the blocking effect disappeared when there was Cl, which forms Pb complexes which are more stable in solution.³⁰ Considering the negative influence of fluorine on the measurement of Pb as well as the possible influence on other metals, fluorine-free membrane, like modified poly(ether sulfone) membrane, maybe a better choice than polyvinylidene fluoride membrane for the quantitatively sampling of metals by IPI samplers.

The carrier solution effects were further tested in soil conditions. When ultrapure water and 10 mM NaCl were used as the carrier solution for soil porewater measurement, a similar phenomenon as in solution experiment was observed. No Pb was detected in samples from either soils with ultrapure water as the carrier solution (Figure S1A,B); however, significant Pb was observed in both soils with 10 mM NaCl as the carrier solution (Figure S1C,D). To test the samplers' performance on Pb measurement, NaCl solution was chosen as the carrier solution in this study.

The Cl in matrix is known to interfere the detection of As by forming $^{40}\text{Ar}^{35}\text{Cl}^+$, which is of the same mass-to-charge ratio of $^{75}\text{As}^+$.³¹ In this study, we also noticed an increase of As counting from 800 to 2500 (Figure S2A,B), when the carrier solution switched from ultrapure water to 10 mM NaCl. The detection limit gets worse when NaCl solution is used but still acceptable because As concentrations are generally high in As-contaminated soils. Thus, the NaCl solution was used as carrier solution to measure As in solution and soil porewater samples (Figure S2C,D).

Effects of Humic Acid. Humic acids are ubiquitous in soil environment, and they may act as natural chelates to complex metals.^{3,9,32} The large HA–metal complex may be rejected by the porewater samplers as a result of their large size.^{26,32,33} The influences of HA on Ni, As, Cd, Sb, and Pb are shown in Figure S3.

The results indicated HA treatment had no significant influence on As and Sb at all levels. Unlike As and Sb, Pb measured by the IPI sampler was significantly reduced by the HA with a concentration of 5–20 mg·L⁻¹. Similar phenomena were found on other metals (Ni, Cd). Moreover, HA also extended the equilibration time of Pb, Ni, and Cd from 3 h to 12–24 h with increasing HA. The longer equilibration time for metals after adding HA is because HA–metal complex has much smaller diffusion coefficient than the free metal.²⁶ Due to the small pores (50 nm) on the IPI sampler, large HA–metal complexes may be rejected during the sampling.^{32–34} Therefore, 24 h equilibration time is recommended for the using of IPI sampler in soils, especially for the environments containing large metal complexes.

Time-Dependent Sample Loading into Hollow Fiber Membrane Tubes. The working procedure of IPI sampler consisted of a passive sampling stage followed by an active sample injection stage. At the passive sampling stage, the ion concentrations across the tube membrane were equilibrated. The equilibration time determines the time resolution of the IPI sampler. The time can be calculated by Fick's second law. Equation 1 yields the time required for a solute to reach a distance x .^{35,36}

$$t = \frac{x^2}{2D} \quad (1)$$

where t is the time (s) that the concentration of solute at distance x (cm) can reach equilibration, and D (cm² s⁻¹) is the diffusion coefficient of solute.

In the IPI sampler, x equals the radius of the tube (1 mm), and D is $\sim 5 \times 10^{-6}$ cm² s⁻¹ for most metal ions at room temperature.²⁷ Thus, we estimated the equilibration time is approximately 17 min (eq 1). However, the calculated duration may be an underestimate, because the extended ion diffusive pathway through the membrane and other factors are not counted in the calculation.³⁷

The time-dependent sample loading process was tested in solution condition. As shown in Figure 2A, all the 5 elements share a similar time-dependent loading process pattern regardless of pH conditions. The elements' concentrations in IPI samplers increased sharply within the first hour, and then increased slowly to a plateau after 3 h. The equilibrium time (hour level) in IPI sampler is consistent with the time (hour level) yielded in a partial resupply mode of analytes when leaving one side of DET gel to the medium.^{27,38} Therefore, it is concluded that the minimum time required to reach equilibrium of the solute across the IPI membrane is 3 h with HA free medium, but ≥ 24 h equilibrium time is recommended for the sampling of porewaters.

Comparison of sample introduction and IPI sampler based introduction in ICP-MS. IPI sampler provides an alternative way to bridge the environmental samples and analytical machines. Compared to direct sample introduction mode for general ICP-MS analysis, IPI samplers contain a hollow fiber membrane tube. The tube serves as a passive sampling tube during the sample loading stage and a conduit in active sample injection stage, as described in Figure 1. On the

basis of the working mechanism, we consider the quantitative measurement of the solutes may be influenced by (1) the diffusion of solute from the sampling tube to the silica tube (side diffusion); and (2) solution leakage/exchange during active sample injection stage.

Side diffusion might lead the total amount of solute inside the sampler increasing with deployment time. In the IPI samplers, diffusion suppressors were placed on each side of the sampling tube to reduce the side diffusion (Figure 1A). According to Figure 2A, the increasement of sample loading into the tube was insignificant after 3 h, which implies the movement of solutes from sampling tube to silica tube was negligible. However, the influence of side diffusion is inevitable, in order to measure elements in environmental samples accurately, it is recommended that the IPI samplers for calibration and testing should be deployed in the standard solutions and environmental samples for a same period to reduce the influence of deployment time on elements' signals.

During the active sample injection stage, the pump may induce a pressure difference across the membrane, therefore an exchange of solution may occur. The positive pressure inside the tube may cause solution leakage and undercount the signal, viz. negative pressure may cause solution suck-in and overcount the signal. Thus, we analyzed the element signals generated from IPI sampling mode and direct sampling mode. Broad peaks of ~ 20 s of every element (e.g., Pb, Figure 2B) were detected in IPI sampling mode. Considering the flow rate of carrier solution was 0.5 mL·min⁻¹, the sample volume for the peak was ~ 170 μ L (0.5 mL/60s \times 20s), which equals to the whole volume inside the sampler (~ 86 μ L) plus another 86 μ L of the internal standard solution. This result indicates the sample in hollow fiber membrane tube (16 μ L) is mixed with the carrier solution in two pipes (35 μ L \times 2) during sample introduction. This indicates IPI sampler always has a dilution coefficient of ~ 5 times of the outer solution, which can be used as a parameter to determine whether a IPI sampler works appropriately. No obvious mass exchange across the hollow membrane was observed during the sample injection.

Calibration Curve and LOD. The calibration curve was generated by deploying the IPI samplers in a series of standard solutions for 24 h. The response of each element was calculated by the peak areas. The data processing method is shown in Figure S4. The points higher than baseline +5SD are selected for peak area integration. The coefficients of determination for all the five elements are >0.995 . According to IUPAC definition,^{39,40} the LODs are 0.12, 0.67, 0.027, 0.029, and 0.074 μ g·L⁻¹ for Ni, As, Cd, Sb, and Pb, respectively.

Comparison of IPI Sampler and Rhizon Sampler. The comparison of IPI sampler and rhizon sampler for measuring Ni, As, Cd, Sb, and Pb was carried out in GZ and QY paddies (Table S3). Cadmium was below the LOD in both samples. The two methods showed no difference in measuring As and Sb. However, lower Ni and Pb were obtained by IPI sampler than rhizon sampler for both soils, which can be explained by the different sampling mechanisms for rhizon samplers and IPI samplers. Tension-free samplers, like IPI sampler, measure the metal species with the molecular size enabling them to pass through the diffusion pores on the sampler freely. In principle, free metals and colloidal metals with the size <50 nm are able to be measured by the IPI sampler. However, larger size particles may be squeezed into rhizon samplers by the tension generated by syringes, which lead to an overestimation of metal concentrations.³³ The experiment on HA addition showed

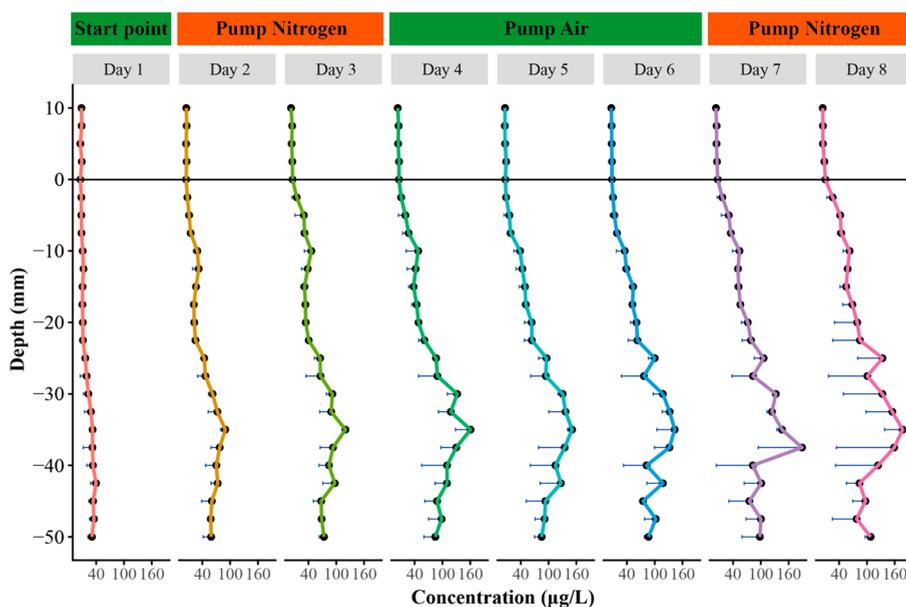


Figure 3. Vertical profile changes of soil porewater arsenic (As) along the 60 mm SWI in 8 days under different conditions. The error bars are standard deviations (SD, $n = 3$).

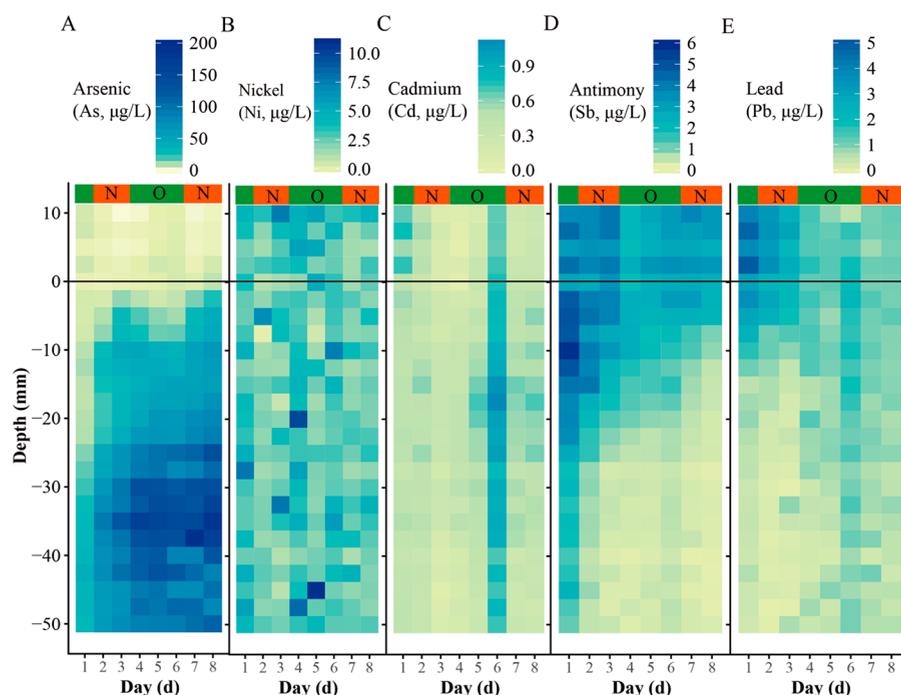


Figure 4. Dynamic vertical profile changes of As (A), Ni (B), Cd (C), Sb (D), and Pb (E) in GZ soils showed in heatmaps. “N” and “O” represent pumping N_2 and air, respectively.

some Ni, Cd, and Pb form complexation with HA and cannot diffuse into IPI samplers, the complexation effect is insignificant for As and Sb (Figure S3). Thus, in soil condition, IPI samplers have comparable performance with rhizon samplers for elements in ions or small moleculars, like As and Sb, but give smaller counts if huge colloidal metals exist.

Nondestructive Spatial and Temporal Metal Measurement by SWI Profiler. With developed calibration curves, the SWI profiler is able to measure the dynamic changes of element profile in two As-contaminated paddy soils. The soils were exposed to different redox conditions by bubbling air or N_2 gases. The vertical changes of As in GZ soil porewater are

depicted in Figure 3. At Day 1, the As concentrations were generally lower than $40 \mu\text{g}\cdot\text{L}^{-1}$ with small variation. The As levels increased slightly with the depth. The deployment of SWI profiler at Day 0 was probably responsible for the low As concentration observed at Day 1 as it may introduce oxygen to soils. Similar As gradients along SWI were clearly observed in other days. The results represented a typical redox controlled element profile, which have been widely reported in other studies.^{2,4,9}

The temporal changes of As profile in SWI were rarely reported. In this study, we are able to track the daily changes of As profile by using SWI profiler. In GZ soil, the As profile below

Table 1. Comparison between Commercial Methods for Soil Porewater Study and SWI Profiler

method	time resolution	spatial resolution	porewater removed (μL) ^a	repeated usage	liquid sample	sample process and analysis time	ref.
rhizon sampler	minutes to hours	~cm	≥ 2000	yes but limited	yes	hour to day	14–16,47,49
DET probe	hours to days	mm to cm	440	no	no	day to week	26,28,34,48
peeper	hours to days	mm to cm	450–10 000	no	yes	hour to day	23–25
SWI profiler	hours to days	mm	400	yes	yes	min to hour	this work

^aThe porewater volume extracted or equivalent porewater volume calculated by the solute diffused into the samplers was used to evaluate the disturbance of sampling techniques to soil/sediment environments. The lengths of DET probes, peeper, and SWI profiler are normalized to 5 cm.

10 mm of SWI was not influenced by the surface water redox condition, but porewater As near SWI was sensitive to anoxic–oxic transition (Figures 4A and S5A). It increased under anoxic conditions (Day 2–3, Day 7–8) and decreased under oxic conditions (Day 4–6). The increase of As after pumping N₂ (Day 2–3, Day 7–8) around SWI could be attributed to the release of As during metal mineral reduction and dissolution when the redox conditions at SWI shifted from oxic to anoxic, and from day 4 to 6, the air pumped into surface water facilitated Fe oxides formation and As(III) oxidation at SWI, thus As was adsorbed by the oxides and decreased in porewater.^{4,41,42} However, no obvious As fluctuation was observed in QY soil (Figure S6A). The result reflects a quick matter movement in sandy GZ soil and a relative slow change in loamy QY soil.⁴³ This finding strongly supports the SWI profiler is a powerful and robust tool to trace the temporal change of elements. However, more tests are essentially needed before applying SWI profiler in other environments, like salty or acidic soils and sediments.

The dynamic changes of other elements, including Ni, Cd, Sb, and Pb, were also tracked and presented in Figures 4 and S5–7. The concentrations of those elements were much lower than As. Nickel profile was constant with time in both soils (Figures 4B and S5–S7B). Spatially, porewater Ni concentrations were higher than Ni in surface water in QY soil. The concentrations of Cd in both soils were as low as $<1 \mu\text{g}\cdot\text{L}^{-1}$ (Figures 4C and S5–S7C). Antimony was found to be mobile in SWI (Figures 4D and S5–S7D), which is consistent with the previous results using DGT probe.^{4,44} Lead showed a fluctuation along with the anoxic–oxic transition in both soils (Figures 4E and S5–S7E), and it tends to be immobilized under anoxic conditions (Day 2–3, Day 7–8).^{45,46}

Comparison with other Commercial Techniques.

Rhizon samplers, peepers, and DET probes are most widely used and commercially available devices for the studies on soil/sediment porewater. Rhizon sampler can extract porewater within minutes to hours.^{14,47} Peeper and DET probe are able to passively collect the solutes in porewater after several hours/days deployment.^{25,28} A comparison of these three methods with SWI profiler is given in Table 1.

The sediment porewater sampling techniques mentioned above have been used to reveal the element gradient along SWI.^{9,41} Horizontal insertion of rhizon samplers can give a good spatial resolution (~cm) of elements along SWI.¹⁵ However, the sampling zone of rhizon sampler strongly depends on the volume of the retrieved fluids,¹⁵ which may cause bias to the element profile. Peeper has a typical resolution of 1 cm, but higher resolution (mm) can be achieved by using small volume chamber.^{23–25} The spatial resolution of DET probe is around 2 mm if the gel was cut before ICP-MS measurement.^{26,48} The spatial resolution of SWI profiler is determined by the size of the hollow fiber membrane tube, which has a comparable spatial

resolution with high resolution peeper (HR-peeper) and DET probe (mm scale) in this study (Table 1).

SWI profiler has great advantages when being applied to the time-dependent element change in soil porewater. The volume of porewater extracted or equivalent porewater was used to compare the disturbance to soil/sediment environment among different sampling techniques in one sampling event (Table 1). The calculation process was provided in the SI. Rhizon sampler extracts porewater directly from the soil via a syringe or vacuum vial, the sample volume is depended on the vacuum pressure and sampling time, generally ≥ 2 mL liquid sample were taken in every sampling event.^{14–16,47,49} Other samplers work passively, i.e., only the dissolved components were extracted, thus the disturbance of passive samplers is evaluated by the equivalent porewater volume. The removed solute in porewater by peeper is determined by the designed chamber volume. Low spatial resolution peeper (1 cm) could extract a large equivalent porewater volume (~10 mL),²³ but HR-peeper only consumes a small volume of porewater (~450 μL).^{24,25} By contrast, the least solute in porewater was consumed by DET (440 μL) and SWI profiler (400 μL).²⁶ The low disturbance of SWI profiler to porewater makes it an ideal tool to repeatedly sample porewater at a certain place. Although HR-peeper and DET probe can be used to study the time series of element change by continuously deploying and taking out of HR-peeper or DET probes, the deployment and take-out cycles may pose disturbances to the sediment, and the coarse sediment may in turn tear the membrane or gel layer on DET probes.^{15,34,50} These influencing factors may cause high variability to the element profile. Low mechanical disturbance of the sediment can be achieved with rhizon sampler method.¹⁵ However, rhizon sampler would be blocked by the suspended soil particles under repeated usage.^{15,16} By contrast, SWI profiler has much longer service life, and no blocking event was noticed after 10 times use in soils.

With SWI profiler, it is easy to monitor the high spatial (mm level) distribution of metals at a certain place repeatedly. However, great care should be taken to sample porewater from SWI profiler in high frequency (e.g., daily), since the buffer capacity to porewater is varying among different soils and sediments.³⁵ This indicates, when sampling in high frequency, underestimation of the components in porewater may happen, especially for the soils or sediments with limited buffer capacity. Therefore, to yield the reliable element profiles, low sampling frequency is recommended for applying SWI profiler in long-term monitoring.

Although all the samplers' quality was checked before application, failed samplers were occasionally found in SWI profiler. A diagnostic graph is shown in Figure S8 to help users to preview the data and remove invalid data. In this test, no peaks were observed in samples 11 and 32, and part of sample 83 peak was missing. A postexperiment check found the blocking

problem was caused by the dropping debris from carbon fiber caps.

The complexity of sample preparation before measurement is a key parameter when selecting analytical methods. There is almost no cost for sample preparation for SWI profiler method, since the samples were directly introduced to ICP-MS. For rhizon sampler and peeper methods, it is common to use a small amount of acid to stabilize the element before instrument analysis.^{25,49} The sample preparation of DET technique is manually intensive.³⁴ In addition, a 24 h elution with NaOH or HNO₃ is needed for the instrument analysis.^{28,48} In comparison with DET, an advantage for peeper, IPI sampler and rhizon sampler is to obtain clean liquid porewater sample directly, which is almost ready for instrument analysis (Table 1). Many alternative solutions were proposed to reduce the sample preparation steps for DET probes, e.g., replacing manually gel slicing with guillotine devices,⁵¹ and coupling DET probe with colorimetric analysis.³⁴ As for SWI profiler, the sample collection and introduction into ICP-MS share the same single hollow fiber membrane tube, which would greatly simplify the sample preparation and analysis. Typically, it takes only 50 min for the multielement sampling and measurement of the whole samples from one SWI profiler when directly connecting to ICP-MS (2 min/sample × 25 samples/SWI profiler). The high sample measurement throughput is only achievable in “on-line” mode by connecting IPI samplers with ICP-MS. If dirt samples are not allowed in clean lab for ICP-MS operation, then the IPI samplers can work in “off-line” mode. The “off-line” mode is time-consuming because soil porewater must be extracted first and sent for ICP-MS lab with proper preparation.

We presented the feasibility of coupling SWI profiler with ICP-MS. When the SWI profiler is applied in field, the solution can be pumped out and stored in tubes for lab-based analysis by the instruments able to measurement a small volume of sample (~100 μL), for examples, ion chromatography (IC), microplate reader, flow cytometer, and dynamic light scattering.^{52–54} More application based on IPI samplers can be foreseen in the future and assist the studies on soil and sediment sciences.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.8b05390.

Calculation of the equivalent porewater extracted by different samplers. Description of soil characteristics, sensitivity of elements in different solutions, performance of ultrapure water and 10 mM NaCl as the carrier solution in soils, signal of As with 10 mM NaCl as the carrier solution in solution and soils, the influence of HA on Ni, As, Cd, Sb and Pb sampling in near-neutral conditions, peak area integration figure, SD profile heatmap of different elements in GZ soil, elements profile heatmap in QY soil, SD profile heatmap of different elements in QY soil, and a preview of sample peaks (PDF)

Raw data and the R scripts used to process and analyze the data (TXT)

Raw data and the R scripts used to process and analyze the data (ZIP)

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Notes

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