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Diffusive gradients in thin films (DGT) technique provided a new predictive method of metal availability in soils. DGT induced translocation of metal includes diffusive process of metal in the soil solution and kinetic resupply processes of metal from the solid phase. In this study, coincident changes were obtained between DGT-measured As and plant-adsorbed As, which demonstrated that DGT is an effective technique for the prediction and assessment of As bioavailability in soils and the feasibility of in situ application of DGT. This study is of great significance to determining an effective method for labile As measurement in soils and to improving the accuracy and precision of As risk assessment.

Assessment of Arsenic Availability in Soils Using Diffusive Gradients in Thin Films (DGT) Technique—A Comparison Study of DGT and Classic Extraction Methods

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Abstract: This study was conducted to evaluate the feasibility and accuracy of available arsenic (As) measurement in soils using the diffusive gradients in thin films (DGT) technique and to shed further light on the risk evaluation of As-contaminated soils. A bio-indicator method was used to evaluate the dependence of As concentrations in plant tissues (edible rape) on the As concentrations measured by different methods. DGT, extraction of soil pore water, 0.5 M $NaHCO_3$, 1 M HCl, 1 M NH_4Cl, 0.5 M NH_4F, 0.1 M NaOH and 0.25 M H_2SO_4 extraction methods, as well as total As content in the soil were employed in this study. Edible rape was grown in 43 soils containing different concentrations of As. A better correlation was obtained between the As concentrations in plant tissues and the As concentrations measured by DGT than between plant concentrations and those measured by other methods. The coefficients of determination (R^2) before and after growth of edible rape were 0.84 and 0.83, respectively. Levels of As in plants and in soil pore water are also closely related: the coefficients of determination (R^2) between these variables before and after growth of edible rape were 0.83 and 0.81, respectively. Measurements from the chemical extraction methods were inferior to those from DGT and soil pore water. Levels of As in plants were more scattered and nonlinear with respect to total soil As content (R^2 = 0.27). The As measured by DGT closely reflected the pool of plant-adsorbed As. From the data obtained in this study, we can conclude that DGT is an effective technique for the prediction and assessment of As bioavailability in soils.

Keywords: DGT, As, availability, extraction, comparison

1. Introduction

The risk assessment of arsenic (As) in contaminated soils must address the bioavailability of the element [1], which has remained a challenge to date [2-4]. Among all As species, total As content has proven to be a poor indicator of As toxicity [5, 6]. Chemical speciation and partition of As are key factors that affect the geochemical processing and availability of As in soils [7]. Total As content does not characterize the element's speciation, mobilization and bioavailability in soils [5, 8], as different As species have unequal impacts on the environment [9] and vary in mobilization and bioavailability. Researchers have determined that total As content embraces large fractions that are unavailable to biota and are moving toward studies that consider the 'available' As fraction as an indicator of risk assessment [5]. Classic chemical extraction methods, such as single and sequential extraction, are frequently used in current assessments of 'bioavailability' of As in soils. These methods are based on the equilibrium principle and extract one or several particular fractions of As from the soil [5, 9]. However, extraction agents are inconsistent across the previous literature, and 0.5 M H_2SO_4, 0.1 M NaOH, 0.5 M $NaHCO_3$, sodium acetate and mixed acids, oxidisable organic matter and 1.0 M HCl all have high efficiencies for defining the available fraction of As [10-14]. An extraction procedure provides a response to a given extraction agent

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rather than a true reflection of the labile As pool. The artificial changes induced during sampling, extraction and analysis may affect As bioavailability, complicating the development of soil test methodologies [5]. The extraction of soil pore water has also been used to determine the available fraction of As in soil. However, the solutes available to plants are widely recognized as derived from both the soil solution and the solid phase [15, 16], which is poorly represented by pore water predictions [1, 17].

Zhang et al. (2001) proposed a new concept known as effective concentration, C_E, to be measured using the Diffusive Gradients in Thin Films (DGT) technique, thereby aiming to provide an easy tool for predicting the availability of metals in soils [1]. Based on a reflection of metal lability, C_E includes both the soil solution concentration and the resupply from the solid phase following the depletion of the soil solution [1]. DGT has been successfully used in previous studies for the measurement of metal cations such as zinc, cadmium, lead and copper in both water and soil [1, 15, 18-20]. However, As generally exists in the environment in its oxyanion form, which differs from metal cations in its chemical properties. Differing from DGT for metal cations which uses Chelex 100 as a binding reagent [18], DGT for oxyanions adopts ferrihydrite (FH) as the binding agent, and previous studies suggested that DGT measurement of phosphorus (P) is a superior predictive method to established soil P tests [21-25]. The first DGT sampler for As was reported by Fitz et al. (2003) [26]. In that study, DGT was used as a monitoring tool to evaluate the efficiency of phytoextraction and to study the potential resupply of labile pools after the cessation of phytoextraction. Cattani et al. (2009) evaluated the availability of As to roots in nine hyperaccumulator planted soils, and demonstrated the sensitivity of DGT to root-induced changes in the soil [27]. Senila et al. (2013) used DGT as a tool to investigate the phytoextraction efficiency of two different plants [28]. However, particular investigations on assessment of As availability in soil using DGT are less available in previous reports, in which DGT was mainly adopted for monitoring phytoextraction efficiency or the kinetic changes of As in rhizosphere soils [26-29]. The objective of this study was to assess the capability of the FH-based DGT technique to predict the bioavailability of As in soils with various physicochemical properties and various concentrations of As. This study is of great significance to determining an effective method for labile As measurement in soils and to improving the accuracy and precision of As risk assessment.

2. Materials and methods

2.1 Soil Samples.

Thirty-eight cultivated soils (0-20 cm depth) used in this study were collected from seven sites throughout China. Among the soils, one was collected from Changchun (CC), one from Beijing (BJ), five from Chengdu (CD), seven from Guiyang (GY), six from Yueyang (YY), nine from Chenzhou (CZ) and nine from Shimen (SM). The soils were air-dried and sieved to <2 mm for all soil testing methods (extractions and DGT) and pot experiments.

All soils, with the exception of the samples collected from Changchun (CC) and Beijing (BJ), were collected from sites threatened by realgar mines or flooding. They were all contaminated by As but to different extents (Table 1). The two soil samples collected from CC and BJ had very low total soil As concentrations (7.4 and 6.5 mg·kg^{-1}, respectively), which were considered as uncontaminated. To simulate As contamination on these two soils, appropriate amounts of Na_3AsO_4 solution were added to the CC and BJ soils to achieve different gradients. The amended soils were left to equilibrate for three months. For the CC soil, the gradient As concentrations were 7.4 and 23.3 mg·kg^{-1}, while for the BJ soil, the gradient As concentrations were 6.5, 9.1, 17.0, 30.0 and 38.1 mg·kg^{-1}.

2.2 Analyses of Soil Properties.

Subsamples of the soils were air-dried and ground (<0.149 mm) for determination of total soil As concentration. Total As concentrations were determined by hydride generation atomic fluorescence spectrometry (HG-AFS) following digestion with $HCl+HNO_3+HClO_4$ (3:1:1, PRC National Standard, GB/T 17135-1997). Soil pH was measured in a suspension of 1:2.5 soil/carbon dioxides–free water. Total organic matter content was estimated using a conversion factor of 1.9 from total carbon, which was determined using the potassium dichromate volumetric method. Particle size analysis was carried out using the combustion hydrometer method.

Table 1 Total As concentrations in soils and in plants and selected physicochemical properties

Site		pH	OM (%)	Clay (%)	$C_{T\text{-}As}$ (mg·kg^{-1})	C_{soln} (mg·L^{-1})	C_E (mg·L^{-1})	C_{plant} (mg·kg^{-1})
CC	1	5.6	23	25	7.4	0.001	0.007	0.115
	amended	5.7	22	23	23.3	0.011	0.107	0.338
BJ	1	7.6	25	15	6.5	0.009	0.056	0.253
	amended-1	7.8	26	15	9.1	0.108	0.511	1.339
	amended-2	7.8	26	4	17.0	0.240	1.214	1.776
	amended-3	7.8	25	10	30.0	0.568	2.066	1.696
	amended-4	7.7	24	14	38.1	1.061	4.612	2.362
CD	1	7.6	17	28	13.2	0.004	0.030	0.162
	2	7.6	18	27	9.1	0.003	0.028	0.408
	3	7.6	12	26	9.3	0.004	0.031	0.840
	4	6.9	20	29	10.0	0.002	0.024	0.143
	5	6.3	19	29	12.9	0.001	0.015	0.135
GY	1	5.6	48	47	16.6	0.001	0.006	0.162
	2	7.5	43	22	7.4	0.002	0.011	0.102
	3	7.5	29	26	5.5	0.002	0.009	0.097
	4	6.1	37	47	22.6	0.001	0.007	0.086
	5	6.2	33	45	20.7	0.000	0.004	0.090
	6	6.6	40	43	27.3	0.002	0.031	0.138
	7	7.5	46	45	25.1	0.002	0.010	0.113
YY	1	4.9	30	17	14.9	0.006	0.040	0.252
	2	5.5	23	18	12.0	0.002	0.027	0.233
	3	5.7	26	16	4.6	0.002	0.030	0.143
	4	5.3	18	13	9.2	0.001	0.013	0.187
	5	5.3	21	17	13.1	0.002	0.013	0.335
	6	5.6	29	20	6.7	0.010	0.048	0.313
CZ	1	6.6	37	30	69.1	0.011	0.122	0.404

	2	6.8	35	27	247.8	0.061	0.518	0.998
	3	7.5	38	28	61.6	0.023	0.070	0.381
	4	7.4	26	27	76.3	0.029	0.126	0.828
	5	7.5	31	28	175.8	0.049	0.315	0.811
	6	7.3	37	27	64.5	0.026	0.165	0.490
	7	7.4	29	28	84.5	0.046	0.242	0.843
	8	7.4	35	36	30.3	0.014	0.072	0.319
	9	7.6	40	15	12.7	0.003	0.017	0.131
SM	1	7	12	28	164.8	0.030	0.264	0.755
	2	6.5	12	33	94.6	0.005	0.031	0.335
	3	7.5	13	22	98.1	0.038	0.294	0.433
	4	7.3	12	27	10.0	0.001	0.011	0.104
	5	6.6	13	33	10.7	0.001	0.008	0.052
	6	6.6	13	35	22.0	0.001	0.011	0.084
	7	7.7	15	25	29.8	0.004	0.041	0.156
	8	6.3	12	29	7.7	0.003	0.017	0.110
	9	5.9	13	25	8.7	0.002	0.020	0.123

$C_{T\text{-}As}$: Total As concentration in soils;

C_{soln}: As concentration in soil pore water;

C_{plant}: As concentration in plant tissues.

2.3 Pot Experiment.

A commonly used amount of macronutrient solution (N:P_2O_5:K_2O = 0.15:0.18:0.12 g·kg^{-1} soil) was added to the soils 7 days before planting. Soil moisture was maintained at approximately 70% of the maximum water holding capacity (MWHC). Soils were left to equilibrate for 7 d before seeding. Edible rape was sown in pots containing 1.5 kg of soil (dry mass, triplicate for each soil). All pots were placed in a glasshouse (20±4 °C, natural light). Eight weeks after germination, the aboveground plant tissues were harvested, rinsed with deionized water and oven-dried at 70°C.

2.4 Measurements of As in plant tissues and soils.

Total As concentrations in the plant tissues were determined by HG-AFS following digestion with HNO_3+$HClO_4$+H_2SO_4 (PRC National Standard, GB/T 5009.11-1996).

For the single extraction procedures, 0.5 M $NaHCO_3$ [14] and 1 M HCl [13] were used to extract As from the soils. A soil sample (5.00 g) was suspended in 50 mL of 0.5 M $NaHCO_3$/1 M HCl and shaken for 2 h at room temperature, and then filtered through 0.45 µm filter paper before As determination by HG-AFS.

The exchangeable As (AE-AS), Al-associated As (Al-As), Fe-associated As (Fe-As), and Ca-associated As (Ca-As) were extracted sequentially using 1 M NH_4Cl, 0.5 M NH_4F, 0.1 M NaOH and 0.25 M H_2SO_4 according to a standard sequential extraction procedure [30]. The As levels in all extracts were determined by HG-AFS.

Soil pore water was collected both before and after the pot experiment using a centrifuge and a soil moisture sampler [31], respectively. Before the pot experiment, the residual soil after the DGT deployment was transferred into a centrifuge tube, and the soil pore water was sampled by centrifugation at 8000 rpm for 3 mins at room temperature (Sigma Laborzentrifugen 3K15, Germany). During DGT deployment after the harvest, a Rhizon SMS 5 cm soil moisture sampler (Rhizosphere Research Products, Wageningen, the Netherlands) was placed in each pot to collect the soil pore water, and the total dissolved As concentration (C_{soln}) in the soil pore water was determined by HG-AFS.

2.5 DGT devices and deployment.

The DGT devices used in this study were purchased from DGT Research Ltd. (Lancaster, UK). A DGT device consists of a plastic assembly containing a binding gel (iron-hydroxide) overlaid with a layer of polyacrylamide diffusive gel, which is well defined in terms of its thickness and pore size, and a protective filter through which ions can freely diffuse [1, 32]. Detailed information about the principles and applications of DGT has been previously reported [1, 15, 18, 32].

The DGT used in this study employed ferrihydrite as the binding agent which measures both As (III) and As (V) [26, 27], besides, the experiment was performed under oxidising conditions which made As(V) the dominant form [33], and therefore total inorganic As was taken into consideration in this study.

Before the pot experiment, appropriate amounts of soil for DGT deployment were first maintained at 60% MWHC for 48 h and then wetted to 80%-100% MWHC for 24 h at room temperature. During the addition of water, the soils were churned and mixed into slurry. A DGT device was placed on each soil and pressed down gently to ensure complete contact between the device and the soil, and then left for 24 h at 25 ± 1 °C. The DGT devices were deployed again after the harvest. Any changes of temperature were recorded during the deployment.

After the DGT devices were retrieved from these two deployments, the binding gels were removed and eluted with concentrated HNO_3 for at least 24 h prior analysis by HG-AFS.

2.6 Calculation of DGT measurements.

The amount of accumulated As in the binding gel, M, was calculated using Eq. (1) [32]:

$$M = C\,(V_{acid} + V_{gel})/f_e \qquad (1)$$

C expresses the As concentration in the elution sample as measured by HG-AFS. V_{acid} is the volume of acid used for elution (2mL) and V_{gel} is the volume of the binding gel (0.18 mL). f_e, the elution factor, is close to 100% when concentrated HNO_3 is used as the extracting solution [32, 34]. From the calculated M, the time-averaged concentration of As at the interface of the DGT device and the soil (C_{DGT}) can be calculated using Eq. (2):

$$C_{DGT} = M\Delta g/(DAt) \qquad (2)$$

Δg is the total thickness of the diffusive gel layer (0.82 mm) and the filter membrane (0.14 mm). D is the diffusion coefficients of As in the diffusive gel, which has been measured previously [20]. A is the surface area (3.14 cm^2) of the DGT sampling window and t is the deployment time (24 h).

The concentration measured directly by DGT (C_{DGT}) can be converted to an effective concentration (C_E) using Eq. (3):

$$C_E = C_{DGT}/R_{diff} \qquad (3)$$

C_E represents the concentration of As that is effectively available from both the soil solution and the solid-phase labile pool [1]. R_{diff} expresses the extent of the concentration depletion at the interface of the device and the soil for the diffusion-only case [1], and has previously been calculated using a dynamic numerical model of the DGT-soil system DIFS (DGT induced fluxes in soils) (DIFS_Basic, Lancaster University) [35]. Details about the principle and application of the DIFS model have been previously reported [35].

2.7 Quality assurance and quality control

During the analysis of As concentration in soil and plant samples, three standard soil reference materials (GBW07401, GBW07404 and GBW 07408) and two standard plant reference materials (GBW10014 and GBW10015) were included in the digest and analytical procedure for quality assurance and quality control. All the reference materials were triplicate during the analysis and determination processes. The average recovery for As in the standard reference soil GBW07401, GBW07404 and GBW 07408 were 84.1%, 80.7% and 84.0%, respectively, while the average recovery for As in the standard reference plant GBW10014 and GBW10015 were 93.9% and 99.3%, respectively. DGT deployment was applied 4 times with 3 blanks each time. The mean DGT value (C_{DGT}) of a total of 12 blanks was 0.21±0.08 $\mu g \cdot L^{-1}$, and the method detection limit (MDL) was 0.63 $\mu g \cdot L^{-1}$.

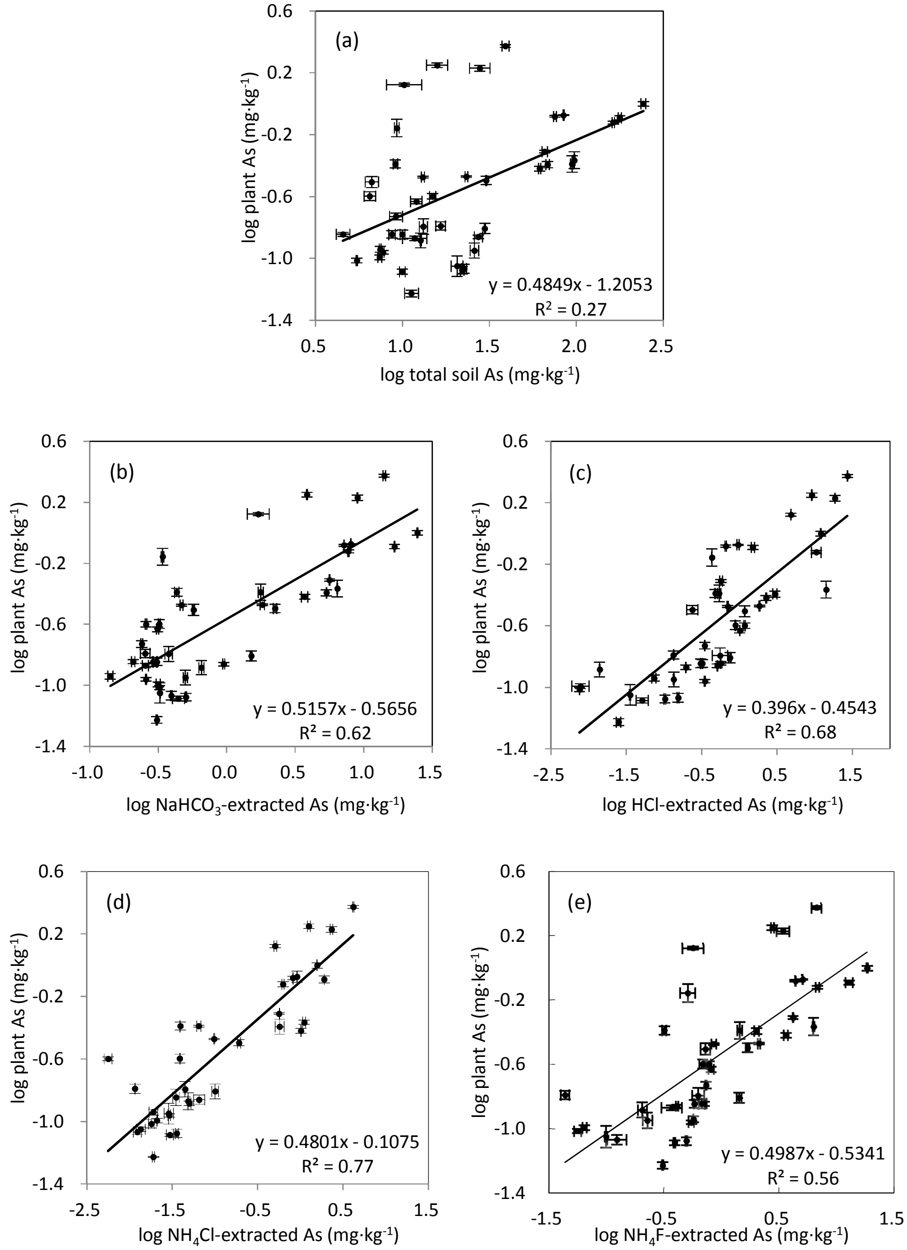
3. Results and discussion

3.1 Different measurements of As and their relationship with plant As

The extracted ranges of As concentration in soils varied considerably after using different extraction methods. DGT-measured As concentrations (C_E) of the soils ranged from 0.004 to 4.612 $mg \cdot L^{-1}$ (before growth) and 0.005 to 5.528 $mg \cdot L^{-1}$ (after growth), which accounted for a small proportion of the total As in the soils. DGT depletes metal in a narrow zone adjacent to the device [1] and this zone is expected to be similar to the volume affected by the plant root [36]. DGT measured As concentration in spiked soils were generally higher (> 0.1 $mg \cdot kg^{-1}$), while in unspiked soils, the higher concentration (> 0.1 $mg \cdot kg^{-1}$) were found in soils collected from Chenzhou (CZ) and Shimen (SM). These two sites are located in Hunan province, China and have been polluted by realgar mines or flooding. Soil pore water As concentration ranged from 0.000 – 1.061 $mg \cdot L^{-1}$ (before growth) and 0.001 to 1.483 $mg \cdot L^{-1}$ (after growth). $NaHCO_3$ extracted As concentration ranged from 0.142 – 24.651 $mg \cdot kg^{-1}$. HCl extracted As concentration ranged from 0.008 – 27.245 $mg \cdot kg^{-1}$. NH_4Cl extracted As concentration ranged from 0.000 – 4.130 $mg \cdot kg^{-1}$. NH_4F extracted As concentration ranged from 0.044 – 18.536 $mg \cdot kg^{-1}$. NaOH extracted As concentration ranged from 0.117 – 135.631 $mg \cdot kg^{-1}$. H_2SO_4 extracted As concentration ranged from 0.171 – 46.493 $mg \cdot kg^{-1}$. Different As concentration ranges measured by different methods indicated the difference of these methods in characterization the available fraction of As in the soil.

To improve data distribution, log-log relationship was used in this study [15]. As concentration in the plant tissues (C_{plant}) was most highly correlated ($p < 0.01$) with DGT-measured concentration

(C_E) and soil pore water concentration (C_{soln}), as displayed in Fig. 1. The correlation coefficients (R^2) between C_{plant} and C_E before and after growth were 0.84 and 0.83, respectively. The correlation coefficients (R^2) between C_{plant} and C_{soln} before and after growth were 0.83 and 0.81, respectively. Furthermore, significant correlations ($p < 0.05$) were found between C_{plant} and the As fractions extracted by 1 M NH_4Cl, 1 M HCl, 0.5 M $NaHCO_3$, 0.5 M NH_4F and 0.25 M H_2SO_4, and the correlation coefficients (R^2) for these methods were 0.77, 0.68, 0.62, 0.56 and 0.53, respectively. C_{plant} was found to be very poorly correlated with both total soil As concentration ($R^2 = 0.27$) and the As extracted using 0.1 M NaOH ($R^2 = 0.16$). Both DGT-measured As concentration and pore water As concentration showed good correlations with the As concentration in plant tissues, indicating that these two methods provided better measurements of labile As concentrations compared to the other extraction methods.



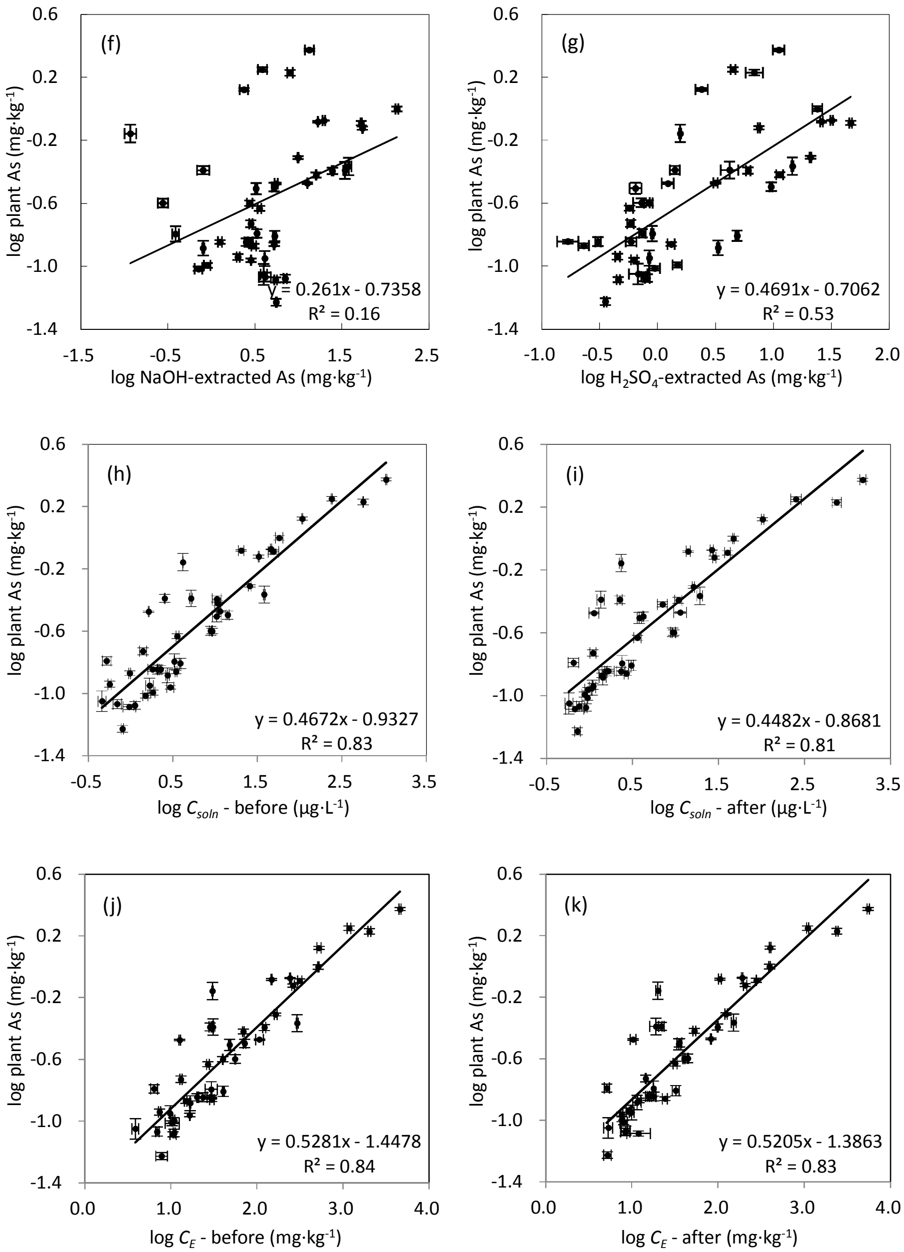


Fig. 1 Dependence of log concentration of As in above ground plant tissues on the log of (a) total soil As, (b) $NaHCO_3$-extracted As, (c) HCl-extracted As, (d) NH_4Cl-extracted As, (e) NH_4F-extracted As, (f) NaOH-extracted As, (g) H_2SO_4-extracted As, (h) soil solution As, before growth, (i) soil solution As, after growth, (j) effective As concentration, C_E, before growth, (k) effective As concentration, C_E, after growth. The linear regression equations and correlation coefficients for the logarithmically transformed data are shown.

As uptake by edible rape from these particular soils had the highest correlations with As measured by DGT. From a predictive perspective, DGT was the best measure in the present study. For P, analogue of As, Menzies et al. (2005) evaluated DGT on 24 soils and suggested that DGT P accumulation reflected plant P uptake accurately [22]. Mason etal. (2010) investigated the ability of DGT and two other established soil P test to predict wheat responsiveness to applied P from 35 field trials, and the results indicated that relationships between DGT and relative yield (%) were significant ($p < 0.05$) for both early dry matter and grain production and a better estimation of plant-available P than established soil P tests was obtained using DGT [23]. Six et al. (2012; 2013) reported that DGT method explained relative yield of maize among soils better ($R^2 = 0.84$) and found no difference in specific activity (SA) between the maize shoot and the soil DGT test [24, 25]. While for As, Cattani et al. (2009) applied DGT on nine soils (total As concentration ranged from 200 to 2000 mg·kg^{-1}) and suggested that the low availability of As measured by DGT in the soils resulted in the small uptake of As observed. This study has proved that DGT is a reliable method for pre-concentration availability of As in 43 soils with a lower As concentration range (4.6 to 247.8 mg·kg^{-1}). The highest correlation between DGT measured As and plant As may due to a true reflection of phyto-available As pool measured by DGT.

The soil pore water concentration method exhibited good performance in predicting the phyto-availability of As in the soil in this study. Similar observations were also obtained previously in Zhang et al.'s (2001) study for Cu and in Nolan et al.'s (2005) study for Zn, Cd and Pb. The As concentration in soil pore water after growth were generally lower than that before growth (data not shown), which indicated that the resupply processes from solid phase after depletion in pore water might be insufficient. Nolan et al (2005) suggested that soil solution concentration may be equally effective as C_E at predicting plant uptake when supply by diffusion becomes unimportant.

3.2 Contribution of different As chemical speciation to different measurements of As

Multiple regression analysis were introduced to study the relationships between different measurements of As and different chemical speciation of As in the soil. The results of the multiple regression analysis are shown in Table 2. C_{plant} was found to have positive relationship with AE-As and Al-As, but negative relationship with Fe-As and Ca-As, which indicated that the phyto-available As pool was mostly derived from AE-As and to a lesser extent from Al-As. Similar relationships were also found between C_E (before and after growth) and different chemical speciation of As in the soil, which indicated that DGT measured labile As pool had a closer reflection of phyto-available As pool than any other methods. DGT measured As includes As soil solution phase and resupply from solid phase after local depletion. Strongly bound chemical speciation of As (Fe-As and Ca-As) in the soil, which could not be utilized by plants, were excluded in the DGT measurement. Similar suggestions were also obtained in previous results from Zhang et al. (2001) [1].

Soil pore water extraction and chemical extraction methods failed to represent precisely the phyto-available fraction of As in the soil. The As concentration in the soil pore water was mainly derived from AE-As, which was the dominant fraction that affecting C_{plant}. However, pore water concentration does not account for the kinetic resupply (Al-As) of the solid phase when local As concentration (AE-As) is depleted [8, 17]. In the present study, As bonded on solid phase (Al-As, Fe-As and Ca-As) were found to have a very small or negative impact on C_{plant} (Table 2); videlicet the resupply processes from solid phase were insufficient. Degryse et al. (2009) suggested that DGT would show benefits over other soil testing methods when the plant uptake was limited by diffusion [38]. However, in the present study, the soils were all collected from areas threatened by As pollution. There are no diffusion limitations due to the high As concentrations and therefore C_{soln} will be just as effective as C_E.

The 0.5 M $NaHCO_3$ method extracted primarily As derived from AE-As and Al-As and to a lesser extent from Fe-As and Ca-As, while the 1 M HCl method extracted mostly As derived from AE-As and to a lesser extent from Al-As and Fe-As. The extracted fractions of As by chemical reagents were different from previous studies [4, 39], and these differences may have been due to the differences in the soils used in these studies or the alterations of labile phase during the sample preparation. The inconsistency in extracted fractions of As by chemical reagents from different studies also indicated the unreliability in characterization the available fraction of As in the soil by chemical extraction methods.

Table 2 Multiple regression analysis for relationship between As species and As measured by different methods

Multiple regression equation	Coefficients of determination (R^2)
$C_{plant} = 0.240 + 0.562\ C_{AE} + 0.03\ C_{Al} - 0.004\ C_{Fe} - 0.008\ C_{Ca}$	0.76
C_E-b $= 0.035 + 1.07\ C_{AE} + 0.029\ C_{Al} - 0.007\ C_{Fe} - 0.033\ C_{Ca}$	0.96
C_E-a $= 0.023 + 1.289\ C_{AE} + 0.013\ C_{Al} - 0.008\ C_{Fe} - 0.038\ C_{Ca}$	0.95
C_{soln}-b $= 6.72 + 265.04\ C_{AE} - 3.184\ C_{Al} - 1.24\ C_{Fe} - 6.846\ C_{Ca}$	0.96
C_{soln}-a $= 4.668 + 362.765\ C_{AE} - 5.267\ C_{Al} - 1.664\ C_{Fe} - 9.949\ C_{Ca}$	0.95
$C_{NaHCO3} = -0.236 + 2.271\ C_{AE} + 0.531\ C_{Al} + 0.063\ C_{Fe} + 0.064\ C_{Ca}$	0.98
$C_{HCl} = 0.596 + 7.295\ C_{AE} + 0.015\ C_{Al} + 0.064\ C_{Fe} - 0.291\ C_{Ca}$	0.92

C_{AE}: Concentration of exchangeable As (AE-As, extracted by 1 M NH_4Cl)

C_{Al}: Concentration of As associated with Al (Al-As, extracted by 0.5 M NH_4F)

C_{Fe}: Concentration of As associated with Fe (Fe-As, extracted by 0.1 M NaOH)

C_{Ca}: Concentration of As associated with Ca (Ca-As, extracted by 0.25 M H_2SO_4)

C_E-b: DGT measured As concentration before pot experiment

C_E-a: DGT measured As concentration after pot experiment

C_{soln}-b: As concentration in soil pore water before pot experiment

C_{soln}-a: As concentration in soil pore water after pot experiment

C_{NaHCO3}: $NaHCO_3$-extracted As concentration

C_{HCl}: HCl-extracted As concentration

This work has demonstrated that DGT method could be used as a predictive tool to assess the availability of As in the soil. Unlike common-used extraction methods, DGT method is founded on kinetic rather than equilibrium principle [26]. Like plant roots, DGT could locally lower As concentration in the soil solution phase and thus induced resupply from the solid phase. The distinguishing feature of DGT measurement is that it combines As concentration in the soil solution phase and kinetic resupply from the solid phase. Furthermore, DGT technique allows for in situ applications [18, 19, 21, 40, 41], thus the soil samples would not be disturbed chemically in that there would be no induced pH change and no large dilution of soil sample with extract. Overall, DGT technique is a continually evolving process aimed at improving the development of better soil testing methodologies [1, 15].

4. Conclusions

The results obtained in this study showed that plant As was better correlated with DGT-measured As concentration, C_E, and with soil pore water concentration than with the As extracted by 0.5 M $NaHCO_3$, 1 M HCl, 1 M NH_4Cl, 0.5 M NH_4F, 0.1 M NaOH and 0.25 M H_2SO_4, as well as total soil As. In all of the soils used in this study, coincident changes were observed between C_{plant} and C_E, indicating that DGT was a reliable and effective method for determining the availability of soil As. In this study, DGT-measured As was derived mainly from AE-As and to a lesser extent from Al-As, rather than from Fe-As and Ca-As, which provided a closer reflection of the plant-adsorbed As pool. The DGT technique showed advantages over the other measurement methods employed in this study. Overall, the DGT technique is a suitable sampling method for labile As measurement in soil and may predict the bioavailability of As species.

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