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Prediction of arsenic accumulation in a calcareous soil-wheat/maize rotation system with continuous amendment of sewage sludge

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Abstract: A potted experiment was conducted to explore the accumulation of arsenic (As) and predict the uptake of As by a wheat-maize rotation system in calcareous soil with different rates of sewage sludge (SS) amendment over two consecutive years. The SS amendment decreased the pH value of calcareous soil but increased the cation exchange capacity (CEC), calcium carbonate (CC), organic carbon (OC) and As accumulation in soil and crops with increasing SS addition. The As bioconcentration factor (BCF) of wheat and maize had a significant negative correlation with pH, CC and a significant positive correlation with OC. Soil CEC had a significant positive correlation only with the As BCF of wheat. Regression analysis showed that soil As, pH, OC, CC and CEC were good predictors of the As concentration in wheat/maize. The regression model for each part of the wheat/maize plants had a high model efficiency value and explained 67~88% of the variability. The R^2 values of the wheat and maize grain prediction models were 79% and 76%, respectively. Thus, these models contribute to the study of As risk assessment for sewage sludge utilisation in calcareous soil-wheat/maize rotation systems.

Keywords: soil properties; crop tissues; contamination; linear relation; pollution

The Agency for Toxic Substances and Disease Registry lists arsenic (As) as the primary chemical poison that is harmful to human health. In China, As is one of the five key elements monitored by the Ministry of Ecology and Environment. In 2014, the national soil pollution survey bulletin reported that as much as 2.7% of China's soil exceeds the risk values (20~40 mg/kg) of As for soils with a different pH range contamination of agricultural land (Li et al. 2014); and inorganic As such as pentavalent arsenate (As^{V}) and trivalent arsenite (As^{III}), is mostly arsenate in soil (Wang et al. 2021). Soil As comes from the mining of arsenic-bearing minerals, arsenic-bearing pesticides, such as methyl sulfur-arsenic pesticides, and the agricultural use of phosphate fertiliser and sewage sludge (SS) (Rahaman et al. 2021). Sewage sludge is an organic by-product from the treatment of municipal wastewater. Agricultural use is an effective way to recycle composted SS (Kacprzak et al. 2017). However, the content of As in SS is 2.9% higher than the agricultural standard limit the standard set for China's agricultural Class A sludge by 30 mg/kg (GB 4284-2018) (Guo et al. 2014, Zhang et al. 2021). It has been proven that As can be transferred from SS-amended soil into crops (Frost and Ketchum 2000). Therefore, the As accumulation risk of SS application in agriculture, especially in calcareous soil, should be considered (Ray et al. 2021) because its toxicity in alkaline soil is much greater than that in acidic soil (Liu et al. 2021).

The main parameters affecting the bioavailability of As in soil include soil pH, organic carbon (OC), cation exchange capacity (CEC), calcium carbonate (CC), and other parameters (Williams et al. 2011).

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For example, under strongly alkaline conditions, a decrease in As availability may be related to the insoluble precipitation of metal ions in the soil. The high CC content in alkaline soil easily forms calcium arsenate precipitates with As. In addition, soil OC plays a complex role in activating or stabilising As in soil. The agricultural use of SS not only increases the As content in the soil but also affects the physicochemical properties of soil and thereby affects the accumulation of As in crops (Eid and Shaltout 2016). Therefore, it is particularly important to understand the effects of soil parameters on As availability and crop absorption to reduce As toxicity and transport in the food chain.

Regression models based on different soil parameters have been widely used to evaluate the uptake of As by crops (Novotná et al. 2015, Zhao et al. 2022). Calcareous soil is predominant across cultivated land types in northern China. Thus, the effect of soil matrix alkaline reactions on exogenous As is a vital concern because there are few reports on the uptake of As in wheat-maize rotation farming that involves the use of SS in calcareous soil. Therefore, we assessed the accumulation characteristics of As in an above-soil crop system, the chief factors affecting As enrichment following sludge application in calcareous soil, and a model for predicting As bioavailability and uptake as a basis for improved As risk assessment and the utilisation of SS in these types of soil.

MATERIAL AND METHODS

Experimental location. A plastic pot experiment was conducted for two consecutive years (from 2016 to 2017) in the Henan University of Science and Technology greenhouse, which is in Luoyang City (34°41'N, 112°27'E), Henan province, China. The climate is semiarid, with an annual average temperature and rainfall of 14.9 °C and 450 mm, respectively.

Experimental design. SS was collected from the Luoyang sludge treatment plant, which utilises an aerobic composting process. The basic physicochemical parameters of the SS are shown in Table 1. The contents of Cd, Hg, Pb, Cr, and As in the selected sludge were 2.17, 0.058, 80.80, 232.87, and 29.08 mg/kg, respectively.

The calcareous soil is a typical Calcic Luvisols, which was collected from the farm near Henan University of Science and Technology, and the physicochemical properties of the soil are shown in Table 1. After air drying, the soil was sieved through a 2 mm sieve, and 10 kg of soil was placed in a plastic pot. SS was mixed with the soil at rates of 0 g/kg (CK), 1.67 g/kg (H1), 3.33 g/kg (H2), 16.6 g/kg (H3), and 33.33 g/kg (H4). The application rates converted into field application amounts were 0, 3.75, 7.5, 37.5 and 75 t/ha (calculated based on the field topsoil weight of 2.25×10^6 kg/ha). Each treatment was repeated three times. The annual plant rotation was winter wheat-summer maize (2016–2017); ten wheat seeds were sown at the beginning of October and harvested in June of the following year (230 days). One maize seed was sown after wheat harvesting and harvested in September (120 days). The cultivars of wheat and maize were Yunong 035 and Zhengdan 958, respectively, and 2.60 g of $CO(NH_2)_2$, 4.2 g of $Ca(H_2PO_4)_2$ and 1.3 g of KCl were applied to each pot in the wheat season.

Sample collection and analysis. The harvested wheat/maize samples were separated into roots, stems and grains, washed with deionised water, oven-dried (at 105 °C) for 30 min, homogenised by grinding in a metal-free plastic mill, passed through a sieve of 0.15 mm mesh size and used for chemical analysis. At the same time, soil samples were collected, and after air drying, they were sieved by 0.85 and 0.15 mm soil sieves. As was determined using a double channel atomic fluorescence ohotometer (Yoshida afs-9120, Yoshida, Japan). Additionally, standard reference samples of known composition were also analysed to check the method's accuracy.

The soil organic carbon content was determined using the potassium dichromate digestion method. The

Table 1. Physicochemical properties and arsenic (As) content of soil and sewage sludge

Material	Total nitrogen	Total phosphorus	Organic carbon	pH_{water}	As
	(g/kg)				(mg/kg)
Sewage sludge	20.23 ± 2.67	15.4 ± 0.70	241.53 ± 4.06	7.74 ± 0.02	29.08 ± 2.23
Calcareous soil	0.54 ± 0.03	0.54 ± 0.03	3.13 ± 0.17	7.61 ± 0.03	12.25 ± 0.65

Values are the mean ± standard deviation (n = 3)

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cation exchange capacity of the soil was determined using the sodium acetate flame photometric method. The soil pH_{water} was determined in soil-water extracts at a ratio of 1:5 (*w*/*v*) using a pH meter (ECP-031, Shanghai, China). The calcium carbonate equivalent was measured with a Bernard calcimeter (Bao 2008).

The As bioconcentration factor and prediction model. The bioconcentration factor (BCF) of As in various parts of crops is the ratio of As content in the various plant parts to soil As content, which reflects the difficulty of the transfer of As from soil into the various parts of plants (Farahat et al. 2017).

$$BCF = C_{plant}/C_{soil} \quad (1)$$

where: C_{plant} – As content in various parts of crops; C_{soil} – As content in the soil.

The model of As content and soil properties (soil As, pH, OC, CC, and CEC) in various parts of crops is established using the regression method as follows:

$$As_{part} = a \times soil_{As} + b \times pH + c \times OC + d \times CEC + e \times CC + k \quad (2)$$

The parameters are normalised to establish the above simulation equation; *a*, *b*, *c*, *d* and *e* represent the influence coefficient of soil parameters on As availability, and *k* indicates the inherent sensitivity index of the crop to As toxicity.

The 15 observed values of As content in roots, stems and grains of wheat and maize in 2017 were selected as the validation datasets, and 15 observed values of As content in the same parts of wheat and maize in 2016 were selected to establish a regression equation. The regression model adopted a single linear regression analysis with soil properties ($soil_{As}$, pH, OC, CC, and CEC) as independent variables to predict As concentrations in distinct parts of wheat and maize. The determination coefficient (R^2) and model efficiency (ME) were used to measure the degree of fit between the predicted concentration and the measured concentration, and the normalised mean error (MNAE) was used to evaluate the quality of the model. Tukey's test was conducted to evaluate the difference between the measured and predicted values of As in wheat and maize tissues.

The model was calculated using the following equations (Novotná et al. 2015):

$$ME = 1 - (\Sigma(C_{model} - C_{measured})^2/\Sigma(C_{model} - C)^2 \quad (3)$$

$$MNAE = \Sigma(|C_{model} - C_{measured}|/C_{measured})/n \quad (4)$$

where: C_{model} – predicted As concentration given by the model; $C_{measured}$ – measured As concentration; C – average value of the measured As concentration; *n* – number of observations.

Data analysis. Data in this study were the average values of three replications and were statistically analysed using Excel 2007 (Washington, USA) and Tukey's test at a $P < 0.05$ probability level using SPSS 17.0 (Chicago, USA).

RESULTS

Effects on soil properties. The application of SS to calcareous soil led to a decrease in soil pH and CC content (Table 2). The soil pH of the H3 and H4 treatments in the 2017 wheat season decreased significantly by 0.26 and 0.31 units, respectively, compared with CK; accordingly, the pH value of the soil decreased significantly in the maize season, and the pH of different treatments in the 2016 season was not statistically significant. In the 2017 maize season, the content of soil CC of H2~H4 decreased significantly by 6.91~11.72% compared with CK. This decrease in soil pH and CC occurred because the organic carbon in SS releases many organic acids in the degradation process, which leads to a decrease in soil pH and a reduction in CC content.

The CEC content was affected by increasing SS amendments. In the 2016 wheat season, the CEC of treatment H4 significantly increased by 0.21 $mmol_+$/kg compared with CK; accordingly, the CEC of H4 in the 2017 wheat season significantly increased by 0.24 $mmol_+$/kg compared with CK. The OC content in calcareous soil increased with increasing SS application rates. In the 2016 and 2017 wheat seasons, only the OC content of H4 significantly increased by 68.67% and 128.64% compared with CK. In the 2016 maize season, the content of soil OC of H3 and H4 significantly increased by 32.72% and 48.43%, respectively. In the 2017 maize season, the OC content of H2, H3 and H4 significantly increased by 25.83, 54.74 and 84.36%, respectively, compared with CK.

Accumulation of As in soil and crops. The SS addition caused As accumulation in the soil (Table 2). In the 2016 wheat and maize seasons, the As content of the H3 and H4 treatments significantly increased by 0.56, 0.84, 0.26 and 0.52 mg/kg compared with CK, but there was no significant difference between the two treatments. Compared with CK, the soil As content significantly increased by 1.43 and 0.89 mg/kg in the H4 treatment in the 2017 wheat and maize seasons. At the same time, the As content of the tested soil was still higher than CK and some treatments; the reason is, on the one hand, due to the As uptake by the plant, the proportion of total As

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Table 2. pH, calcium carbonate (CC), cation exchange capacity (CEC), organic carbon (OC) and arsenic (As) content of soil for different harvest seasons

Parameter	Treatment	2016		2017	
		wheat season	maize season	wheat season	maize season
pH	CK	7.73 ± 0.07^{a}	7.74 ± 0.03^{a}	7.56 ± 0.17^{a}	7.66 ± 0.12^{a}
	H1	7.70 ± 0.05^{a}	7.73 ± 0.02^{a}	7.46 ± 0.03^{ab}	7.47 ± 0.01^{b}
	H2	7.66 ± 0.19^{a}	7.71 ± 0.04^{a}	7.40 ± 0.08^{ab}	7.42 ± 0.04^{b}
	H3	7.58 ± 0.17^{a}	7.65 ± 0.15^{a}	7.30 ± 0.06^{b}	7.38 ± 0.01^{bc}
	H4	7.50 ± 0.37^{a}	7.54 ± 0.30^{a}	7.25 ± 0.19^{b}	7.27 ± 0.05^{c}
CC (g/kg)	CK	40.31 ± 0.72^{a}	40.42 ± 0.52^{a}	39.31 ± 0.25^{a}	40.80 ± 1.71^{a}
	H1	39.63 ± 2.30^{a}	39.83 ± 0.95^{a}	38.50 ± 2.36^{a}	38.33 ± 1.23^{ab}
	H2	39.13 ± 0.53^{a}	39.73 ± 0.25^{a}	37.83 ± 0.76^{a}	37.98 ± 0.69^{b}
	H3	39.00 ± 0.71^{a}	39.33 ± 1.04^{a}	37.33 ± 1.04^{a}	36.39 ± 0.67^{b}
	H4	38.88 ± 1.59^{a}	39.32 ± 016^{a}	36.33 ± 0.76^{a}	36.02 ± 0.36^{b}
CEC ($mmol_+$/kg)	CK	320.53 ± 0.08^{b}	348.24 ± 17.46^{a}	344.60 ± 9.53^{b}	349.87 ± 5.78^{a}
	H1	329.17 ± 7.26^{ab}	348.95 ± 7.04^{a}	349.62 ± 4.96^{ab}	350.43 ± 7.07^{a}
	H2	334.01 ± 6.60^{ab}	352.63 ± 28.77^{a}	356.12 ± 3.80^{ab}	354.85 ± 1.41^{a}
	H3	337.23 ± 5.60^{ab}	353.78 ± 10.25^{a}	360.50 ± 4.16^{ab}	355.84 ± 6.76^{a}
	H4	341.52 ± 1.98^{a}	354.01 ± 4.08^{a}	368.01 ± 7.63^{a}	362.22 ± 5.98^{a}
OC (g/kg)	CK	4.15 ± 0.07^{b}	3.82 ± 0.25^{c}	4.26 ± 0.13^{b}	4.22 ± 0.29^{d}
	H1	4.72 ± 1.23^{b}	3.94 ± 0.33^{c}	4.86 ± 0.48^{b}	4.47 ± 0.06^{cd}
	H2	4.95 ± 1.04^{ab}	4.10 ± 0.05^{c}	5.63 ± 1.38^{b}	5.31 ± 0.06^{c}
	H3	5.35 ± 0.09^{ab}	5.07 ± 0.09^{b}	6.90 ± 0.13^{b}	6.53 ± 0.53^{b}
	H4	7.00 ± 0.47^{a}	5.67 ± 0.05^{a}	9.74 ± 0.82^{a}	7.78 ± 0.23^{a}
$Soil_{As}$	CK	11.64 ± 0.09^{b}	10.98 ± 0.18^{c}	12.03 ± 0.51^{b}	11.31 ± 0.33^{c}
	H1	11.79 ± 0.10^{b}	11.03 ± 0.01^{bc}	12.36 ± 0.49^{ab}	11.66 ± 0.01^{bc}
	H2	11.83 ± 0.03^{b}	11.05 ± 0.02^{bc}	12.43 ± 0.54^{ab}	11.69 ± 0.09^{bc}
	H3	12.20 ± 0.20^{a}	11.24 ± 0.03^{ab}	12.97 ± 0.04^{ab}	11.89 ± 0.04^{abc}
	H4	12.48 ± 0.09^{a}	11.50 ± 0.06^{a}	13.46 ± 0.08^{a}	12.20 ± 0.08^{a}

Values are the mean ± standard deviation (n = 3). CK – sewage sludge mixed with soil at rates of 0 g/kg; H1 – sewage sludge mixed with soil at rates of 1.67 g/kg; H2 – sewage sludge mixed with soil at rates of 3.33 g/kg; H3 – sewage sludge mixed with soil at rates of 16.6 g/kg; H4 – sewage sludge mixed with soil at rates of 33.33 g/kg. The same parameters with different lowercase letters in the same column for the same growing season were significantly different between different treatments ($P < 0.05$)

absorption by wheat and corn to total As in soil every year as followed 0.078~0.18%, on the other hand, due to the leaching of available As, but the specific amount and form of the leaching of As need to be further studied.

The As content in different tissues of wheat and maize also was affected by increasing SS application rates (Table 3), and the As content occurred in the following order: root > stem > grain. At the same time, the As content in wheat and maize grains of each treatment did not exceed the standard value (0.5 mg/kg) for food safety (GB2761-2017) in China, and therefore SS can be safely applied on calcareous soil in the short term. However, with the increase in the application amount and period, the increase in As risk should be considered. When the SS application occurred in the H3 and H4 treatment rates, the As content in wheat and maize roots significantly increased compared with CK in the four growing seasons. The stem As the content of H1~H4 treatments in the 2016 and 2017 wheat seasons and H2~H4 treatments in the 2016 and 2017 maize seasons significantly increased compared with the CK. In the 2016 wheat and maize seasons, the grain As the

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Table 3. The concentration of arsenic (mg/kg) in tissues of wheat/maize in different harvest seasons

Tissue	Treatment	2016		2017	
		wheat season	maize season	wheat season	maize season
Root	CK	0.66 ± 0.03[c]	0.64 ± 0.03[c]	0.73 ± 0.09[c]	0.67 ± 0.05[c]
	H1	0.74 ± 0.02[c]	0.66 ± 0.03[c]	0.86 ± 0.01[c]	0.71 ± 0.02[c]
	H2	0.82 ± 0.05[c]	0.67 ± 0.02[c]	0.88 ± 0.06[c]	0.75 ± 0.01[bc]
	H3	1.09 ± 0.09[b]	0.83 ± 0.08[b]	1.24 ± 0.03[b]	0.92 ± 0.09[b]
	H4	1.29 ± 0.07[a]	1.05 ± 0.06[a]	1.42 ± 0.06[a]	1.17 ± 0.10[a]
Stem	CK	0.43 ± 0.02[d]	0.20 ± 0.003[d]	0.48 ± 0.08[d]	0.23 ± 0.01[d]
	H1	0.59 ± 0.07[c]	0.25 ± 0.01[d]	0.70 ± 0.04[c]	0.26 ± 0.02[d]
	H2	0.79 ± 0.05[b]	0.43 ± 0.02[c]	0.83 ± 0.04[bc]	0.45 ± 0.03[c]
	H3	0.86 ± 0.06[ab]	0.52 ± 0.01[b]	0.95 ± 0.03[ab]	0.54 ± 0.02[b]
	H4	0.99 ± 0.04[a]	0.60 ± 0.04[a]	1.05 ± 0.05[a]	0.63 ± 0.04[a]
Grain	CK	0.036 ± 0.002[c]	0.023 ± 0.002[c]	0.039 ± 0.003[d]	0.024 ± 0.002[d]
	H1	0.040 ± 0.001[bc]	0.025 ± 0.001[bc]	0.046 ± 0.003[ac]	0.029 ± 0.001[cd]
	H2	0.043 ± 0.002[ab]	0.03 ± 0.002[ab]	0.049 ± 0.002[bc]	0.034 ± 0.001[bc]
	H3	0.046 ± 0.0001[a]	0.032 ± 0.003[a]	0.056 ± 0.0003[ab]	0.040 ± 0.004[ab]
	H4	0.048 ± 0.001[a]	0.033 ± 0.002[a]	0.060 ± 0.0005[a]	0.045 ± 0.003[a]

Values are the mean ± standard deviation (n = 3). CK – sewage sludge mixed with soil at rates of 0 g/kg; H1 – sewage sludge mixed with soil at rates of 1.67 g/kg; H2 – sewage sludge mixed with soil at rates of 3.33 g/kg; H3 – sewage sludge mixed with soil at rates of 16.6 g/kg; H4 – sewage sludge mixed with soil at rates of 33.33 g/kg. The same tissues with different lowercase letters in the same column for the same growing season were significantly different between different treatments (P < 0.05)

content of H2, H3 and H4 treatment significantly increased compared with the CK. Accordingly, in the 2017 wheat and maize seasons, the grain As content was significantly higher than that of CK when the SS application occurred in the H1 and H2 treatment rates, respectively. Under the same SS dosage, the As content of maize roots, stems and grains in the same year was less than that of wheat.

BCF of As in various parts of crops. The SS addition effected the BCF of As in various parts of crops (Table 4). Compared with CK, the root BCF of wheat and maize of the H3 and H4 treatments increased by 25.42~80.70%, and at the same SS application rate, the As BCF of wheat roots was less than that of maize roots in the same year. The BCF of As by stem was significantly higher than that of CK when the SS dosage in the wheat and maize seasons occurred in the H1 and H2 treatment rates, respectively. The As BCF of wheat stems in the same year was lower than that of maize under the same SS application rate. When the amount of SS in the wheat and maize seasons occurred in H2, and H3 treatment rates, respectively, the BCF of As in grains was significantly higher than that of CK.

Relationship between the As BCF of crops and soil parameters. The soil's properties can affect As's bioavailability (Figure 1). The BCF decreased with increasing pH and significantly correlated with the As BCF of wheat and maize tissues. There was a significant correlation between wheat and maize soil OC and As BCF. Only the As BCF of wheat root stems and grains reached a significant correlation with CEC, respectively. The As BCF of wheat and maize decreased with increasing CC content. This is because a high CC content in calcareous soil easily forms calcium arsenate precipitation and reduces the absorption of As by crops. It significantly correlates with the As BCF of each part of wheat/maize.

Wheat/maize-specific As a model. The predictive results and accuracy of the model are summarised in Table 5. The correlation between measured and predicted values is reflected by a high determination coefficient (R^2) and an average error of low model efficiency. In all prediction models, there was a significant correlation between the measured and predicted values of As. Overall, the R^2 of the regression model significantly changed, but the ME value of the model did not. For example, these models

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Table 4. The bioconcentration factor of arsenic from soil to wheat and maize tissues

Tissue	Treatment	2016		2017	
		wheat season	maize season	wheat season	maize season
Root	CK	0.057 ± 0.003^{b}	0.059 ± 0.004^{c}	0.061 ± 0.006^{b}	0.059 ± 0.003^{c}
	H1	0.063 ± 0.001^{b}	0.060 ± 0.003^{bc}	0.069 ± 0.002^{b}	0.061 ± 0.001^{c}
	H2	0.069 ± 0.004^{b}	0.060 ± 0.002^{bc}	0.071 ± 0.002^{b}	0.064 ± 0.001^{bc}
	H3	0.090 ± 0.007^{a}	0.074 ± 0.008^{b}	0.096 ± 0.002^{a}	0.078 ± 0.007^{b}
	H4	0.103 ± 0.006^{a}	0.091 ± 0.005^{a}	0.106 ± 0.004^{a}	0.096 ± 0.008^{a}
Stem	CK	0.037 ± 0.002^{d}	0.018 ± 0.0003^{d}	0.040 ± 0.006^{d}	0.020 ± 0.002^{c}
	H1	0.050 ± 0.005^{c}	0.022 ± 0.0009^{d}	0.056 ± 0.002^{c}	0.022 ± 0.001^{c}
	H2	0.067 ± 0.004^{b}	0.039 ± 0.0022^{c}	0.067 ± 0.001^{bc}	0.038 ± 0.003^{b}
	H3	0.071 ± 0.005^{ab}	0.046 ± 0.0007^{b}	0.073 ± 0.002^{ab}	0.046 ± 0.002^{ab}
	H4	0.079 ± 0.003^{a}	0.053 ± 0.0035^{a}	0.078 ± 0.004^{a}	0.051 ± 0.004^{a}
Grain	CK	0.0031 ± 0.0002^{a}	0.0021 ± 0.0001^{a}	0.0033 ± 0.0002^{c}	0.0021 ± 0.0002^{d}
	H1	0.0034 ± 0.0002^{b}	0.0022 ± 0.0001^{a}	0.0038 ± 0.0001^{b}	0.0025 ± 0.0001^{cd}
	H2	0.0037 ± 0.0002^{c}	0.0027 ± 0.0002^{b}	0.0040 ± 0.0001^{b}	0.0029 ± 0.00010^{bc}
	H3	0.0038 ± 0.0001^{c}	0.0028 ± 0.0002^{b}	0.0043 ± 0.00002^{a}	0.0034 ± 0.0003^{ab}
	H4	0.0038 ± 0.0001^{c}	0.0029 ± 0.0001^{b}	0.0045 ± 0.00003^{a}	0.0037 ± 0.0003^{a}

Values are the mean ± standard deviation (n = 3). CK – sewage sludge mixed with soil at rates of 0 g/kg; H1 – sewage sludge mixed with soil at rates of 1.67 g/kg; H2 – sewage sludge mixed with soil at rates of 3.33 g/kg; H3 – sewage sludge mixed with soil at rates of 16.6 g/kg; H4 – sewage sludge mixed with soil at rates of and 33.33 g/kg. The same tissues with different lowercase letters in the same column for the same growing season were significantly different between different treatments (P < 0.05)

have high ME values (0.67~0.88), and the explanation of variation can reach 76~95%; simultaneously, the MNAE value is low and ranges from 0.25~0.51.

DISCUSSION

Soil properties are affecting As accumulation in crops. Previous studies have shown that pH, OC, CEC, CC, and other parameters are the main aspects affecting the accumulation of As in soils and crops (Eid et al. 2018). The addition of SS affects changes in pH, CEC, OC, CC and other parameters in the soil. Additionally, As availability in an alkaline environment is greater than in an acidic environment (Fitz and Wenzel 2002). In this study, the addition of SS led to a decrease in the soil pH value, but the BCF of As in crop grains decreased with increasing pH (7.2~8.0). This may be related to the high content of CC and other carbonates in high-pH calcareous soil, which easily forms insoluble As-Ca complexes ($CaHAsO_4$ and ($Ca_3(AsO_4)_2$) (Hartley et al. 2004). SS contains a large amount of OC, which can alter the properties of soil. However, there are different research conclusions regarding the effect of OC on As, including reports that OC can reduce the availability of As in soil (Bauer and Blodau 2006), OC improves the bioavailability of As (Tessema and Kosmus 2001), and there is no relationship with OC (Livesey and Huang 1981). In this study, the correlation coefficient between OC and the As BCF in wheat and maize was high, and with an increase in soil OC, the BCF of As in crop grains also increased. This may be because the polar groups in OC form chelates with complex structures and high availability of As, which increases As availability in soil (Khan et al. 2021). Furthermore, adding SS increased the content of fulvic acid (an unpublished result) because fulvic acid is acidic, which may lead to a decrease in the carbonate concentration in calcareous soil. Thus the carbonate-bound state of As would decrease, and the available state of As would increase. Soil CEC mainly affects the bioavailability of As from positive and negative aspects, and its impact is also related to crop species (Palansooriya et al. 2020). In this study, soil CEC played a positive role in the concentration of As in crops. However, compared with other parameters, CEC has a poor correlation with the As bioconcentration of maize.

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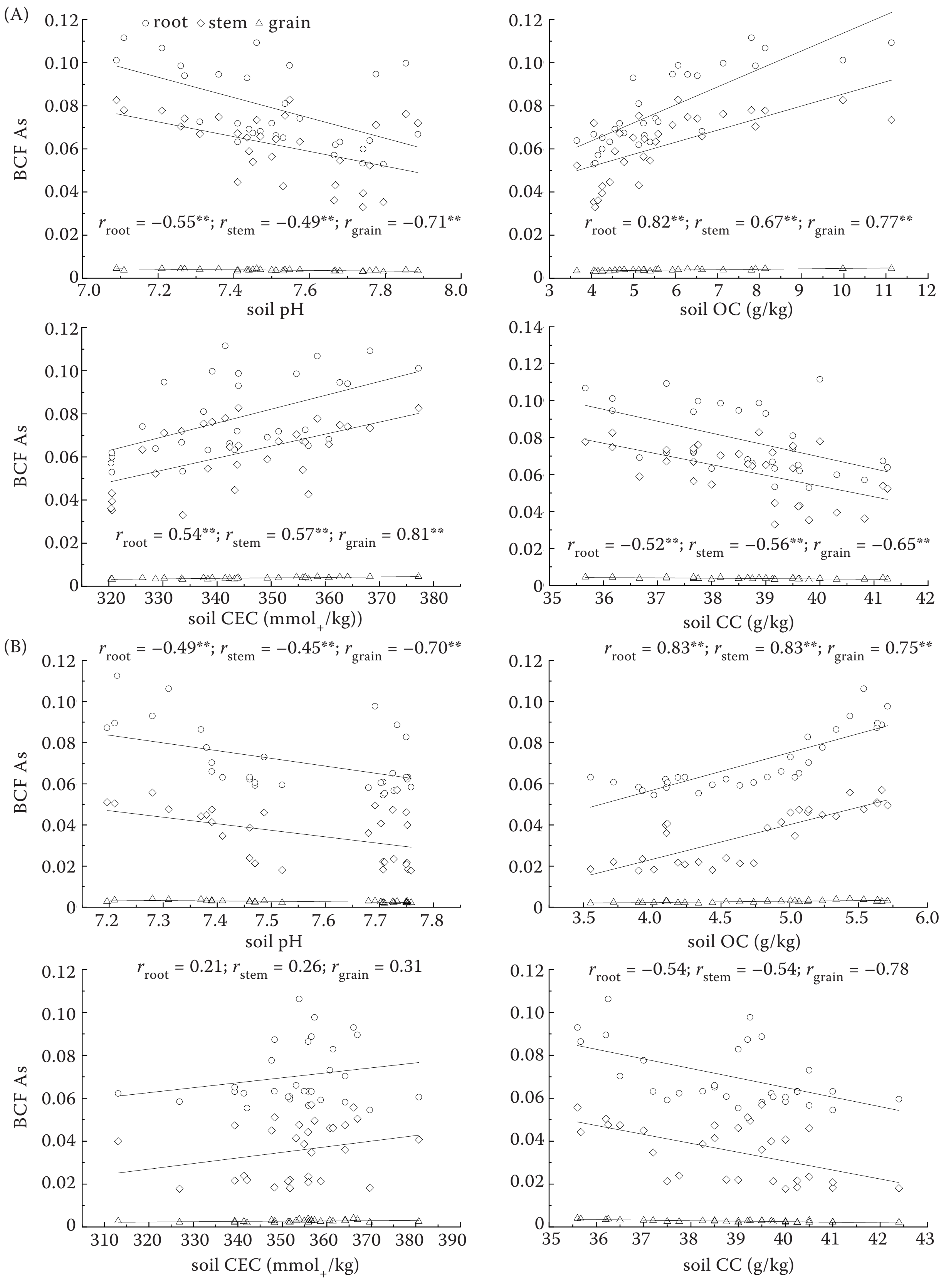

Figure 1. Linear relationship (*r*-value) between the bioconcentration factor (BCF) of arsenic (As) in (A) wheat and (B) maize tissues and soil parameters. OC – organic carbon; CEC – cation exchange capacity; CC – calcium carbonate; **indicates a significant correlation at the 0.01% level; *indicates a significant correlation at the 0.05% level

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Table 5. Regression models between the concentration of arsenic (As) in wheat/maize and soil As, pH, organic carbon (OC), calcium carbonate (CC) and cation exchange capacity (CEC) content

	Equation	R^2	ME	MNAE	Tukey's test	
					F_{value}	P
Wheat	As_{root} = 0.25 + 0.82 × As_{soil} – 0.32 × pH + 0.088 × OC – 0.035 × CC – 0.042 CEC	0.95	0.86	0.25	33.58	< 0.01
	As_{stem} = –0.056 + 0.57 × As_{soil} + 0.078 × pH + 0.050 × OC + 0.030 × CC + 0.43 CEC	0.86	0.75	0.40	11.16	< 0.01
	As_{grain} = 0.57 + 1.25 × As_{soil} – 0.45 × pH –0.36 × OC – 0.39 × CC + 0.014 CEC	0.79	0.68	0.51	6.92	< 0.01
Maize	As_{root} = –0.051 – 0.18 × As_{soil} + 0.070 × pH + 0.98 × OC – 0.030 × CC – 0.0048 CEC	0.85	067	0.40	10.25	< 0.01
	As_{stem} = 0.17 – 0.30 × As_{soil} + 0.027 × pH + 1.05 × OC – 0.21 × CC + 0.095 CEC	0.83	0.88	0.31	9.03	< 0.01
	As_{grain} = 0.38 + 0.34 × As_{soil} – 0.15 pH + 0.34 × OC – 0.14 × CC + 0.098 CEC	0.76	0.81	0.34	3.48	< 0.05

ME – model efficiency; MNAE – normalised mean error

Prediction model. A regression prediction model was established according to the main soil parameters, which can identify the main controlling factors and predict the concentration of As in crops. Therefore, choosing the appropriate model algorithm is especially important for successfully modelling data. When there are many variables or data, more complex models are needed to improve the fitting degree of the equation (Povak et al. 2014). In contrast, some models based on simple algorithms have lower data requirements and are more stable (Bi and Jeske 2010). The pot experiment is different from the spatial heterogeneity of field soil conditions. A linear regression algorithm is used to predict the concentration of heavy metals in plant crops (Römkens et al. 2011), and there is a significant linear relationship between dependent variables and independent variables (Liu et al. 2016). In this study, the generated prediction model has high prediction performance for As content in distinct parts of wheat/maize. At the same time, all parameters indicating the high performance of the model (R^2, ME, MNAE, F and P-values) were considered, and the selected soil factors (As concentration, pH, OC, CC, and CEC) had a certain effect on the As concentrations in wheat/maize tissues. Other researchers have reported that the above-related parameters impact the As absorption of crops (for example, Zeng et al. 2022). The prediction models for As absorption of wheat/maize used in this study are comparable or better than those for As absorption of many other crops. For example, in our study, the percentage of explanatory variability (R^2) of As was between 76% and 95% in each part of wheat/maize plants. Whereas Yang et al. (2018) found that the R^2 value of the As concentration prediction model in maize stalks after continuous sludge application was 69%.

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