Journal of the Serbian Chemical Society
JSCS-info@shd.org.rs • www.shd.org.rs/JSCS

J. Serb. Chem. Soc. 82 (7–8) 943–954 (2017)
JSCS–5014

UDC 549.73’755+544.723.2:504.53.054+
504.4.054
Original scientific paper

Arsenate and arsenite adsorption in relation with chemical properties of alluvial and loess soils

SHAH RUKH[1]*, MOHAMMAD SALEEM AKHTAR[1], AYAZ MEHMOOD[2], SAYED HASSAN[3], KHALID S. KHAN[1], SYED M. S. NAQVI[4] and MUHAMMAD IMRAN[1]

[1]Department of Soil Science & SWC, PMAS-Arid Agriculture University Rawalpindi-46000, Pakistan, [2]Department of Agricultural Sciences, University of Haripur, Haripur-22620, Pakistan, [3]Department of Crop and Soil Sciences, University of Georgia, Athens-30602, GA, USA and [4]Institute of Biochemistry and Biotechnology, PMAS-Arid Agriculture University Rawalpindi-46000, Pakistan

(Received 9 February, revised 18 March, accepted 20 March 2017)

Abstract: Arsenic is one of the most toxic elements in the soil environment. Understanding of the arsenic adsorption chemistry is essential for evolving the extent of soil and groundwater contaminations. This research was conducted to determine the variation in adsorption behaviour of arsenite and arsenate with depth in different lithology soils. We sampled two parent materials at genetic horizons, and within a parent material, we selected two soils. Besides basic soil characterizations, a laboratory batch experiments were carried out to study the adsorption of arsenate and arsenite. Freundlich adsorption approaches were employed to investigate the adsorption of arsenate and arsenite in the soils. Freundlich isotherms fit arsenate and arsenite sorption data well with r^2 values of 0.88–0.98 in most soils. Arsenate and arsenite adsorption varied with the soil properties, especially in clay composition and in the oxides of iron and aluminum. Arsenic adsorption parameters also varied with depth in parent materials, and loess derived soils had greater adsorption capacity as compared to alluvial soils in most of the adsorption parameters. This research concludes that the loess soils had higher arsenic adsorption capacity than the alluvial soils.

Keywords: arsenic species; parent material; Freundlich isotherm.

INTRODUCTION

Arsenic is one of the most toxic trace element present in soil and water. Naturally As occurs in rocks and mineral weathering and it can contaminate soil and groundwater.[1] Anthropogenic activities, including the application of agricultural pesticides, industrial waste and land filling of sewage sludge add As to soil and cause As mineral weathering. Mineralization of organic matter and cyclic oxid-

---

* Corresponding author. E-mail: shahrukhshah86@hotmail.com

https://doi.org/10.2298/JSC170209042R

ation–reduction release As in the soluble form into the soil immediately after addition.[2]

Arsenic forms a variety of inorganic and organic compounds in soils.[3] Inorganic As occurs dominantly as pentavalent arsenate (As(V)) and trivalent arsenite (As(III)). Arsenate species is predominant over As(III) and organic As and it may be up to 40 percent of total As content in contaminated soils.[4] The inorganic As phases are hundreds times more toxic than the organic phases; and among the inorganic As forms, As(III) are twenty five to sixty times more toxic than As(V).[5,6] Therefore, the correct estimation of As form in soil is important for understanding bioavailability of As and its effects on biota.[7]

The adsorption of As is probably initial on metal oxides especially iron oxides, *i.e.*, goethite, lepidocrocite and less crystalline ferrihydrite. A large portion of As becomes adsorbed on metal oxides and only a small portion remains in soil water.[8] The arsenic adsorption process controls the toxicity, fate, mobility and bioavailability of As in soils. Soil solution of As can be significantly different although the same amount of As exists in different soils due to its adsorption with the soil matrix. Therefore the understanding of the adsorption of As is important for predicting the As behaviour in the soil environments.[9]

Arsenic adsorption on clay, metal oxides of iron and aluminum and organic matter is the most common process for As solid phase formation generally.[10,11] It is reported that oxides and hydroxides of iron and aluminum are major constituents which controls As adsorption in soils.[12,13] Calcite possibly has a role in the retention and the solubility of arsenic in carbonate rich environment. Phosphate, organic matter and clay contents are the two important soil factors which significantly affect the adsorption of As in soils.[14,15]

Arsenate and As(III) adsorption studies used variety of adsorbents such as metal oxides, clays and soils. Studies was conducted on As(V) and As(III) adsorption by amorphous iron and aluminum oxides, as well as on clay minerals, *i.e.*, kaolinite and montmorillonite.[16] For the modeling of As(V) and As(III) adsorption the most widely used analytical isotherms are the Langmuir isotherm[17] and the Freundlich isotherm.[18] The studies on the arsenic adsorption in relation with lithology and development are scarce. We assumed that the adsorption behaviour of As(V) and As(III) may vary with the soil lithology and within a same lithology parent material, the soil development controls the arsenic forms adsorption. We sampled the two parent materials at genetic horizon level, and we selected two soils in each parent material. The objectives of the study were to evaluate the adsorption behaviour of As(V) and As(III) of different parent materials soils and the effect of soil properties on As(V) and As(III) adsorption.

EXPERIMENTAL

Soil sampling and characterization

Soils were taken from the Pothwar Plateau, having different parent material, and we selected alluvium and loess parent material for the present study. The GPS location and USDA taxonomy of selected soils is given in Table I. Triplicate profile for each soil was dug and soil samples were taken from each of the genetic horizon. Samples were air dried and crushed to pass through a 2-mm sieve.

TABLE I. Selected soils loess and alluvium parent materials

Soil	Location	USDA Classification	Parent material
Rawal	33°38'46.28''N and 73°04'57.82''E	Fine silty, mixed, hyperthermic Typic Hapludalfs	Alluvium
Kotli	33°37'11.13''N and 73°42'53.92''E	Fine, mixed, hyperthermic Entic Chromosterts	
Guliana	33°33'22.12''N and 72°38'30.82''E	Silty, mixed, thermic Udic Haplustalfs	Loess
Mansehra	34°24'56''N and 73°14'06''E	Fine loamy, mixed hyperthermic Typic Hapludalfs	

Each sample was analyzed for texture, pH, calcium carbonate, cation exchange capacity (*CEC*), $Na_2S_2O_4$-extractable Fe and Al and dissolved organic carbon (*DOC*). The soil particle size distribution was determined by the dispersion in $(NaPO_3)_6$ solution and the soil pH of saturated soil paste was measured. Soil $CaCO_3$ was determined by the acetic acid consumption.[19] The *DOC* was extracted with K_2SO_4 and determined by consumption of $K_2Cr_2O_7$.[20] Soil iron and aluminum oxides were dissolved in $Na_2S_2O_4$ and $C_6H_5Na_3O_7$ and $NaHCO_3$ buffer solution. The concentrations of Fe and Al in the extracts were measured by ICP-MS.[21] Cation exchange capacity was determined by saturating soil with an index cation.[22] Amorphous iron and aluminum were determined by extracting soil in acidified ammonium oxalate solution in dark.[23]

Batch experiment for arsenate and arsenite sorption

Sorption isotherms for As(V) and arsenite were constructed to estimate Fruendlich model parameters employing the batch sorption experiments.[24,25] In triplicate, 3.0 g of soil was equilibrated with 30 mL 0.01 M KNO_3 solutions containing graded concentration of As(V) 0, 0.1, 2.5, 5, 8, 10, 15, 20, 25, 40 and 100 mg L^{-1} (Na_2HAsO_4). The suspension was shaken for 48 h at room temperature and centrifuged for 20 min at 3000 rpm. The supernatant was filtered through 0.45 µm cellulose membrane and analyzed for total arsenic. Separately, three g soil was equilibrated with 30 ml of 0.01 M KNO_3 solution containing graded concentration of As(III) 0, 0.1, 0.5, 1, 3, 5, 7 and 8 mg L^{-1} from $NaAsO_2$. The suspension was shaken for 48 h at room temperature and centrifuged for 20 min at 3000 rpm. The cellulose membrane of 0.45 µm was used to filter the supernatant and total arsenic was analyzed in the extract. Sorbed amount of As(V) and As(III) was calculated from the change in the solution phase concentration.

The adsorption isotherm was fitted to the Freundlich equation:[26]

$$x / m = K_{\mathrm{f}} c_{\mathrm{w}}^{1/\beta} \tag{1}$$

where x/m is the equilibrium concentration adsorbed by the soil (mg kg^{-1}), c_w is the equilibrium concentration in solution (mg L^{-1}), β is an adsorption exponent related to adsorption intensity and K_f is the Fruendlich adsorption coefficient (L kg^{-1}).

Chemical analysis

Soil pH and pH change for $CaCO_3$ were determined by using Cole Parmer pH meter. For *CEC* analysis, NH_4^+ determination was carried out using shimadzu UV–Vis spectrophotometer. Elemental analysis of Fe, Al, and total arsenic were determined by using Perkin Elmer's ICP-MS.

Statistical analysis

The variety of the adsorption parameters were ascribed to the soil parent material at different depths. The multivariate analysis was implemented using Proc General Linear Model in SAS version 9.4 (SAS Institute Inc., 2014).[27] The parent material and soil (parent material) were class variable and the soil depths were multiple dependent variables. Stepwise multiple regression analysis was applied to correlate the adsorption parameters and the soil properties that determine adsorption of As(V) and As(III) in soils derived from loess and alluvium.

RESULTS AND DISCUSSION

Soil characteristics

Soils varied in chemical and physical characteristics which are important for As(V) and As(III) adsorption (Table II). The soils were dominantly silt loam. Overall, the alluvium derived Kotli soil had larger clay content, followed by the Guliana, Mansehra and Rawal soils. Clay leaching and accumulation caused by the soil development processes was observed in Bt horizon of all the soils except for the Kotli, developed in clayey parent material. Most soils were non-calcareous with lower *DOC*. Rawal soil under forest conditions showed higher *DOC* content. Dissolved organic carbon varied in most soils with higher contents in surface horizons and decreased with depth, in all the soils due to the accumulation of organic material at the surface horizons. Most of the soils were non-calcareous except for the Rawal soil which had $CaCO_3$ in the range of 35 to 100 g kg^{-1} and increased with depth. The similar values for $CaCO_3$ were reported earlier.[28] The *CEC* was in the range of 10 to 30 cmol+/kg. Higher *CEC* was observed in the Guliana soil with the increasing trend with depth and seemed to increase at Bt horizon level in all the soils. Amount of citrate bicarbonate dithionate extractable iron seems increased with depth in all the soils. Overall, the Guliana soil showed greater amount of Fe due to soil development process which results in the iron release from primary mineral. In the Rawal, Guliana and Mansehra soils high Fe content at Bt horizon was due to the translocation and the accumulation at Bt horizon level. Amount of citrate bicarbonate dithionate aluminum was greater in the loess derived soils, as compared to alluvium derived soils indicating the significant change in Al with the change in parent material.[29] Amount of citrate bicarbonate dithionate aluminum seems to be increased with the soil depth in all the soils. Loess derived Guliana and Mansehra were highly weathered soils, as supported by greater content of Fe and Al, compared to alluvium derived Rawal and Kotli soils. Oxalate-extractable iron also varied with parent material. The loess derived Guliana and Mansehra soils had higher concentration of Fe compared to the alluvial Rawal and the Kotli soils. High Fe content was observed in soils at relatively higher stage of development and accumulated in Bt horizon, whereas in the Rawal and Kotli soils higher Fe was observed in the surface horizons due to less leaching.[30] High amorphous iron contents in Mansehra soils may attribute to high rainfall which reduces the crystallinity while dry climate promote crystallinity.[31] Oxalate-extractable aluminum was higher in soils at higher stage of development since the weathering processes result in an increase in hydrolytic breakdown and release of iron and aluminum from the primary minerals. Oxalate-extractable aluminum content also increased with an increase in the depth. Overall iron and aluminum oxides were present in greater amount as a result of weathering in Guliana and Mansehra soils. Total As content varied between 3.4 to 6.92 mg kg^{-1} in most soil samples. In almost all the soils total As content increase with depth, which may indicate subsurface accumulation.

TABLE II. Chemical properties of studied soils; *CEC*, cation exchange capacity; *DOC*, dissolved organic carbon; Fe_d, Al_d, dithionate extractable Fe and Al; Fe_o, Al_o, oxalate-extractable Fe and Al; mean of $n = 3$; standard deviation in the parentheses

Horizon	Depth, cm	pH	Clay, g kg^{-1}	$CaCO_3$, g kg^{-1}	CEC, cmol+/kg	DOC, mg kg^{-1}	Fe_d	Al_d	Fe_o	Al_o	Total As, mg kg^{-1}
							g kg^{-1}				
Rawal: Fine silty, mixed, hyperthermic, Typic Hapludalfs											
A	0–10	7.05	190	$34_{(5.27)}$	$9_{(0.60)}$	$300_{(1.23)}$	$5.0_{(0.33)}$	$1.3_{(0.08)}$	$0.10_{(0.02)}$	$0.62_{(0.02)}$	$3.52_{(0.05)}$
Bw	10–18	7.35	215	$35_{(3.50)}$	$12_{(2.37)}$	$170_{(0.40)}$	$6.6_{(0.40)}$	$1.7_{(0.10)}$	$0.09_{(0.04)}$	$0.82_{(0.07)}$	$3.40_{(0.10)}$
Bt	18–30	7.57	265	$53_{(6.57)}$	$14_{(1.19)}$	$180_{(0.55)}$	$9.4_{(0.33)}$	$2.5_{(0.10)}$	$0.09_{(0.00)}$	$1.06_{(0.01)}$	$3.57_{(0.13)}$
Bk	30–46	7.63	215	$102_{(24.7)}$	$10_{(1.45)}$	$160_{(0.41)}$	$8.8_{(0.38)}$	$2.3_{(0.06)}$	$0.03_{(0.02)}$	$0.83_{(0.04)}$	$3.97_{(0.07)}$
Kotli: Fine, mixed, hyperthermic Entic Chromostert											
Ap	0–10	7.93	345	$5.9_{(0.30)}$	$17_{(0.24)}$	$150_{(0.78)}$	$4.9_{(0.05)}$	$1.4_{(0.02)}$	$0.40_{(0.12)}$	$0.69_{(0.04)}$	$4.17_{(0.09)}$
Bw	10–18	8.40	345	$7.3_{(0.32)}$	$16_{(2.46)}$	$113_{(0.10)}$	$5.8_{(0.29)}$	$1.6_{(0.06)}$	$0.51_{(0.02)}$	$0.67_{(0.04)}$	$3.75_{(0.20)}$
C	18+	8.20	445	$5.6_{(0.24)}$	$18_{(0.10)}$	$46_{(0.36)}$	$8.7_{(0.10)}$	$2.6_{(0.02)}$	$0.24_{(0.04)}$	$0.79_{(0.05)}$	$4.43_{(0.35)}$
Guliana: Silty, mixed, thermic Udic Haplustalfs											
Ap	0–10	7.70	210	$7.8_{(0.45)}$	$26_{(0.65)}$	$75_{(0.24)}$	$8.0_{(0.41)}$	$2.4_{(0.07)}$	$0.21_{(0.02)}$	$0.91_{(0.02)}$	$5.21_{(0.04)}$
Bw	1–20	7.37	210	$7.8_{(0.70)}$	$18_{(0.85)}$	$70_{(0.48)}$	$7.7_{(0.40)}$	$2.4_{(0.10)}$	$0.22_{(0.05)}$	$0.96_{(0.05)}$	$5.48_{(0.18)}$
Bt1	20–30	7.48	295	$6.4_{(1.05)}$	$30_{(0.14)}$	$60_{(0.08)}$	$9.7_{(0.23)}$	$3.3_{(0.06)}$	$0.31_{(0.01)}$	$1.25_{(0.04)}$	$6.92_{(0.07)}$
Bt2	30–50	7.50	320	$6.1_{(1.35)}$	$26_{(1.46)}$	$60_{(0.67)}$	$9.3_{(0.38)}$	$3.5_{(0.15)}$	$0.27_{(0.01)}$	$1.39_{(0.10)}$	$6.66_{(0.08)}$
Mansehra: Fine loamy, mixed hyperthermic Typic Hapludalfs											
Ap	0–20	7.00	200	$5.6_{(1.18)}$	$17_{(0.60)}$	$110_{(0.40)}$	$7.2_{(0.80)}$	$2.0_{(0.62)}$	$0.53_{(0.03)}$	$0.91_{(0.03)}$	$3.87_{(0.10)}$
Bw	20–40	7.10	200	$5.2_{(0.74)}$	$13_{(0.60)}$	$88_{(0.21)}$	$5.8_{(0.29)}$	$2.5_{(0.07)}$	$0.56_{(0.04)}$	$0.43_{(0.03)}$	$3.50_{(0.05)}$
Bt	40–70	7.08	310	$6.2_{(0.17)}$	$22_{(0.08)}$	$66_{(0.75)}$	$8.7_{(0.10)}$	$4.0_{(0.10)}$	$0.69_{(0.04)}$	$1.48_{(0.06)}$	$4.73_{(0.21)}$

Arsenate and arsenite sorption isotherm

The isotherms for As(V) and As(III) sorption depict variation in the shape of isotherms with the diversity in soil characteristics (Fig. 1). Overall, As(V) adsorption was greater than As(III). Both As(V) and As(III) had fast rise in sorption, with a small increase in concentration in equilibrium solution. Several scientists reported a fast sorption initially and a moderate increase at the later part of the isotherm.[9,18] Maximum sorption increase for As(V) was less than 150 mg kg^{-1}. The Bt horizons, especially in the case of the Mansehra and the Guliana soils, had faster adsorption rise compared to Ap and Bw horizons. In case of As(III), where the concentration maxima was ≈ 30 mg kg^{-1} generally, had greater rise in the adsorbed concentration in case of Bt horizons of all the soils. It appears that the clay content had a stronger role in the adsorption of both As(V) and As(III). Several studies indicated a strong correlation of clay content with the adsorption of As(V) and As(III).[32,33]

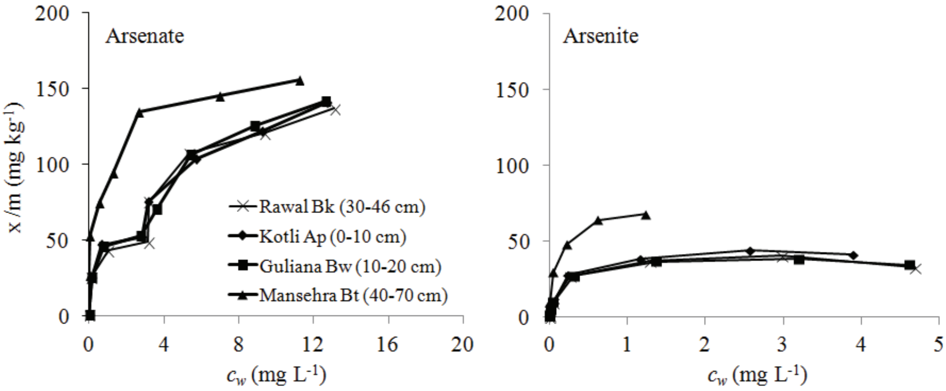

Fig. 1. Adsorption isotherms for arsenate and arsenite constructed between adsorbed concentrations at ordinate and solution concentration at abscissa in, indicating a fast initial rise especially in case of Bt horizon and the Bk horizon of Rawal had noteable low in adsorption.

Freundlich equation sorption parameters

Freundlich equation (Eq. (1)) fit the isotherms with most of the $r^2 > 0.95$ (Fig. 2). Adsorption of As(V) and As(III) in these soils was well fitted by the Freundlich isotherm model.[34] The maximum average adsorption intensity of As(III) (β) was lower than the adsorption intensity of As(V) in most soils, while the adsorption capacity (K_f) was greater for As(V) than As(III). It appears that As(V) had higher adsorption capacity than As(III), but with lesser binding intensity than most soils. The distribution of β and K_f for As(V) and As(III) remained similar to the soil depth in both of the parent materials (Fig. 3), as the hypothesis of nonsignificant depth–PM interaction was accepted through MANOVA test criteria. Fruendlich adsorption parameters increased with soil depth in loess and alluvium. The loess derived soils had higher adsorption parameters (β and K_f) than alluvial soils at all soil depths. Variation in β and K_f of As(V) and As(III) with the soil depth in each parent material was also remained similar (Table III).

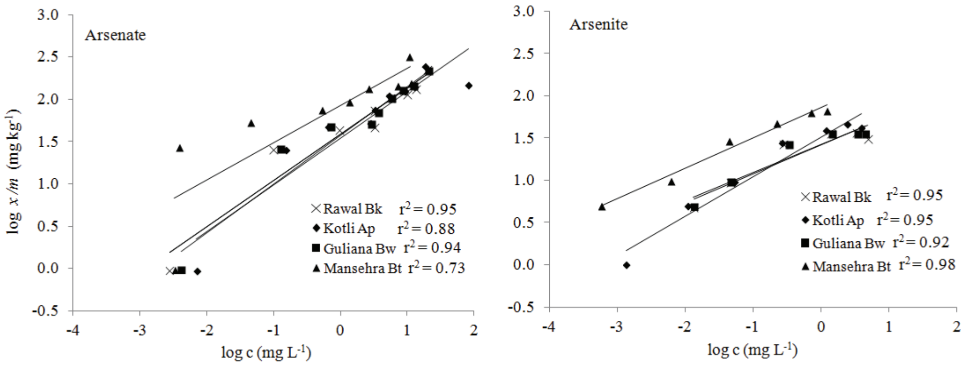

Fig. 2. Freundlich equation (Eq. (1)) fit for arsenate and arsenite isotherms in the selected soil horizons. Arsenate and arsenite adsorption parameters were calculated from the trendline.

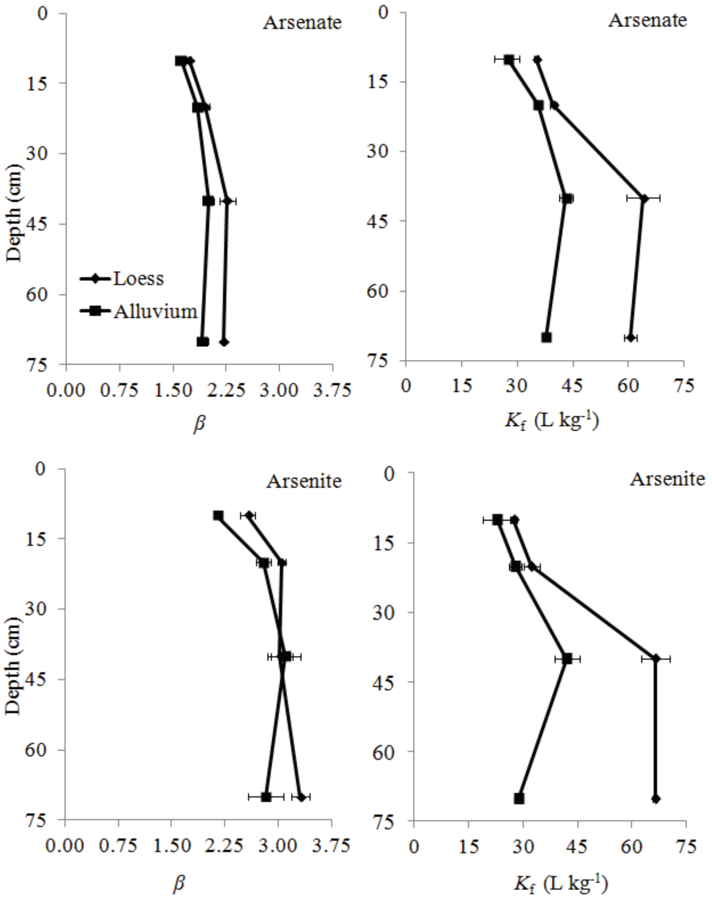

Fig. 3. Distribution of adsorption parameters (β and K_f) of arsenate and arsenite in each parent material (mean = 6, and bars show standard error).

TABLE III. Fitted Freundlich sorption model parameters for arsenate and arsenite of each soil; adsorption intensity, β, and maximum adsorption capacity, K_f, both in L kg^{-1}, were calculated from the respective regression equation. Values in parentheses are standard deviations

Horizon	Arsenate		Arsenite	
	β	K_f	β	K_f
Rawal: Fine silty, mixed, hyperthermic, Typic Hapludalfs				
A	$1.43_{(0.06)}$	$19_{(0.34)}$	$2.20_{(0.02)}$	$13_{(0.36)}$
Bw	$1.88_{(0.01)}$	$35_{(0.55)}$	$2.93_{(0.14)}$	$24_{(0.70)}$
Bt	$1.82_{(0.02)}$	$40_{(0.62)}$	$2.77_{(0.35)}$	$34_{(0.80)}$
Bk	$1.91_{(0.08)}$	$38_{(0.76)}$	$2.82_{(0.25)}$	$29_{(0.10)}$
Kotli: Fine, mixed, hyperthermic Entic Chromosterts				
Ap	$1.80_{(0.06)}$	$35_{(1.40)}$	$2.07_{(0.04)}$	$32_{(0.18)}$
Bw	$1.81_{(0.01)}$	$36_{(0.45)}$	$2.65_{(0.14)}$	$32_{(0.29)}$
C	$2.18_{(0.05)}$	$47_{(1.20)}$	$3.43_{(0.21)}$	$50_{(1.68)}$
Guliana: Silty, mixed, thermic Udic Haplustalfs				
Ap	$1.73_{(0.03)}$	$34_{(0.59)}$	$2.74_{(0.18)}$	$27_{(2.29)}$
Bw	$1.90_{(0.11)}$	$37_{(0.85)}$	$2.98_{(0.04)}$	$27_{(0.42)}$
Bt1	$2.03_{(0.11)}$	$53_{(0.50)}$	$3.43_{(0.10)}$	$57_{(0.58)}$
Bt2	$2.22_{(0.02)}$	$61_{(1.61)}$	$3.31_{(0.13)}$	$66_{(0.61)}$
Mansehra: Fine loamy, mixed hyperthermic Typic Hapludalfs				
Ap	$1.74_{(0.013)}$	$36_{(0.24)}$	$2.40_{(0.02)}$	$27_{(0.20)}$
Bw	$2.01_{(0.031)}$	$42_{(0.38)}$	$3.11_{(0.12)}$	$37_{(0.85)}$
Bt	$2.50_{(0.05)}$	$75_{(1.96)}$	$2.61_{(0.14)}$	$76_{(1.80)}$

The adsorption intensity ranged from 1.45 to 2.50 and K_f of As(V) ranged from 19 to 75 L kg^{-1} and. These results are in line with the findings of Roy *et al.*,[35] Payne and Abdel-Fattah[36] and Zeng *et al.*[37] Arsenate β increased with depth in all the soils with the increase in clay content (r 0.48). As β is the intensity of adsorption, it is related to the abundance of metal oxides. It was evidenced that As(V) had high affinity for metal oxides from positive correlation of β with Fe_d (r 0.77), Al_d (r 0.80), Fe_o (r 0.42) and Al_o (r 0.71). Similarly, K_f, increased with depth with increase in clay content as evidenced by the positive correlation with clay (r 0.46). The CEC is largely related to clay content[38] because there are more exchange sites for adsorption, so that As(V) K_f values positively correlated with *CEC* (r 0.59). The K_f had showed strong relation with iron (Fe_d (r 0.83) and Fe_o (r 0.50)) and aluminum (Al_d (r 0.89) and Al_o (r 0.87)) oxides as the increase in As(V) K_f and in the metal oxides with increase in soil depth. Several studies reported the role or iron and aluminum oxides in the As(V) adsorption.[13,18] Overall, As(V) β and K_f were increased linearly with the increase in metal oxide contents. Loess derived Guliana and Mansehra soils, which are more weathered soils, had greater amount of clay in Bt horizons and ultimately higher iron and aluminum oxides, resulted in greater adsorption of As(V) when compared to alluvium derived Rawal and Kotli soils. The adsorption intensity, β, ranged from

2.07 to 3.43 and K_f ranged from 13 to 76 L kg^{-1}. The adsorption parameters vary widely with the change in soil properties especially due to the differences in iron oxides.[39] The β values showed non-significant relation with the metal oxides indicating the weak binding of As(III) on the metal oxide surfaces. However, As(III) β was positively related with clay content (r 0.38) and CEC (r 0.36). The adsorption capacity of As(III) was higher in weathered horizons of the Guliana and the Mansehra soils while β values are greater in Bw/Bt horizons of all the soils compared to remaining horizons. The K_f for As(III) increased with depth in all the soils except for the Kotli soil. Similar values for K_f of As(III) were observed by Elkhatib *et al.*[39] in loamy soils. Arsenite K_f showed similar behaviour as As(V) in the positive correlation with Fe_d (r 0.77), Al_d (r 0.87), Fe_o (r 0.46) and Al_o (r 0.82). The Bt horizons of the Guliana and the Mansehra soil had higher K_f values due to the higher clay and metal oxides content.

Prediction of adsorption parameters

We selected the soil properties (independent parameters) by the stepwise regression maximizing r^2 and predicted the adsorption parameters of As(V) and As(III) obtained from the fitting of the isotherm to the Fruendlich equation. Soil was included as an independent parameter. Intercept differed with the soil type in case r^2 improves significantly, due to the addition of a soil type as a variable. The multiple regression equations have more significance in the understanding of processes rather than as predictive tools. The regression equations for As(V) and As(III) adsorption parameters are given in the Table IV. It is apparent that β for As(V) is positively related with Al_d while negatively correlated with CEC, $CaCO_3$, which confirms the observation of Raven *et al.*[18] that the adsorption intensity was more related to metal oxides. Freundlich coefficient related to the adsorption capacity K_f in all soils was more related to Fe_o and Al_o as compared to Fe_d and Al_d.[40] However, β for As(III) is suppressed by aluminum oxides (Al_d and Al_o) whereas it is increased in the presence of iron oxides and *CEC* related to clay content.[38] The regression equation for As(III) K_f showed that the adsorption capacity of As(III) increases with the increase in Al_d, whereas it was suppressed by the increase in $CaCO_3$ and *CEC*.

TABLE IV. Regression equations for different properties estimate for each adsorption parameter

Arsenic form	Regression equations	r^2
Arsenate	$\beta = 3.63 + 12.24Al_d - 89.92CEC - 7.76CaCO_3 - 0.26Clay$	0.82
	$K_f = 236.33 + 17.80Fe_o - 72.44Al_o$	0.15
Arsenite	$\beta = 1.10 + 0.0055Fe_o - 0.052Al_o - 0.021Al_d + 0.23CEC$	0.57
	$K_f = 21.77 + 8.66Al_d - 66.50CEC - 5.21CaCO_3 - 0.22Clay$	0.82

CONCLUSIONS

From our results, it can be concluded that As(V) adsorption was greater than As(III) in all the soils and varied with the soil properties, among which clay content and iron and aluminum oxides exhibited the most important influence on As(V) and As(III) adsorption. Freundlich isotherms fit As(V) and As(III) sorption data well with r^2 values of 0.88–0.98 in most soils. Loess soils had higher adsorption capacity than alluvial soils. Metal oxides and clay contents are the major predictor for As(V) and As(III) adsorption parameters. This study may help to understand the soil and groundwater contamination phenomena.

Acknowledgment. The authors thank the Higher Education Commission of Pakistan for financial assistance.

ИЗВОД

УТИЦАЈ ХЕМИЈСКИХ СВОЈСТАВА ЛЕСНИХ И АЛУВИЈАЛНИХ ЗЕМЉИШНИХ НАСЛАГА НА АДСОРПЦИЈУ АРСЕНАТА И АРСЕНИТА

SHAH RUKH[1], MOHAMMAD SALEEM AKHTAR[1], AYAZ MEHMOOD[2], SAYED HASSAN[3], KHALID S. KHAN[1],
SYED M. S. NAQVI[4] и MUHAMMAD IMRAN[1]

[1]*Department of Soil Science & SWC, PMAS-Arid Agriculture University Rawalpindi-46000, Pakistan,* [2]*Department of Agricultural Sciences, University of Haripur, Haripur-22620, Pakistan,* [3]*Department of Crop and Soil Sciences, University of Georgia, Athens-30602, GA, USA и* [4]*Institute of Biochemistry and Biotechnology, PMAS-Arid Agriculture University Rawalpindi-46000, Pakistan*

Арсен је један од најтоксичнијих загађивача земљишта. Познавање адсорпционе хемије арсена је суштински важно за одређивање степена загађења земљишта и подземних вода. Представљена су истраживања помоћу којих је одређена промена адсорпционог понашања арсената и арсенита са литосферном дубином. Узоркована су два матична материјала кроз различите типове земљишних наслага, а у оквиру та два одабрана су по два узорка земљишта. Уз серијско лабораторијско испитивање адсорпције арсената и арсенита, урађена је и основна карактеризација земљишта. Примењен је Фројндлихов приступ анализи адсорпционих процеса. Фројндлихова изотерма задовољавајуће описује сорпционе податке за арсенат и арсенит, са r^2 вредностима у опсегу 0,88–0,98 за већину узорака земљишта. Адсорпциони параметри зависе од својстава земљишта, посебно од садржаја глине и оксида гвожђа и алуминијума. Ови параметри су се мењали и у зависности од дубине слоја у оквиру матичног материјала, и закључено је да лесно-засnована земљишта поседују већи адсорпциони капацитет од алувијалних.

(Примљено 9. фебруара, ревидирано 18. марта, прихваћено 20. марта 2017)

REFERENCES

1. H. Garelick, H. Jones, A. Dybowska, E. Valsami-Jones, *Rev. Environ. Contam. Toxicol*. **197** (2008) 17
2. E. Moreno-Jiménez, J. M. Peñalosa, E. Esteban, M. P. Bernal, *J. Environ. Monit*. **11** (2009) 1375
3. G. T. Vaughan, *The environmental chemistry and fate of arsenical pesticides in cattle dip sites and banana plantations*, CSIRO Division of Coal Industry, Center for Advanced Analytical Chemistry, NSW, Melbourne, 1993, p. 123

4. A. Giacomino, M. Malandrino, O. Abollino, M. Velayutham, T. Chinnathangavel, E. Mentasti, *Environ. Pollut*. **158** (2009) 416
5. X. C. Le, X. Lu, M. Ma, W. R. Cullen, V. Aposhian, B. Zheng, *Anal. Chem*. **72** (2000) 5172
6. C. K. Jain, I. Ali, *Wat. Res.* **34** (2000) 4304
7. C. J. Ng, N. Barry, S. Bruce, H. Crawley, M. R. Moore, in *Proceedings of the Fifth National Workshop on the Assessment of Site Contamination*, Australia, EPHC, Adelaide, 2003, p. 163
8. P. O'Neill, in *Heavy metals in soil*, B. J. Alloway, Ed., 2nd ed., Blackie academic and professional, London, 1995, p. 105
9. H. Zhang, H. M. Selim, *Environ. Sci. Technol*. **39** (2005) 6101
10. M. Sadiq. *Water, Air Soil Pollut*. **93** (1997) 117
11. V. Matera, I. L. Hecho, A. Laboudigue, P. Thomas, S. Tellier, M. A. Astruc, *Environ. Pollut*. **12** (2003) 51
12. B. J. Lafferty, R. H. Loeppert, *Environ. Sci. Technol*. **39** (2005) 2120
13. H. J. Shipley, S. J. Yean, A.T. Kan, M. B. Tomson, *Environ. Toxicol. Chem*. **28** (2009) 509
14. A. Mehmood, R. Hayat, M. Wasim, M. S. Akhter, *J. Agri. Biol. Sci*. **1** (2009) 59
15. J. Alvarez-Benedi, S. Bolado, I. Cancillo, C. Calvo, D. Garcia-Sinovas, *Vadose Zone J.* **4** (2005) 282
16. S. Goldberg, *Soil Sci. Soc. Am. J*. **66** (2002) 413
17. S. Kundu, A. K. Gupta, *Chem. Eng. J*. **122** (2006) 93
18. K. Raven, A. Jain, R. Loeppert, *Environ. Sci. Technol.* **32** (1998) 344
19. R. H. Leoppert, C. T. Hallmark, M. M. Koshy, *Soil Sci. Soc. Am. J*. **48** (1984) 1030
20. D. W. Nelson, L. E. Sommers, in *Methods of Soil Analysis. Part 2. Chemical and microbiological properties*, A. L. Page, R. H. Miller, D. R. Keeney, Eds., ASA, Madison, WI, 1982, p. 574
21. O. P. Mehra, M. L. Jackson, *Clay Mineral* **7** (1960) 317
22. H. D. Chapmen, in *Methods of Soil Analysis. Part 2. Chemical and microbiological properties*, C. A. Black,Ed., ASA, Madison, WI, 1965, p. 891
23. M. L. Jackson, C. H. Lim, L. W. Zelazny, in *Methods of Soil Analysis. Part 1*, A. Klute, Ed., ASA, Madison, USA, 1986, p. 101
24. C. L. Castro, D. L. Rolston, *Soil Sci. Soc. Am. J*. **41** (1977) 1085
25. J. K. Syers, R. F. Harris, D. E. Armstrong, *J. Environ. Qual*. **2** (1973) 1
26. H. Freundlich, *Kapillarchemie. eine Darstellung der Chemie der Kolloide und verwandter Gebiete,* Akademische Verlagsgellschaft, Leipzig, 1909
27. SAS Institute Inc. 2003. SAS Version 9. Cary (NC): SAS Institute Inc.
28. R. Amin, M. Ikram, *Keys to Soils of Punjab and Sindh*. Soil Survey of Pakistan, Multan Road, Lahore, 2007
29. A. Mehmood, *PhD Thesis*, PMAS-Arid Agriculture University, Rawalpindi, 2014
30. H. Jenny, *Factors of Soil Formation*, McGraw-Hill, New York, 1941
31. A. Mehmood, M. S. Akhtar, R. Hayat, M. Memon, *J. Chem. Soc. Pak*. **32** (2010) 129
32. N. Ghorbanzadeh, W. Jung, A. Halajnia, A. Lakzian, A. N. Kabra, B. Jeon, *Geosystem Eng*., DOI: 10.1080/12269328.2015.1062436
33. Wu, P., W. Wu, S. Li, N. Xing, N. Zhu, P. Li and Z. Dang, *J. Haz. Mat*. **169** (2009) 824
34. Q. Feng, Z. Zhang, Y. Chen, L. Liu, Z. Zhengjie, C. Chen, *Procedia Env. Sci*. **18** (2013) 26
35. W. R. Roy, J. J. Hassett, R. A. Griffin, *Soil Sci. Soc. Am. J*. **50** (1986) 1176
36. K. B. Payne, T. M. Abdel-Fattah. *J. Environ. Sci. Health* **40** (2005) 723
37. X. Zeng, P. Wu, S. Su, L. Bai, Q. Feng, *Plant Soil Environ*. **58** (2012) 405

38. H. L. Bohn, B. L. McNeal, G. A. O'Connor, *Soil Chemistry*, 2nd ed., John Wiley & Sons, New York, 1985
39. E. A. Elkhatib, O. L. Bennett, R. J. Wright, *Soil Sci. Soc. Am. J.* **48** (1984) 1025
40. W. Jiang, S. Zhang, X. Shan, M. Feng, Y. Zhu, R. McLaren, *Environ. Pollut*. **138 (**2005) 278.