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Boron and zinc sorption and transport in calcareous soils

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Abstract

Boron (B) and zinc (Zn) are essential plant-micronutrients recommended for field application where leaching losses can be significant and cause economic losses as well as contamination of shallow groundwater. Boron and Zn sorption and transport was studied using two calcareous soils, i.e. Lyallpur (clay loam) and Sultanpur (loam). Boron and Zn sorption isotherms were constructed and data was fitted to Langmuir adsorption model. In addition, B and Zn transport experiment was carried out using intact soil columns (8.4 cm dia and 28 cm length) to determine the relative characteristics of breakthrough curve and the transport parameters. The Lyallpur had slightly greater adsorption partition coefficient (kd) both for B (1.17 vs. 1.10) and Zn (21 vs. 18) than the Sultanpur. In the Lyallpur columns, B arrival was immediate but the peak concentration lower than the Sultanpur. The breakthrough of B in Sultanpur occurred after about 10 cm of cumulative drainage in both the columns, the rise in effluent concentration was fast and the peak concentration was almost one. Zinc leaching through the soil columns was very limited as only one column from Lyallpur showed Zn breakthrough in the effluent where the peak concentration ratio was only 0.05. The study demonstrates effect of soil structure on B transport and has implications for the nutrient management in field soils.

Keywords: Zinc, Boron, sorption, transport, calcareous soils.

Introduction

Numerous studies have shown that water and solutes often travel rapidly through small fractions of the total pore volume of the soil having macropores and bypass much of the matrix (Radulovich *et al.*, 1992). Simulation models used for predicting water and solute movement often fail to predict arrival time accurately (Steenhuis *et al.*, 1994; Hatfield *et al.*, 1997; Wildenschild *et al.*, 1994; Vervoort *et al.*, 1999). Boron in soil and water poses ecological and environmental problems and, in case by-pass flow is significant, loss of agricultural productivity can also occur. Kang et al (2002) ascribed B deficiency to cabbage to leaching in humid areas. Therefore, the research area merits further work.

The preferential pathways are small fraction of total porosity through which solutes travel rapidly by passing the soil matrix (Radanovich *et al.*, 1992), causing a rapid and accelerated breakthrough of both adsorbing and non-adsorbing solutes (Butcher *et al.*, 1995; Gaber *et al.*, 1995; Gupta *et al.*, 1999). Accurate estimation of solute velocities in soil profile is essential for the prediction of subsoil and groundwater contamination. Solute parameters transport can only be predicted accurately once breakthrough over a range of flow rates are known partly because the matrix (intra-aggregate porosity) has different hydraulic properties than the preferential flow paths (inter-aggregate porosity) (Mahmood-ul-Hassan, 1998).

Studies on B transport are limited in calcareous soils. Boron adsorption is considered to be reversible but the use of models based on the assumption of local equilibrium often provides poor descriptions of B transport in soil columns. Also, B transport is strongly related to the soil pH (Communar and Keren, 2005). It appears that soil pH and occurrence of macropores are two important characteristics controlling leaching of B. Similarly, leaching of Zn which affects its distribution soil fractions and availability to plants depends on soil physical properties (Alvarez *et al.*, 2001; Voegelin *et al.*, 2003).

Adsorption coefficient (kd) by batch technique helps explain the results of leaching studies and, given pore water velocity, leaching experiments can also yield kd (Schweich *et al.*, 1983; Bond and Phillips, 1990a; Barnett *et al.*, 2000). The batch experiment has disadvantages of breakdown of soil aggregates during sample

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agitation, the soil/solution ratio being relatively small, and there are differences in mass-transfer and hydrodynamic conditions; which cumulatively result in inappropriate estimates of the degree of adsorption (Schweich *et al.*, 1983). The column technique however, overcomes some of these limitations where solution of CDE help obtain kd by fitting BTC but the disadvantage of the column technique is the absence of an accurate solution for a nonlinear CDE with equilibrium adsorption (Veldhuizen *et al.*, 1995). The disadvantage of column study can be partly overcome by application of semi-analytical solutions of a nonlinear transport CDE (Bond and Phillips, 1990b).

Boron application is widely recommended for to field crops (Rashid *et al.*, 2002) but little information is available on B adsorption and transport in calcareous soils. As a part of a bigger study on leaching fertilizer nutrients, objectives of this experiment were to determine whether preferential flow of B and Zn actually does occur in these calcareous soils and to determine the transport parameters for these fertilizer nutrients.

The Langmuir Equation

The adsorption isotherms are fitted to the Langmuir equation (Castro and Rolston, 1977), which has the form:

$$X = \frac{bKCw}{1 + KCw} \qquad [1]$$

or rearranged in linear form

$$\frac{Cw}{X} = \frac{1}{Kb} + \frac{Cw}{b} \qquad [2]$$

where X is sorption by soil (mg kg^{-1}), C_w is concentration in solution at equilibrium (mg L^{-1}), K is the constant related to binding strength (when C = 1/K then X = b/2 or half of the sites on the soil are filled with adsorbate) (L mg^{-1}), and b is maximum sorption on the soil (mg kg^{-1}).

Tangent to the Langmuir isotherm at application concentration gives adsorption partition coefficient, kd (Akhtar *et al.*, 2003). Differentiating Eq. [1] with respect to C_w gives:

$$\frac{\partial x}{\partial Cw} = \left[\left(\frac{1}{1 + KCw} \right) + \left\{ bk - \left(\frac{bK^2Cw}{(1 + KCw)^2} \right) \right\} \right] \qquad [3]$$

or:

$$kd = \left[\left(\frac{1}{1 + KCw} \right) + \left\{ bk - \left(\frac{bK^2Cw}{(1 + KCw)^2} \right) \right\} \right] \qquad [4]$$

Convective Dispersive Equation (CDE)

The CDE model for one-dimensional transport of reactive solutes subject to adsorption in one or two domains has been solved for several boundary conditions given in Parker and van Genuchten (1984) and other textbooks:

$$\mathrm{R}\,\frac{\partial \mathrm{C}}{\partial \mathrm{t}} = \mathrm{D}\,\frac{\partial^2 \mathrm{C}}{\partial \mathrm{x}^2} - \mathrm{v}\,\frac{\partial \mathrm{C}}{\partial \mathrm{x}} \qquad [5]$$

where R is retardation factor for adsorbing solute, D is dispersion coefficient (L^2/t), *v* is velocity of the solute and equals $q/(\beta(\rho k_d + \theta)$ where β is mobile water fraction (Parker and van Genuchten, 1984). In order to solve the differential equation a constant adsorption partition coefficient is employed, resulting in solutions in which the movement of solutes can be scaled with a retardation coefficient of the form (Toride *et al.*, 1995):

$$R = 1 + \frac{\rho k_d}{\theta_s} \qquad [6]$$

where ρ is bulk density Mg m^{-3} and Θs is total porosity (m m^{-1}).

Material and methods

A leaching study on B and Zn was carried out at Institute of Natural Resources and Environmental Sciences, National Agricultural Research Center, Islamabad using intact columns from two calcareous soils. Solutes containing $ZnSO_4$ and H_3BO_3 were applied with 0.01 M $CaCl_2$ at constant flow rate under 20 mm water head. In addition, B and Zn adsorption isotherms were developed by batch experiment and the flow paths were marked by blue dye to explain the breakthrough curves. The breakthrough curves for B were fitted to CDE and the parameters were described in relation to soil structure.

Description of Site and Soils

The soils were located between longitude 73° 10' and 73° 45' and latitude 31° 10' and 31° 30' in Bari Doab, an alluvial landmass between Ravi and Sutloj rivers in semi-arid subtropical continental climate (Mian, 1968). The Lyallpur and Sultanpur soil series, from the columns were taken, are Typic Camborthids: used for Maize-Potato-Maize cropping sequence. The Lyallpur soil is a very deep, clay loam, well drained, calcareous, weak coarse and medium sub-angular blocky and developed on late Pleistocene. The Sultanpur soil is a deep, sand loam, well drained, calcareous, weak coarse sub-angular blocky and developed on sub-recent level floodplain.

Saturated hydraulic conductivity of the Sultanpur and Lyallpur was 125 and 152 mm per day, respectively. pH of the Sultanpur was 8.2 and of Lyallpur 8.0. Bulk density of Sultanpur and Lyallpur was 1.49 and 1.42 Mg m^{-3}, respectively. The calculated mean pore volume was 290 and 330 mm for Sultanpur and Lyallpur, respectively. Total porosity was 0.43 and 0.46 m^3m^{-3} for Sultanpur and Lyallpur, respectively.

Column preparation

The column had 8.4 cm diameter and was 28.0 cm long, excavated from each soil by inserting PVC pipes, and brought to laboratory. The bottom and surface of the column were leveled by removing 1.5 cm soil layer from each side. The bottom soil layer was supported by small gravels and plastic netting fixed on a support PVC pipe of relatively large diameter resting on a ceramic funnel. The column was saturated from bottom by 0.01 M $CaCl_2$ electrolyte solution.

Leaching experiment

Ten mg L^{-1} solution containing $ZnSO_4$ and H_3BO_3 prepared in 0.01 M$CaCl_2$ was applied at the column surface at constant flow rate controlled by 2 cm water head. The leachate collected in plastic containers at time interval was analyzed for B and Zn.

Batch experiment for B and Zn Sorption

Boron and Zn adsorption coefficients for the soils were determined from adsorption isotherms developed through batch experiments (Syers *et al.*, 1973; Castro and Rolston, 1977). Surface soil from the each series was passed through a 2-mm sieve and 5 g soil was equilibrated in triplicate with 30 mL 0.01 M $CaCl_2$ aqueous solutions containing 0, 8, 20, 40, 80, 120, 160, 240, 320, 400, 480 µg B L^{-1} as H_3BO_3. The suspension was shaken overnight on an end to end shaker at room temperature and then centrifuged. The pH of the supernatant was recorded and B in the supernatant was analyzed calorimetrically. Separately, 5 g soil in 30 ml of 0.01M $CaCl_2$ with 0, 25, 50, 100, 200, 300, 400, 500, 600, 700, and 800 µg Zn $5g^{-1}$ soil was shaken over night and the supernatant was analyzed for Zn. The amount of B or Zn added but not recovered in solution was assumed to be adsorbed. Sorption was expressed on a dry-soil weight basis.

Characterisation of Flow Paths

In addition to the leaching experiment, the flow paths were marked by applying brilliant blue dye to the columns. Two cm of 1% FD&C blue dye No. 1 was applied on the column surface without causing runoff (Flury *et al.*, 1994). After 24 hours, each column was cut perpendicularly with 3 cm increment towards the center and faces were photographed successively.

Analytical methods

Boron was analyzed calorimetrically using the Azomethine-H and the absorbance read at 420 nm (Bingham, 1982). Zinc was analyzed by Atomic Absorption Spectrophotometer.

Parameter Estimation

Boron and Zn adsorption isotherms as determined from the batch experiment were plotted as C_w/X versus C_w and regressed linearly. The reciprocal of the slope of the regression line yielded b, the maximum B (or Zn) sorption and the Langmuir constant K was obtained by dividing the slope (1/b) by the intercept (1/Kb). To investigate the degree of adsorption at the application concentration of 10 mg L^{-1}, we determined the adsorption partition coefficient, kd, by finding the tangent to the Langmuir isotherm at this concentration using Eq. 4.

All the breakthrough curves were fitted to CDE with partitioning Θ into mobile/immobile fractions using STANMOD, a Windows based computer code which uses analytical solutions of deterministic non-equilibrium CDE (Simunek *et al.*, 1999; Toride *et al.*, 1999). The input data consisted of solute concentration ratio and drainage depth (cm) as proxy for solute concentration and time, respectively. The boundary conditions included characteristic length of 0.28 m and the total pulse input equal to drainage depth of application phase. We used the R coefficient calculated from the Eq. 6. No decay or production terms were included.

Further, uniqueness of the fitted parameters was verified by repeatedly STANMOD run for each experiment varying the initial values of the input parameters (Langer *et al.*, 1999). The fitted parameters from the analytical solution were accepted once the goodness of fit (r^2) was the highest and the T-value for the individual parameter was at least one (Kim *et al.*, 2005). Mean square of error for model was < 0.01 in most cases. The fitted flow parameters for the breakthrough of B and Zn were: $V_{(m)}$, velocity in the mobile region defined as $\theta_m v/\theta$ (L L^{-1}); $D_{(m)}$, dispersion in the mobile region defined as $\theta_m D/\theta$ (L^2 L^{-1}); β, mobile water partitioning coefficient θ_m/θ; and ω, mass transfer function (Simunek *et al.*, 1999; Toride *et al.*, 1999).

Results and discussion

Flow Path Characteristics

The columns from both soils showed differences in flow paths as marked by the blue dye. Preferential flow of blue dye was visible after uniform wetting of the surface 2 cm column depth but the nature of flow was different in each soil. In the Sultanpur, a massive loam soil, blue dye after uniformly wetting surface 2 cm soil flowed through 3 cm wide fingers and had no association with any pedological feature (Fig. 1a,b) indicating existence of finger flow in this loamy soil. In the Lyallpur, the blue dye moved through macropores and, then, moved outward perpendicular to the flow paths suggesting diffusion into the matrix (Fig. 1c,d). The distribution of dyed area reflected differences in nature of dye paths in the soils: (a) fingering and, possibly, macropore flow in the massive loam Sultanpur and only macropore flow in the clay loam Lyallpur soil. Instability in the wetting front causes finger flow and it occurs in homogenous soils (Wang *et al.*, 2003) while macropore flow is associated with biopores (earthworm burrows, decayed root channels) and the interpedal voids and fissures formed due to shrinking and swelling (Beven and Germann, 1982).

Boron Sorption

Boron adsorption isotherms for both the soils are depicted in Fig. 2a. Initially there was a rapid increased in B adsorption associated with adsorption on the solids' surface in both the soils. Then, it followed a slow rise of isotherm associated with diffusion of B into the clay mineral. Boron adsorption isotherm had steeper slope for Lyallpur compared to the Sultanpur. It also had greater clay than Sultanpur. Previously, Couch and Grim (1968) proposed a two-step mechanism for B retention in soils. Griffin and Burau (1974) and Sharma *et al.* (1989) observed a slow B desorption from clay soil and assumed that it could be due to a slow B diffusion from the interior surfaces of clay mineral to the solution phase.

Table 1. Langmuir adsorption parameters calculated from the linear adsorption isotherm for B and Zn.

Soils	r^2	Intercept	Slope	b (mg kg^{-1})	k (L mg^{-1})	kd (L kg^{-1})	R
				Boron			
Lyallpur	0.75	0.081	0.069	14.43	0.86	1.17	4.1
Sultanpur	0.81	0.102	0.070	14.25	0.69	1.10	3.9
				Zinc			
Lyallpur	0.88	0.338	0.0096	104	0.25	20.80	65.10
Sultanpur	0.85	0.044	0.0104	94	0.23	18.00	63.37

Intercept is 1/kb; slope of the regression line between Cw/X vs. Cw is 1/b; then, b, is the maximum sorption (mg kg^{-1} soil) and k is as binding strength (L mg^{-1}); r^2 is the regression coefficient; and kd is the adsorption partition coefficient (L kg^{-1}) tangent to isotherm at the concentration applied (10 mg L^{-1}) and R is retardation coefficient (Eq. 6).

The adsorption isotherems fitted the Langmuir equation (Eq. 2) well (Fig. 3b,c) with an r^2 of 0.75 in Lyallpur and 0.81 in Sultanpur. The maximum B sorption and the binding strength determined from inverse of slope and the intercept, respectively, of the regression line of Langmuir equation were greater in case of Lyallpur compared the Sultanpur (Table 1). This difference appears to be related to clay content as previously reported (Communar and Keren, 2005).

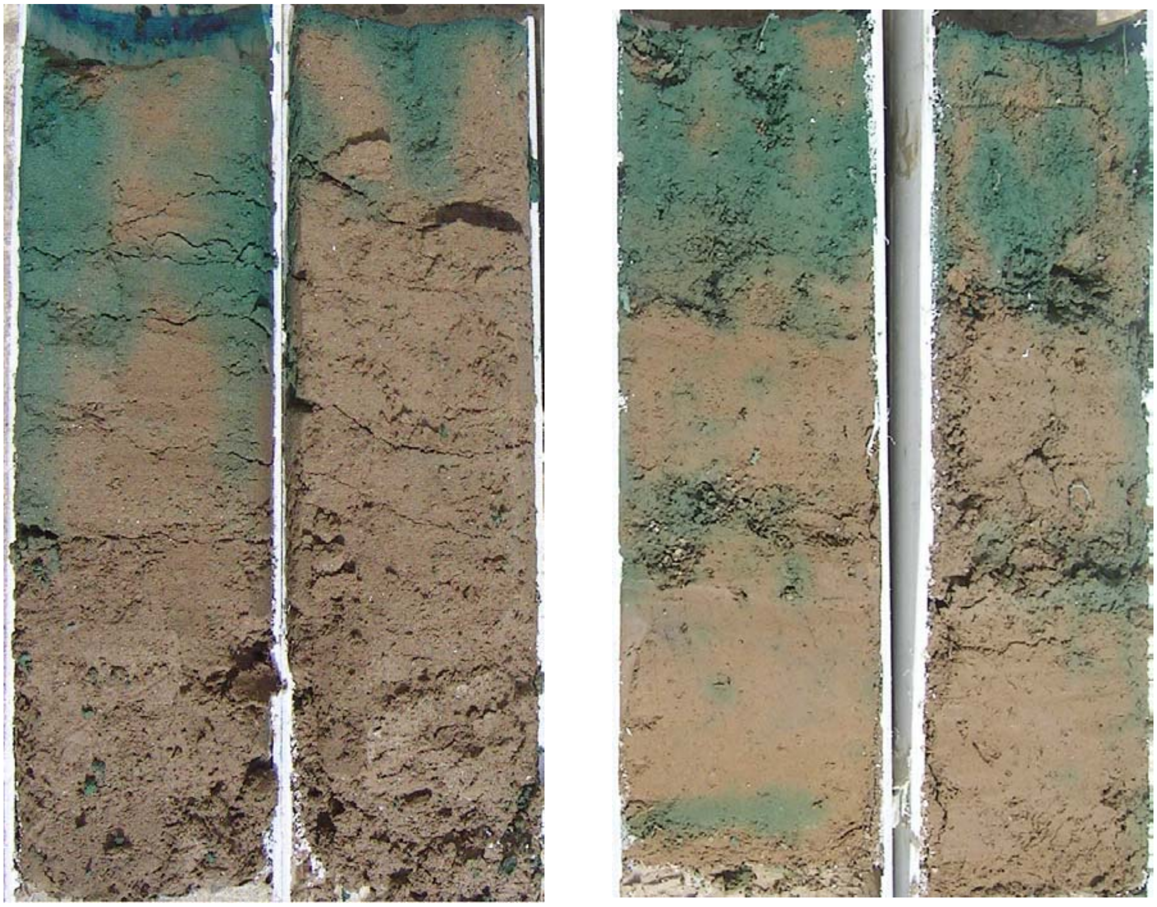

Figure 1. Patterns of blue dye staining in two columns from each soil: (a and b) Sultanpur, a massive loam exhibits blue dye vertical fingers; (c & d) Lyallpur clay loam exhibit macropore flow.

Adsorption partition coefficients at C_w 10 mg L^{-1} which was the concentration applied during the leaching experiment calculated with Eq. [4] by using the fitted Langmuir parameters is given in Table 1. The adsorption partition coefficient is assumed to be constant over the range of concentration that occurs in the soil. The surface soils had the adsorption partition coefficient in the range of 1.17 in case of Lyallpur to 1.10 in case of Sultanpur (Table 1). Similarly, the retardation coefficient calculated from the Eq. 6 was slightly greater in the Lyallpur compared to the Sultanpur soil (Table 1). Therefore, all the indication exist that the Lyallpur soil had slightly greater B adsorption potential than the Sultanpur which relates to the difference in clay content while both soils have very similar pH.

Zinc Sorption

Zinc sorption isotherms for the soils are shown in Fig. 3a. Initially there was a rapid increased in Zn adsorption associated with adsorption on the solids' surface followed a slow rise of isotherm associated with diffusion into the clay mineral (Couch and Grim, 1968; Griffin and Burau, 1974; Sharma *et al.*, 1989). Both the soils had similar sorption trend in at low concentration ($\leq 0.1 \mu g\ mL^{-1}$), while at greater concentrations, the Lyallpur sorbed relatively greater Zn than the Sultanpur. For example, the Lyallpur sorbed about 80 $\mu g\ g^{-1}$ soil and Sultanpur approximately 70 µg g-1 soil at the equilibrium concentration of 11 µg mg L^{-1} and there was no further increase in sorption with increase in solution concentration after 12 µg Zn mL^{-1} solution.

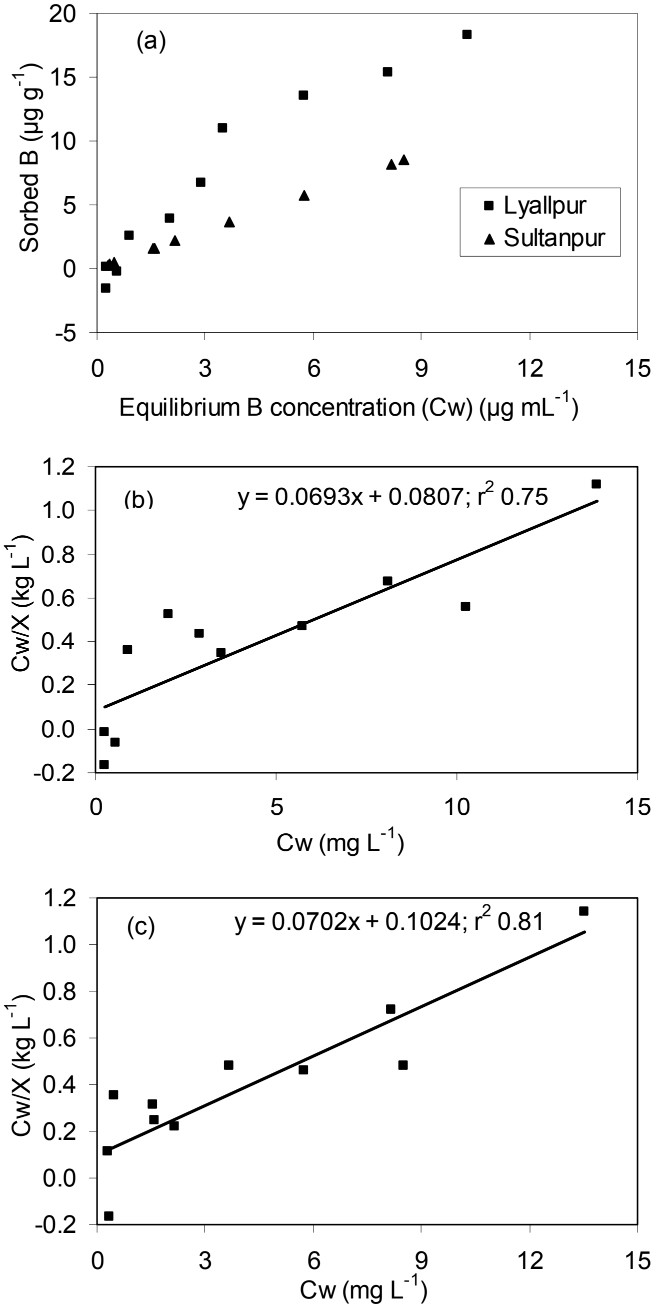

Figure 2. B adsorption isotherms depicting mean of three replicate for each soil (a) and Langmuir equation fit in Lyallpur (b) and Sultanpur (c).

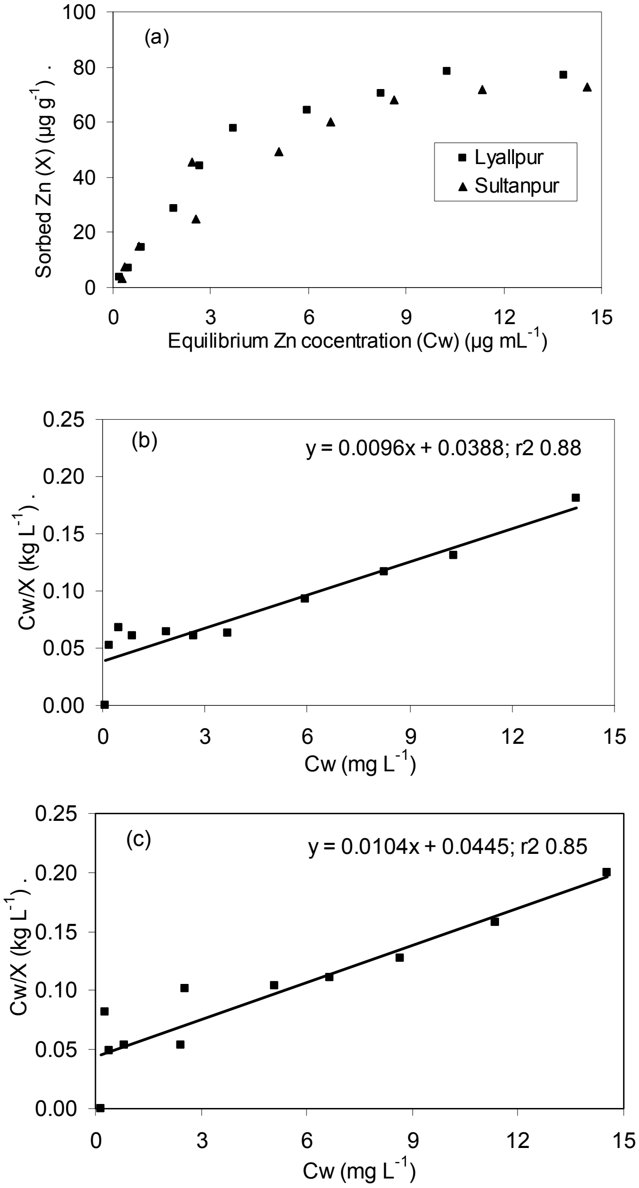

Figure 3. Zinc adsorption isotherms depicting mean of three replicate for each soil (a) and Langmuir equation fit in Lyallpur (b) and Sultanpur (c).

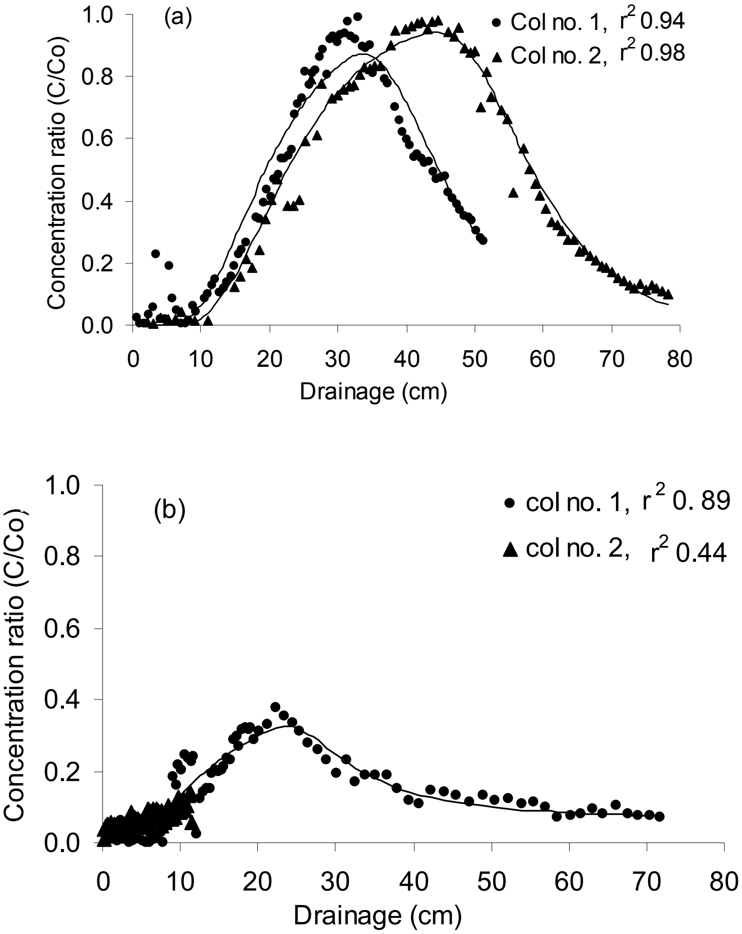

Figure 4. Boron breakthrough curve in two columns from each soil: (a) Sultanpur and (b) Lyallpur.

The isotherms fitted to Langmuir equation are depicted in Figure 3b,c for both soils. Langmuir equation fitted the data well with a r^2 of 0.88 in Lyallpur and 0.85 in Sultanpur. The Lyallpur had greater maximum Zn sorption capacity (b) and the binding strength (K) than the Sultanpur (Table 1). The adsorption partition coefficients (kd) calculated with Eq. [4] by using the Langmuir parameters (Table 1) at C = 10 mg L^{-1}, which is the tangent to the slope at this concentration, was 21 in case of Lyallpur and 18 in case of Sultanpur (Table 1). Therefore, the Lyallpur soil had slightly greater Zn adsorption capacity than the Sultanpur and appeared it may be related to clay content.

Boron Breakthrough

Breakthrough curves plotted as a function of time, pore volumes of effluent, or cumulative drainage are common tool to determine the transport properties (Jardine *et al.* 1988, Vereecken *et al.* 1999; Zurmuhl, 1998). Boron breakthrough in Sultanpur soil columns occurred after 10 cm of commutative drainage and relative concentration (C/Co) peaked to 0.9 after 32 cm of cumulative drainage in column 1 and to 1.0 after 40 cm of cumulative drainage in column 2 (Fig. 4a). In both the soils B breakthrough occurred earlier than one pore volume. In the Lyallpur columns the breakthrough was immediate due to high preferential flow but after initially steep slope and C/Co reached only 0.4 after 24 cm of cumulative drainage in column one. Also, this curve showed long tail (Fig. 4b) implying that concentration decrease was slow during the flushing phase. Diffusion of solutes perpendicular to the flow path into matrix during application phase and seeping back into the macropore during flushing causes long-tail to BTC. The blue dye pattern in the soil also showed diffusion perpendicular to the macropore (Fig. 1c,d). Although in Lyallpur column-2 also the B breakthrough was immediate due to high preferential flow, the C/Co reached at peak 0.1 after 13 cm of cumulative drainage (Fig. 4b). Therefore, we see delay in terms of concentration but in terms of arrival time. In contrast, there was relatively sharp decline in percolate B in Sultanpur columns (compared to Lyallpur) during the flushing phase when B application had stopped and B-free water was started. Macropore flow usually occurs near saturation, yet, it does not depend on water content of the bulk matrix unless it was close to saturation but depended instead principally upon surface boundary conditions (Mahmood-ul-Hassan, 1998).

Table 2. Solute transport parameters determined by non-equilibrium CDE using CXTFIT (Toride *et al.*, 1999).

Soil	Column	r^2	β	ω	$V_{(m)}$	D_m ($cm^2\ cm^{-1}$)
Sultanpur	1	0.94	0.97	0.51	5.64	16.76
	2	0.98	0.97	99.00	4.91	12.47
Lyallpur	1	0.88	0.30	0.87	5.28	42.45
	2	0.44	0.07	79.44	2.23	458.66

$V_{(m)}$ velocity of the mobile liquid phase, ($V_{(m)} = V(\theta_m/\theta$, cm cm^{-1}); $D_{(m)}$ dispersion coefficient of the mobile liquid phase, ($D_{(m)} = D(\theta_m/\theta$, $cm^2\ cm^{-1}$); β, dimensionless water partitioning coefficient ($\beta = \theta_m + f\rho_b K_d/\theta + \rho_b K_{d^3}$ where f is fraction of exchange site in equilibrium and ρ_b is bulk density and K_d is adsorption coefficient); and ω, dimensionless mass transfer coefficient.

Zinc Breakthrough

Breakthrough of Zn was very limited within the drainage depth in these weakly developed coarse blocky structured soils. Only one column from the Lyallpur soil showed C/Co of 0.05 toward end of leaching experiment (data not presented). Transport parameters for Zn were not determined because of lack of breakthrough; however, we have R factor calculated from Eq 6 using the kd values from the batch experiment (Table 1).

Model Fitting

The two-domain CDE fitted well to the B breakthrough data except for one column of the Lyallpur soil where r^2 was only 0.44 (Table 1). Boron under 20 mm water head moved 5.3 cm per cm of drainage in the Sultanpur soil as determined by fitting the breakthrough curves. One column of Lyallpur soil was as fast as the Sultanpur but the other was relatively slow. Water partitioning coefficient (θ_m/θ) in Sultanpur was 0.97 compared to 0.30 and 0.07 for the two columns of Lyallpur, which mean larger volume fraction of Sultanpur had taken part into the flow process implying lesser degree of preferential flow compared to Lyallpur which conformed to blue dye flow patterns, i.e., finger flow in Sultanpur and macropore flow in Lyallpur. However, the Lyallpur soil had high dispersion in the mobile region (Table 2). We believe the rapid breakthrough of solutes due to preferential flow paths – with solute appearing before the water that initially contained them (if uniform flow is assumed)–forces CXTFIT to assign low velocity and to attribute solute movement to high dispersion. Therefore, we see low velocity in Lyallpur beside it had greater macropore flow as seen from the dye pattern.

Conclusion

We investigated leaching of B and Zn through two soils by taking replicated intact column. We also marked the flow paths in the columns used and determined B and Zn sorption potential by batch experiment. This study provided a comparison of observed (from breakthrough curves) calculated first arrival time (by fitting CDE solute transport model) and showed that both the soils the Sultanpur series and the Lyallpur have the preferential flow that vary in nature and magnitude. The Lyallpur soil due to its greater clay content sorbed greater B and Zn compared to the Sultanpur but because of macropore flow it had early breakthrough of B. However, solute velocity in Lyallpur was not higher than that of Sultanpur mainly because the solute movement was attributed to high dispersion. The study demonstrates effect of soil structure on solute transport and has implications for the nutrient management in field soils.

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