Short title: *Solute transport through agricultural soils*

Transport characteristics of heavy metals, metalloids and pesticides through major agricultural soils of Bangladesh as determined by TDR

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29 **Summary**

30 The transport parameters of soluble chemicals through soils are needed to assess the
 31 pollution risks of soil and groundwater resources. The transport parameters of seven heavy
 32 metal or metalloid compounds (NaAsO_2 , $\text{Cd}(\text{NO}_3)_2$, $\text{Pb}(\text{NO}_3)_2$, $\text{Ni}(\text{NO}_3)_2$, ZnCl_2 , CuSO_4
 33 and $\text{Co}(\text{NO}_3)_2$), two pesticides (cartap and carbendazim) and an inert salt (CaCl_2) were
 34 determined in repacked columns of eight agricultural soils of Bangladesh. The relation
 35 between the physicochemical properties of the soils and solutes, and the solute-transport
 36 parameters was investigated by TDR using bulk soil electrical conductivity (EC) as a
 37 proxy. With the increase in clay content of the soils, velocity of the solutes (V) decreased
 38 and dispersivity (λ) increased, both linearly. Solute retardation factor (R) was negatively
 39 and nonlinearly related to the clay content. Dispersivity was negatively related with the
 40 median grain diameter following power law. Both Peclet number (P) and velocity of
 41 solute, V , were negatively correlated with soil bulk density, but dispersion coefficient (D)
 42 and dispersivity, λ , were positively correlated with it. V , R and P were positively
 43 correlated with soil organic carbon (OC) content. V , D and P were positively correlated
 44 with soil pH while R and λ were negatively correlated with it. In most cases, the
 45 correlations were significant ($p \leq 0.05$). D , R and λ increased with the increase in solute
 46 travel path in the soil. Based on R , the general adsorption affinity of the solutes in the soils
 47 was: $\text{As} > \text{Co} > \text{Cd} > \text{carbendazim} > \text{Pb} > \text{Cu} > \text{cartap} > \text{Zn} > \text{Ni} > \text{Ca}$. In some soils,
 48 however, Cd and carbendazim showed a lower adsorption compared to Pb and Co, and Zn
 49 and cartap were more strongly adsorbed than Ni. The relationships between
 50 physicochemical properties of the soils and solutes, and the solute-transport parameters
 51 established in this study, contribute to the better interpretation of TDR data as a
 52 preliminary assessment of pollutant mobility in soils with different textures. An additional
 53 plus point of this study is that information was obtained concerning the transport of two

pesticides (cartap and carbendazim) through soil that is still limited.

Introduction

The urgent need to increase food production to feed the growing population in many countries, such as in Bangladesh, has resulted in a rapid increase in the use of pesticides and chemical fertilizers. The use of chemical fertilizers in Bangladesh increased seven-fold from 1977–1978 to 1997–1998 (UNEP, 2001) and nearly double (182%) from 1992–1993 to 2012–2013 (MoA, 2014). In a similar way, the application of pesticides increased five-fold from 1989 to 1998 (UNEP, 2001) and threefold (328%) from 2000 to 2010 (BRRI, 2010). Carbendazim is a systemic broad spectrum fungicide that controls various fungal pathogens and is the most widely used fungicide in Bangladesh. The farmers cultivating fields adjacent to rivers passing through the major industrial areas are irrigating with polluted surface water, and others are irrigating with polluted groundwater. Applications of chemical fertilizers and pesticides along with irrigation water contaminated by industry cause soil pollution by heavy metals and pesticide residues. Islam *et al.* (2004) reported elevated concentrations of arsenic (As), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn) in agricultural soils of Bangladesh. Dhar *et al.* (1997) reported possible risks of heavy metal contaminated groundwater due to antropogenic activities. A grave concern about soil and groundwater contamination by agricultural chemicals and industrial wastes is thus increasing.

The transport characteristics of soluble chemicals through soil are an important aspect to assess the pollution of soil and groundwater resources (Porro *et al.*, 1993). For a correct assessment through modeling, solute-transport parameters such as dispersion coefficient, residence time, velocity of transport, dispersivity and retardation factor have to be determined. The models simulate solute transport through soils in a region

contaminated by heavy metals and pesticides as well as waste disposal, and allow quantifying the potential pollution and working out remediation measures for a degraded agricultural land. The models can guide both future research efforts and current management practices in an objective and quantitative manner.

Understanding of solute-transport processes in the subsurface is important in agricultural soils and underlying aquifers. Especially, they are necessary for optimum application of agrochemicals in the field, and selection and design of sustainable leaching/reclamation methods during irrigation in order to avoid degradation of soils and aquifers. Because the properties of soils affect the transport of solutes in subsurface media, it is necessary to know the transport behaviour of different solutes through agricultural soils as a function of their properties (texture, organic carbon content, pH). However, due to the lack of comprehensive data sets on the transport behaviour of solutes through different soils, the effects of soil physicochemical properties on solute-transport parameters are not fully understood. Models to estimate solute transport in soil are often soil-specific and cannot simply be extrapolated to soils with a different texture. Moreover, Koestel *et al.* (2013) showed that it should be possible to estimate solute-transport properties from soil properties (e.g., texture, bulk density). In Bangladesh, solute transport through soils, especially agricultural soils, has not been investigated yet. So, the fate of heavy metals, metalloids and pesticides in the soils is not known. Under this context, the general objective of this study was set to characterize solute transport through major agricultural soils, with different textures, of Bangladesh. Although the solute-transport process through subsurface soil governs the fate of the contaminants, and soil and groundwater quality, this study focuses on topsoil only because of limitations of the measurement technique. Also, because of the enormous heterogeneity of the natural field soil, it is not possible to derive exact relations between the solute-transport parameters and

various soil properties. Therefore, this study was done on sieved and repacked soils. The results obtained under this simplification need to be up-scaled by further study for practical application in the field condition.

One approach to achieve the objective of the study could be to sample soil solution during a breakthrough or an impulse-response experiment and to analyse for concentrations of dissolved solutes. This would require both sophisticated extraction equipment and chemical instrumentation to analyse the small water samples. Since such facility is not available in Mymensingh, we employed TDR. Hereby, the bulk EC inside soil columns is measured as a proxy for the solute concentration. The advantage is that this is a low-cost screening method for determining the transport characteristics of solutes. The disadvantage is that ion exchanges in the soil solution might lead to an apparent lower retardation factor. The major drawback is that we were forced to work with single solutes because TDR does not allow distinguishing between different solutes. Competitive sorption of several interacting solutes results in complex breakthrough patterns, which cannot be analysed in a meaningful way. Therefore, competitive adsorption phenomena were not considered in the present study. Because the solutes under study can replace another more mobile ion absorbed in the soil, the resulting increase in bulk EC is caused by both the solute and the replaced ions. By sufficiently leaching the soil columns before the experiment this effect is kept minimal. Previous studies already indicated that TDR can be used to monitor cation exchange and solute transport through soil when the percolate solution causes a sufficient change in electrical conductivity (Vogeler, 2001).

The specific objectives were (i) to determine the transport parameters of several commonly used solutes containing heavy metal compounds and pesticides by measuring their breakthrough data in repacked soil columns, and (ii) to investigate the relations of pertinent soil properties with the solute-transport parameters for a range of agricultural

soils in Bangladesh.

Materials and method

Site selection and soil sampling

Agricultural land with intensive use of agrochemicals was selected for soil sampling within Bangladesh. Soil samples were collected from seven administrative districts, each located in a different agro-ecological zone (AEZ) in the country. The districts were Mymensingh, Gazipur, Comilla, Satkhira, Bogra, Rajshahi and Dinajpur (Figure 1) that were in the AEZ 9, 28, 19, 13, 25, 11 and 3, respectively (BARC, 2008). Eight soil samples were collected from the seven districts: two from Mymensingh and one from each of the other districts. For Mymensingh (where the research was done), soil samples were collected at three different times over a two-year period and used for different experiments. As plowing upper soil layers is a common practice and soil structure is affected during irrigation and/or rainfall, repacked soil columns were used in solute-transport experiments to reduce variability due to heterogeneity. Soil samples were collected from 0–15 cm top layer covering an area of one square meter and were air dried. These were sieved to pass through 2-mm mesh sieve after desegregation by crushing; soils with aggregate size of ≈ 2 mm are regarded representative for characterizing good physical quality indicators (Stavi *et al.*, 2011). All the soil samples were analyzed for texture, grain size, EC, pH and organic carbon (OC). Soil texture was determined from particle size distribution determined by Hydrometer Method and grain size was determined by sieve analysis following British Standards, BS 1377 (1990). Soil EC and pH were determined by a glass electrode EC/pH meter following Jackson (1962) on a saturation extract (air-dry soil to water ratio of 1:2.5 at 25°C). Soil organic carbon was determined following the

method described by Walkey-Black (Nelson and Sommers, 1982).

Selection of solutes

Based on the composition of the most frequently used agrochemicals and waste products discharged by industries in Bangladesh, ten chemicals with extensive propensity to cause soil and groundwater contamination were selected for the transport experiments. In addition, Arsenic (As) causes concern because As-contaminated groundwater used as drinking water and for irrigation is a serious problem in Bangladesh (Anawar *et al.*, 2003). Therefore one metalloid (As), six heavy metals (Cd, Ni, Pb, Co, Zn and Cu) and, for comparison, laboratory grade calcium chloride (CaCl_2) were included. The CaCl_2 serves as a conservative/inert reference solute. In addition, cartap and carbendazim, extensively used as insecticide and fungicide, respectively in Bangladesh, were selected as organic solutes. The EC of these solutes was measured in 2, 5, 10, 15 and 20 mM solutions. The solutions of the solutes were prepared in separate clean glass beakers and kept for 48 hours in a control room at 25°C to achieve homogeneous solutions. The EC of the solutions were measured by an EC meter. Tables 1 and 2 provide some properties of the CaCl_2 salt, seven heavy metal/metalloid salts, and two pesticides, respectively.

Solubility and EC of solutes

Electrical conductivity of solutes depends on their solubility in water. As given in Tables 1 and 2 for 5 mM electrolyte concentration, cartap resulted in the maximum EC of 241 mS m^{-1} and carbendazim resulted in the minimum EC of 77 mS m^{-1} . The solubility of carbendazim in water at pH 7–8 is 5–7 mg l^{-1} (Dang and Smit, 2008), whereas the solubility of cartap in water at 20°C is 200 g l^{-1} (PPDB, 2008). The electrolyte

concentrations and EC of the solutes were linearly related. Of the heavy metals and metalloid salts, NaAsO₂ solution resulted in the highest EC and CuSO₄ solution resulted in the lowest EC. The transport of a solute through soils is largely controlled by its water solubility and sorption properties. The chemicals that readily dissolve in water are more easily transported with soil water than less soluble pesticides, such as carbendazim. An increased ionic strength of the soil solution reduces metal adsorption capacity of soils (Fike, 2001). However, electrolytic cation composition has a more pronounced effect on element adsorption than ionic strength (Fike, 2001).

Solute-transport experiments

Experimental set-up. Following Mojid *et al.* (2004), four PVC columns, each 34 cm long and 15 cm in diameter, were placed on four 1.2-m high supporting columns that were uniformly filled with a sandy loam soil. The upper columns were filled uniformly and compactly with four air-dried and sieved soils out of the eight soils to be used for solute-transport experiments; the remaining four soils were used in a second batch of experiments. Each column was packed to 32 cm depth with uniform bulk density ($\rho_b = 1.29 - 1.40 \text{ g cm}^{-3}$) by incrementally packing same masses of soil in 8 cm layers; the bottom of the columns was closed with nylon cloths. This was done by using a flat-tipped rod, which was of nearly the same diameter as the interior of the column. A 2-cm clearance was kept on the top of the columns to maintain ponding water during their conditioning. Following complete packing, the columns were saturated with tap water (EC = 17 mS m^{-1} , pH = 7.08) placing the soil columns in a large flat-bottom plastic bowl and adding water in the bowl slowly in 48 hours. In that way, water entered from the bottom upwards so that air bubbles and grain size separation due to gravity in the supernatant aqueous phase in the columns were minimized. After saturation, a sufficient quantity of

tap water was leached from the top through the soil in the columns following six wetting and drying cycles in the next three months. After settlement of the soils, the experimental soil columns, four simultaneously, were placed on the top of the supporting columns vertically. The nylon cloths from the bottom of the soil columns were removed to make good contact with the soil of the supporting columns. For the remaining four soils, experimental soil columns were prepared following the similar procedure in a second batch of experiments.

Constant flux experiment. Two 3-wire TDR sensors (10 cm long, 3 cm spacing of centre to centre of the outer wires and 0.2 cm wire diameter) were inserted horizontally and glued to each column to prevent leaking of water. One sensor was at 8 cm and the other at 28 cm below the top of the upper column; the vertical distance between the two sensors (Z) was 20 cm. It is noted that the top few centimetres of the soil profile are critical for strong-sorbing compounds. But, because of the volume of influence of the TDR sensors (volume over which water and EC are measured) and also to avoid the effect of development of the upper boundary conditions on the sensor we inserted the top sensor at 8 cm depth. The concentration of solutes at the upper depth is the input and that at the lower depth is the response. Measuring concentrations between the two sensors in a sample rather than from the top of the sample to one sensor has several advantages (Mojid *et al.*, 2006). Firstly, it allows measurement over a well-defined horizon from a soil without having to remove the upper layers. Secondly, it is difficult to supply a small solute pulse correctly in order to satisfy the boundary conditions under unsaturated conditions. Thirdly, it is easier to measure the input correctly in the soil after some mixing that otherwise would be erroneous. Following every wetting and drying for eight weeks, a sufficient quantity of tap water was leached through the columns to enhance the contact

between sensors and soil and to create a good pore connectivity environment between the supporting and experimental soil columns. After that, a cartridge pump applied tap water at a constant rate ($0.32 \pm 0.02 \text{ cm h}^{-1}$) to ensure unsaturated flow. Water flow continued until equilibrium between the applied and drainage water was attained. A constant hanging water table, maintained at 20 cm above the base of the lower columns, created suction in the upper soils.

The breakthrough experiments were conducted as an impulse response by spreading a solution of solute, instantaneously and uniformly, as a pulse by maintaining a steady water flow over the surface of the experimental soils in the columns. Before using the solutes under study, calcium chloride (CaCl_2) was used in the breakthrough experiments for the non-reactive and conservative solute in the eight soils. CaCl_2 did not degrade the structure of the soils during the experiments. At steady-state water flow condition, a pulse of 5 ml CaCl_2 solution of concentration 250 g l^{-1} was introduced, uniformly, by a syringe on each column and the selected rate of water flow ($0.32 \pm 0.02 \text{ cm h}^{-1}$) continued until the solution was completely eluted from the columns. Although the applied solute pulse was of relatively high concentration, the small pulse (5 ml) spread uniformly over a soil surface of 15 cm diameter and was diluted with the water flux along its travel distance. Consequently, there was no density effect of the solutes on their transport process, and also the link between TDR-measured ECs and breakthrough solute concentrations remained valid.

A TDR100 and CR10X datalogger were programmed with Logger net datalogger-support software (Campbell Scientific INC, Logan, UT) that recorded water content and bulk electrical conductivity of the soils at selected intervals. The measurements continued until the whole of the applied solute leached out from the upper columns. Measurements of water content and bulk EC were done for the ten solutes (Tables 1 and 2); the pulse

volume and concentration were the same as that for CaCl_2 (5 ml, 250 g l^{-1}). A solute required 5 -10 days to leach completely through the soil columns depending on the texture of the soils and properties of the solute. After completion of the experiments with the eight soils in two batches, soil samples were collected from the columns by inserting a 5 cm $\times$ 5 cm core sampler through the surface of each of the eight columns. One sample was collected from each column; the sampling depth was from the soil surface to 5 cm depth. First, saturated hydraulic conductivity of the soil samples was determined by constant-head method through permeameters. Each permeameter was constructed by a PVC column of length 22 cm and diameter 5.25 cm. Two holes were cut at opposite sides of the PVC column and two plastic tubes were fitted to them. One tube continuously supplied water to the sample while the other discharged water and maintained a constant water head over the soil sample. The permeameters were placed on a wooden structure supported by steel bands. The core samples were attached to the bottom of the permeameters and water was supplied continuously through the supply tubes under a constant head maintained by the discharge tubes. The soil samples with the permeameters were kept for 48 hours to attain steady state water flow condition after which the drainage water from the samples was collected for a known period of time for each of the sample. The hydraulic head both at the bottom and top of each soil sample was measured by setting two piezometer tubes. The saturated hydraulic conductivity was calculated from Darcy's law, that is, by multiplying the volume of water collected per unit time by the length of the soil sample in the column and dividing them by the product of the cross-sectional area of the soil core and hydraulic head difference between the two ends of the soil sample. Subsequently, the bulk density of the samples was determined from the core samples by drying them in the oven at 105°C for 24 h. The bulk density was calculated from the mass of the oven dry soil samples and their volumes.

277

278 *Experiment on depth dependence.* The measurements of depth-dependent solute
 279 breakthrough data were done in the silt loam soil of Mymensingh for the ten solutes under
 280 investigation (Tables 1 and 2). The organic carbon content, pH and EC of the soil were
 281 0.82%, 6.31 and 5.10 mS m⁻¹, respectively. The bulk density of soil in the column was
 282 maintained at 1.33 g cm⁻³. It is noted that Mymensingh silt loam and Mymensingh loamy
 283 sand were collected from two specific agricultural fields, and soil sampling was done at
 284 three different times over a two year period. Between the periods of soil sampling, crops
 285 were grown in the fields. Consequently, the organic carbon content, pH and EC of the
 286 soils differed at different sampling times. Six TDR sensors were inserted in the column
 287 successively at 6, 11, 16, 21, 26 and 31 cm depth from top of the soil surface. The distance
 288 between the adjacent sensors was 5 cm. The mean water flux was maintained at $0.51 \pm$
 289 0.031 cm h^{-1} . The experimental procedure was similar to that of the constant flux
 290 experiment. A larger water flux ($0.51 \pm 0.031 \text{ cm h}^{-1}$) than in the previous set of
 291 experiments ($0.32 \pm 0.02 \text{ cm h}^{-1}$) substantially shortened the duration of experiments, but
 292 did not affect the flow conditions and objective of the experiments.

293

294 *Experiment on flux dependence.* The flux-dependent solute-transport experiments
 295 were done in the two soils of Mymensingh for five water fluxes and four solutes (CaCl₂,
 296 NaAsO₂, cartap and carbendazim). The length and inner diameter of the PVC columns was
 297 30.0 and 12.15 cm, respectively in this case. Two TDR sensors were inserted horizontally
 298 in each soil column at 8 and 23 cm from top of the soil surface; the distance between the
 299 sensors was 15 cm. The bulk density of the loamy sand and silt loam in the columns was
 300 1.36 and 1.34 g cm⁻³, respectively. In this case, the organic carbon content, pH and EC of
 301 the loamy sand were 0.13%, 7.66 and 4.15 mS m⁻¹, respectively. The corresponding

properties of the silt loam were 0.35%, 7.17 and 5.98 mS m⁻¹. The average unsaturated steady-state water fluxes were 0.09 ± 0.011 , 0.19 ± 0.014 , 0.25 ± 0.008 , 0.34 ± 0.013 and 0.53 ± 0.040 cm h⁻¹ for both soil columns.

Data analysis

The analysis of TDR-measured EC is based on the relation between the concentration of a solute in soil water and the EC of soil water, which is linearly related to the EC of bulk soil (Kachanoski *et al.*, 1992; Ward *et al.*, 1994) for a constant water content. The initial concentration of solute in the soil water before applying the pulse of solute is deducted from the time-dependent concentrations. The resulting concentrations are then normalized with respect to the total measured concentration. If the initial and time-dependent concentrations of solute in the soil water are represented by C_i and C_t , respectively, and the corresponding bulk electrical conductivities of the soil by $E_{a(i)}$ and $E_{a(t)}$, respectively, then,

$$C_t = \alpha_1 + \alpha_2 E_{a(t)} \quad (1)$$

$$\text{and} \quad C_i = \alpha_1 + \alpha_2 E_{a(i)}, \quad (2)$$

where α_1 and α_2 are calibration constants. The time-dependent normalized concentration $[C_{0(t)}]$ for the initially relaxed (non-zero initial concentration) system is then computed by

$$C_{0(t)} = \frac{C_t - C_i}{\sum_{t=0}^T (C_t - C_i)}, \quad (3)$$

where T is the total duration of the experiment. Substituting Equations 1 and 2 into Equation 3, the normalized concentration is calculated by

$$C_{0(t)} = \frac{E_{a(t)} - E_{a(i)}}{\sum_{t=0}^T [E_{a(t)} - E_{a(i)}]} \quad (4)$$

The bulk ECs of the soils in Equation 4 were expressed at 25°C by employing a temperature correction factor, f_T , expressed (Heimovaara *et al.*, 1995) as

$$f_{T'} = \frac{1}{1 + 0.019(T' - 25)} \quad (5)$$

where T' is the temperature of soil water (°C). The BTCs were drawn by plotting the normalized concentration, $C_{0(t)}$, against time, t . Figure 2 displays the normalized input and response BTCs for $\text{Co}(\text{NO}_3)_2$ in Mymensingh loamy sand as an example.

The mean travel time, τ , mass-dispersion number, $N (=D/ZV)$, and retardation factor, R , of the solutes were fitted from the BTCs by a transfer-function method (Mojid *et al.*, 2004; their Equations 5 and 7) using a non-linear least-square fitting technique. For CaCl_2 , we expected the retardation factor, R , to be unity assuming it to be a non-reactive solute. The fitting was good with large coefficient of determination ($r^2 \geq 0.97$) and small root-mean square error ($\text{RMSE} \leq 0.08$) between the measured and estimated BTCs. The other solute-transport parameters, such as the velocity of solute/pore water, V (Z/τ), dispersion coefficient, D ($= VZN = Z^2N/\tau$, Van Genuchten and Wierenga, 1986), and dispersivity, λ ($= D/V = ZN$), were calculated from τ , N and the distance, Z , between the input and response BTCs. The column Peclet number, P was calculated by ZV/D .

Results and discussion

Soil properties

According to the USDA soil classification, five soils were classified as silt loam, one was loamy sand, one was sandy loam and one was silt. Table 3 lists the physicochemical properties of the eight soils. The range of sand, silt and clay contents of the soils was 4.92 – 79.48%, 14.48 – 77.96% and 6.04 – 19.12%, respectively. The uniformity coefficients (C_u) of the soils were >2.0 , implying that the soils were well-graded with a good drainage environment. The dry bulk density of the repacked soil columns for constant water flux experiment varied from 1.40 g cm^{-3} for silt loam of Gazipur to 1.29 g cm^{-3} for silt loam of Bogra. The soil at Satkhira was characterized by the highest OC content (0.84%), while the soil at Comilla had the lowest OC content (0.37%). The bulk density of the soils decreased with increasing OC (Curtis and Post, 1964); the correlation between them ($r^2 = 0.26$) was insignificant ($p = 0.05$). Soil pH varied from slightly acidic (6.32) to slightly alkaline (7.58). The pH decreased with the increase in clay content of the soils; the correlation between them ($r^2 = 0.53$) was significant. Chukwuma *et al.* (2010) also reported a similar relation between pH and clay content of soils. EC of the eight soils ranged from 3.95 to 17.74 mS m^{-1} . A significant positive association between EC and clay content with a strong correlation ($r^2 = 0.72$) existed that was also supported by Hartsock *et al.* (2000). The saturated hydraulic conductivity of the soils varied from 15.56 to 133.68 cm d^{-1} , with the highest value for loamy sand of Mymensingh and the lowest value for silt loam of Satkhira. A strong negative correlation ($r^2 = 0.69$) existed between the saturated hydraulic conductivity and the clay content of the soils.

Solute-transport parameters as affected by soil types

The pore velocity of solutes, V , was positively correlated with median grain diameter of the soils. Uniformity coefficient, C_u , of the soils (Table 4) also influenced V ; there was a

weak linear relation ($r^2 = 0.32$) between V and C_u . Soils having a wider pore-size distribution resulted in a higher variation in V , and, consequently, higher dispersion coefficient, D .

Dispersivities, λ , of the solutes were <1 cm for the eight soils (Table 5). Such dispersivities were in agreement with Nielsen & Biggar (1962), Kirda *et al.* (1973), Bresler & Laufer (1974) and Wierenga & van Genuchten (1989), who reported λ of the order of 1 cm or less for laboratory scale experiments with homogeneous and repacked soils in small columns (≈ 30 cm). Dispersivity generally increased from coarser to finer textured soils. Because of the lower soil-water content associated with lower clay content in the loamy sand of Mymensingh, λ in this soil was lower than in the other soils. Increased tortuosity of flow paths of a solute with increasing clay content in the soil augmented λ . Huang *et al.* (2009) also reported an increased λ and its variance with increasing clay content of the soils. Vanderborght & Vereecken (2007) also observed larger dispersivities in fine-textured soils; the difference between the dispersivities in fine- and coarse-textured soils was however insignificant. Median grain diameter (D_{50}) decreased with increasing clay content of the soils. According to the grain size distribution (Table 4), loamy sand having a greater median grain diameter than the other soils provided lower dispersivity (Table 5). Figure 3 illustrates a curvilinear decrease of dispersivity with increasing D_{50} . Dispersivity of the solutes systematically increased with increasing clay content following power law relation except for CaCl_2 , for which a linear relationship held.

Clay content of the soils significantly controlled transport of the solutes since an increased velocity of solute, V , obtained in coarser soils than in finer soils revealed high mobility of the solutes in soils with low clay content. Especially for soils with low organic matter content, clay minerals can play a decisive role in the sorption processes of heavy

metals and arsenic. Heavy metals are adsorbed by clay minerals by inner and outer sphere complexes, and the extent of adsorption mainly depends on the cation exchange capacity and pH of the soil (Lukman *et al.*, 2013). Since pH of all the soils in this study was around neutral (6.32 – 7.58; Table 3) a strong adsorption of heavy metals on negatively charged clay mineral surfaces can be expected. Consequently, their retardation factors, as depicted in Figure 4, increased with increasing clay content following power law, indicating that clay content is a determining factor for heavy metal retention in the studied soils. Several other studies showed that clay minerals play an important role in heavy metal retention in soil (e.g. Srivastava *et al.*, 2005; Covello *et al.*, 2007). This is also reflected in positive correlations found between total heavy metal contents, such as Cd, Ni, Pb, Cu and Zn, and clay contents of soils described by Shuman (1979), Lee *et al.* (1997) and Tarakcioglu *et al.* (2006). Arsenite is sorbed by inner and outer sphere complexes on clays (Arai *et al.*, 2001), which explains for the positive correlation between clay content and the retardation factor for As.

The mobility of the two pesticides through the soils was studied in a similar way as the heavy metals and arsenic. A very few studies on the sorption and transport of carbendazim and cartap in soils are available for comparison. In a study on four Vietnamese soils, Berglöf *et al.* (2002) showed that the sorption of carbendazim was strongest in soil with the highest OC content (9.8%) and the highest clay content (49.8%). Paszko (2012) showed that, in the pH range between 3 and 7, the adsorption of carbendazim was inversely correlated to the pH of the soil. In the present study, the pH range of the soils was too narrow to check the relationship between carbendazim sorption and pH.

It is noted that the retardation factors of the solutes were relatively small. The most plausible reason was that the breakthrough concentrations of the solutes were measured at

8 and 28 cm below the soil surfaces, and most cation sorption occurred in the top of the column. In such case, instead of only two depths, the breakthrough concentrations can be measured at several depths starting from as close to the soil surface in the column as possible with TDR sensor taking into account the area of influence of measurement by the sensor, and depth-dependent retardation factor can be established. Such relationships will be more realistic in assessing leaching risk in the field condition. Peclet number, P , decreased with increasing clay in the soils, revealing a large contribution of dispersive transport relative to advective transport in finer texture as compared to coarse textured soils.

Solute-transport parameters as affected by solute types

The largest velocity obtained with the non-reactive CaCl_2 solution (Table 5) can be assumed to deliver the best estimate for the average pore-water velocity. Velocity of the reactive solutes depended on their retardation against the soils and was always smaller than the pore-water velocity. Cartap moved with the largest velocity that varied over $0.60 - 0.88 \text{ cm h}^{-1}$ in five of the the eight soils (Table 5). It was more soluble in water and spread easily in soils, and hence transported with less retardation. Of the other metals and metalloids, nickel was transported with the largest velocity, 0.49 to 0.57 cm h^{-1} , in the three other soils due to its low retardation in these soils. The smallest velocity obtained for arsenic varied from 0.41 cm h^{-1} in Satkhira silt loam to 0.73 cm h^{-1} in Mymensingh loamy sand. The mobility of arsenic through the soils was small due to its high adsorption by clay particles, which was also reflected in large retardation factors.

The smallest dispersion coefficient, 0.12 to $0.13 \text{ cm}^2 \text{ h}^{-1}$, was obtained for carbendazim in five of the eight soils (Table 5). This solute was less soluble in water and had poor spreading ability in soils with lower clay content. Nickel, characterized by small

retardation, also showed small D (0.10 to 0.11 cm² h⁻¹) in the other soils with relatively high clay contents. The low pore-water velocities in the soils with high clay content resulted in small D . Similar to D , carbendazim also provided the smallest dispersivity that varied from 0.14 to 0.16 cm. Ni was more sensitive to dispersion than carbendazim in soils with large clay content. Cobalt was characterized by the largest D (0.20 – 0.26 cm² h⁻¹) and consequently also by the largest dispersivity (0.28 – 0.35 cm) in the soils. The sequence of magnitude of dispersivity of the solutes was: Co > As > Ca > Pb > Zn > cartap > Cd > Cu > Ni > carbendazim.

The retardation factor, R , of arsenic was larger than the other solutes and varied from 1.30 to 1.44 according to small to large clay-containing soils. As(III) adsorption on kaolinite, illite, montmorillonite, has been shown to increase gradually with increasing pH from 3.5 up to 8–9 (Manning & Goldberg, 1997) with an adsorption maximum around pH 8.5 (Goldberg, 2001), which is comparable to the pH of the soils in this study. Moreover, under aerobic conditions, As(II) will be oxidized to As(V), a species that is even more strongly sorbed to soil (Manning & Suarez, 2000). The oxidation of As(III) to As(V) also results in a lower mobility of As.

There were moderate positive linear correlations ($r^2 = 0.43 - 0.52$) between retardation factors and molecular weights of the solutes for the eight soils. The increasing retardation factors of carbendazim and cartap with the increase in clay and organic matter contents implied that the affinity of these solutes to adsorb to soils increased with increasing clay and organic matter contents of the soils. Nemeth-Konda *et al.* (2002) also reported large adsorption coefficients of carbendazim, which provided positive correlation with soil organic carbon and clay contents.

The residence time of the solutes, defined by the ratio of length of soil column to pore-water velocity and multiplied by the retardation factor, depends on pore-water

velocity and retardation factors. Due to large retardation factor, arsenic had the largest residence time that varied from 49.5 to 27.4 h for traveling a 20-cm long column of fine to medium textured soils. Arsenic had a tendency to travel in soils for a prolonged time, thus requiring more time for reaching the groundwater. As a conservative solute, CaCl_2 had the smallest residence time (34.3 – 23.2 h) in the soils. Cartap had a smaller residence time than carbendazim and, consequently, can reach groundwater in a shorter time.

Travel length variation of solute-transport parameters

Dispersion coefficients significantly increased with the increase in length/depth of travel (5 to 25 cm). The increase of D over the travel length was different for different solutes; CaCl_2 , due to its high solubility in water, had the highest increase (137 – 281%) and Co, a solute with a large absorption rate to clay, had the lowest increase (6.1 – 26.1%) in D . The increase in D with travel length was logarithmic for CaCl_2 , NaAsO_2 and ZnCl_2 , power function for Pb and cabendazim, exponential for Cu and cartap, and linear for Cd, Ni and Co (Table 6). The correlation between D and length of travel was strong for all solutes ($r^2 = 0.97 - 0.99$) except for cartap, for which $r^2 = 0.92$. In the homogeneous soil columns, pore-water velocities were uniform at all depths and the increase of dispersion coefficient was governed by the properties of the solutes only.

The increase in travel length of the solutes enlarged dispersivity, λ . Costa & Prunty (2006) reported obtaining increased dispersivity in their field experiments at steady state unsaturated condition at higher flow rates. Gelhar *et al.* (1992) and Vanderborght & Vereecken (2007) also reported finding scale dependency of λ , which increased with increasing transport distance. The trend of variation of λ with travel length was similar to that of the dispersion coefficient for the solutes (Table 6); the correlation between λ and length of travel was significant. The increasing rate of dispersivity of the solutes, except

for Co and cartap, decreased and followed a different pattern with increasing traveling length. Jury & Roth (1990) reported that when spatial scale across which particles travel with a constant velocity is smaller than the transport distance, the rate of increase in the dispersivity decreased with travel distance and the dispersivity reached an asymptotic value.

The retardation factor, R , is a unit less index (Kookana *et al.*, 1994) expressing the retention of solutes by the soil that leads to a lower mobility of the solutes. The retardation factor of the solutes increased with increasing travel length through the soils. The largest variation in R (2.85 – 2.92) was observed for Co. Retardation was an important controlling factor in the behaviour of both the bulk solution and its component ions. When a solute was transported through a soil, its cations were adsorbed to the clay particles while the anions were repelled, causing increased retardation of the cations/metals. The retardation factors increased, non-linearly, with increasing travel length except for cadmium, which showed a linear increase in R with travel length (Table 6). The correlation between R and length of travel was strong and significant except for CaCl_2 and cartap.

Solute-transport parameters as affected by water flux

Dispersion coefficient of the solutes increased with the increase in water flux; the relationship being power law function (Figure 5) was strong ($r^2 > 0.95$) and significant ($p = 0.05$). D was always larger in loamy sand than in silt loam at higher water fluxes. It was directly related to soil-water content, possibly due to that the range of pore sizes reduced when the larger pores were emptied. This reasoning was in line with the capillary tube model of Aris (1956), which brought forward the idea that the dynamic part of mechanical dispersion would be reduced as the media was desaturated.

Dispersivity of the solutes increased with the increase in water flow rate. For

NaAsO₂, a significant linear relation between λ and water flux for loamy sand (LS), and logarithmic relation for silt loam (SL) held (Figure 6) with large coefficients of determination ($r^2 > 0.96$). For cartap, the relationship was linear and for carbendazim, it was power function; in both cases the relationships were strong ($r^2 > 0.94$) and significant. The flux-dependent dispersivities were larger for silt loam than for loamy sand soils for all solutes. Vanderborght & Vereecken (2007) reported that for unsaturated flow experiments, dispersivity distributions did not depend on flow rate in soils with a coarser texture, whereas λ increased with increasing flow rate in soils with a finer texture. In soils with a finer texture, the pores in the soil matrix or the intra-aggregate pores are small so that the soil matrix has a low hydraulic conductivity. When leaching rate exceeds the hydraulic conductivity of the intra-aggregate pores, the inter-aggregate pores, which are continuous across a much larger distance than the intra-aggregate pores, are activated. Consequently, λ increases with increasing flow rate. In soils with a coarser texture, the pore sizes and hydraulic conductivity are much higher and more soil matrix pores are activated with increasing flow rates. As a result, the water-filled pore network becomes better connected and the tortuosity of the flow paths decreases. This may even lead to a decrease in dispersivity with increasing flow rate. At low water flux, variation of dispersivity was not pronounced for CaCl₂, but at high water flux, it was remarkable. This scenario was observed at intermediate water flux for NaAsO₂, but at low and high water fluxes, λ was pronounced in both soils (Figure 6). For the two pesticides, there were distinct differences in dispersivities between low and high water fluxes for both soils.

Retardation factors of the solutes decreased as water flux increased (Figure 7), revealing non-equilibrium conditions of the transport process (Pang *et al.*, 2002). For slow water velocities, diffusion can become a major transport mechanism resulting in lower retardation factors. However, for the water flux (0.09 – 0.55 cm h⁻¹) used in this study

diffusion should not be the main process. So, high water velocities resulted in the lower retardation factors since the solute did not have sufficient time to adsorb to the soil, i.e., chemical equilibrium was not obtained (Selim & Amacher, 2001). A longer retention time, due to a lower pore-water velocity, leads to a longer contact time, while shorter retention times might occur at higher superficial velocities (velocities of pore water on the particle surface). This relationship was also observed previously by several investigators (Schulin *et al.*, 1987; Pracek & Gillham, 1992; Pang *et al.*, 2002). The residence time decreased with increasing pore-water velocity following curvilinear relation, while pore-water velocity was linearly related to water flux. As a result, the water flux had an impact on R . The retardation factor also depended on clay content; it was higher in silt loam than in loamy sand. At higher water fluxes ($>0.5 \text{ cm h}^{-1}$), the difference in R between the soils however diminished. R for NaAsO_2 provided a strong correlation ($r^2 > 0.95$) with the water flux in both soils. For cartap, this relationship was governed by power function ($r^2 = 0.90$) for loamy sand and exponential function ($r^2 = 0.99$) for silt loam; both relations were significant ($p \leq 0.05$). In case of carbendazim, R versus water flux relation followed logarithmic function ($r^2 = 0.92$) and power function ($r^2 = 0.97$) for the corresponding soils; both relations were significant.

Potential mobility of the solutes

The preferred adsorption of one solute with soils over another species is called selective adsorption, and it is dominantly influenced by ionic size of the heavy metals (Elliott *et al.*, 1989). As explained by Adriano (2001), the ionic size and ionic charge as well as hydrolysis properties of the heavy metals influence their sorption to the soil surfaces. The adsorption selectivity sequence of the heavy metals and pesticides in the soils was derived based on their retardation factors. The potential mobility of the heavy metals and pesticides in soils and towards groundwater are summarized in Table 7. Arsenic had the

largest retardation factor while calcium had the lowest value in all soils (Table 5). Arsenic had the lowest potential for transport to groundwater in the soils of the present study, followed by Co. The heavy metals Co, Pb, Cd and the pesticide carbendazim were transported more slowly through the soils compared to Cu, Ni, Zn and cartap. Cartap appeared to be more mobile in soils due to high solubility in water (200 g l^{-1}) and was more easily transported with soil water than less soluble carbendazim. Mobility of the solutes cartap and carbendazim seemed also governed by their organic carbon partition coefficients (K_{oc}) and organic carbon content in addition to by the clay content of the soils. K_{oc} is defined by the ratio of the mass of a chemical that is adsorbed in a soil per unit mass of organic carbon in the soil to the equilibrium chemical concentration in solution. Chemicals having low organic carbon partition coefficients ($K_{oc} < 300 \text{ } \mu\text{g g}^{-1}$) bind less to soil organic matter and are more susceptible to leaching than chemicals having higher K_{oc} values. K_{oc} of carbendazim is in the range 200 – 246 (Dang & Smit, 2008), while the K_{oc} of cartap is much lower (0.12) (PPDB, 2008). However, chemicals with high K_{oc} values may be more susceptible to transport via runoff (McCauley & Jones, 2005). According to the retardation factors, the adsorption affinities of the solutes to the soils were in the order: As > Co > Cd > carbendazim > Pb > Cu > cartap > Zn > Ni > Ca, with Cd and carbendazim exchanging places with Pb and Co, respectively, and Zn with Ni and cartap for some soils. These results agreed well with those of Gomes *et al.* (2001) who showed that heavy metal selectivity sequences varied among soils but the most common sequence was Pb > Cu > Cd > Zn > Ni, with Zn exchanging places with Cd for some soils. This is also in accordance with the selectivity sequence of heavy metal sorption in a natural clay soil containing montmorillonite (single component scenario): Pb > Cu > Cd > Zn (Covelo *et al.*, 2007).

Conclusions

The transport velocity of the solutes, V , of seven heavy metal compounds (NaAsO_2 , $\text{Cd}(\text{NO}_3)_2$, $\text{Pb}(\text{NO}_3)_2$, $\text{Ni}(\text{NO}_3)_2$, ZnCl_2 , CuSO_4 and $\text{Co}(\text{NO}_3)_2$), two pesticides (cartap and carbendazim) and an inert salt (CaCl_2) through eight agricultural soils in Bangladesh decreased and dispersivity, λ , increased, both linearly, with the increase in clay content of the soils. Dispersivity of the solutes decreased with increasing median grain diameter of the soils following power law. Retardation factor, R , also increased with the increase in clay content. The velocity of solute, V , and Peclet number, P , were negatively correlated with the bulk density of soils. Both dispersion coefficient, D , and dispersivity, λ , were positively correlated with the bulk density. V , R and P were positively correlated with soil organic carbon. V , D and P were positively correlated while R , and λ were negatively correlated with soil pH. In most cases, the correlations were significant ($p \leq 0.05$). D and R increased with the increase in the length of travel. Dispersivity of the solutes also increased, but at a decreasing rate, with the length of travel. At higher water fluxes, the difference in R between silt loam and loamy sand became insignificant. Based on retardation factor, the adsorption affinities of the solutes in the soils were obtained as: $\text{As} > \text{Co} > \text{Cd} > \text{carbendazim} > \text{Pb} > \text{Cu} > \text{cartap} > \text{Zn} > \text{Ni} > \text{Ca}$; Cd and carbendazim exchanged places with Pb and Co, respectively, and Zn exchanged place with Ni and cartap for some soils.

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Figure captions

Figure 1 Map of Bangladesh showing the sites of soil sampling.

Figure 2 Measured input and response breakthrough curves of $\text{Co}(\text{NO}_3)_2$ in Mymensingh Loamy sand.

Figure 3 Relationship between dispersivities and median grain diameters of different textured soils for different solutes at average water flux of 0.32 cm h^{-1} .

Figure 4 Variation of retardation factor with the clay content for different solutes through different textured soils at average water flux of 0.32 cm h^{-1} .

Figure 5 Dispersion coefficients (D) for different solutes in two different soils as a function of water flux.

Figure 6 Dispersivity (λ) of different solutes as a function of water flux in two different textured soils.

Figure 7 Retardation factor (R) of different solutes as a function of water flux in two different soils.

Table 1 Properties of CaCl_2 , NaAsO_2 , $\text{Pb}(\text{NO}_3)_2$, $\text{Cd}(\text{NO}_3)_2$, ZnCl_2 , CuSO_4 , $\text{Ni}(\text{NO}_3)_2$ and $\text{Co}(\text{NO}_3)_2$

Sl. No	Solute	Metal salt	Formula	Mol. wt g mol^{-1}	*EC mS m^{-1}
1	Ca	Calcium chloride	$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	147.02	166
2	As	Sodium arsenite	NaAsO_2	312.01	236
3	Pb	Lead nitrate	$\text{Pb}(\text{NO}_3)_2$	331.21	213
4	Cd	Cadmium nitrate	$\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	308.47	207
5	Zn	Zinc chloride	ZnCl_2	136.28	152
6	Cu	Copper sulphate	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	249.68	116
7	Ni	Nickel nitrate	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	290.81	211
8	Co	Cobalt nitrate	$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	291.03	153

* EC was measured at concentration 5 mM and at a temperature of 25°C

Table 2 Some properties of two pesticides (cartap and carbendazim)

Active ingredient	Chemical group	Commercial name	Mol. wt. g mol ⁻¹	Solubility (water) mg l ⁻¹	*EC mS m ⁻¹
Cartap	Cartap hydrochloride	Bravo	273.8	2.0 × 10 ⁵	241
Cabendazim	Carbamate-benzimidazole	Bavistin	191.2	8.0	77

Source: Shanghai Skyblue Chemical Co. Ltd., China

* EC was measured at concentration 5 mM

Table 3 Classification and physicochemical properties of the eight sampled agricultural soils of Bangladesh. The bulk density and saturated hydraulic conductivity of the soils were determined from the repacked samples after solute-transport experiments. The other soil properties were determined by taking samples before using the soils in transport experiments.

Locations	Textural classes	USDA classification	Bulk density (g cm ⁻³)	Organic C (%)	%Clay	Soil pH	Soil EC (mS m ⁻¹)	Saturated hydraulic conductivity (cm d ⁻¹)
Mymensingh (LS)	Loamy sand	AericHaplaquepts	1.36	0.767	6.04	7.36	3.95	133.68
Mymensingh (SL)	Silt loam	AericHaplaquepts	1.33	0.686	11.44	7.45	5.53	21.06
Dinajpur	Sandy loam	UdicUstochrepts	1.33	0.452	8.50	7.58	4.78	83.41
Bogra	Silt loam	AericFluvaquents	1.29	0.753	10.68	7.38	4.63	51.33
Gazipur	Silt loam	AericFluvaquents	1.40	0.523	12.68	7.01	16.45	17.32
Rajshahi	Silt	AquicEutrochrepts	1.34	0.787	13.36	7.07	9.48	17.68
Comilla	Silt loam	AquicUdifluvents	1.37	0.372	15.48	6.32	15.24	16.36
Satkhira	Silt loam	AquicEutrochrepts	1.32	0.840	19.12	6.85	17.74	15.46

Table 4 Clay content and grading parameters of eight agricultural soils of different locations in Bangladesh. Also given in this table is the dispersivity of NaAsO_2 as an example

Sl. No.	Locations	%Clay	D_{10} (mm)	D_{50} (mm)	D_{60} (mm)	Uniformity coefficient (C_u)	Dispersivity (cm) of As (λ)
1	Mymensingh (LS)	6.04	0.085	0.235	0.278	3.271	0.26
2	Mymensingh (SL)	11.44	0.048	0.101	0.157	3.257	0.31
3	Dinajpur	8.50	0.073	0.200	0.261	3.575	0.28
4	Bogra	10.68	0.052	0.112	0.173	3.302	0.30
5	Gazipur	12.68	0.035	0.095	0.135	3.857	0.32
6	Rajshahi	13.36	0.029	0.069	0.085	2.982	0.32
7	Comilla	15.48	0.031	0.066	0.082	2.629	0.34
8	Satkhira	19.12	0.028	0.062	0.079	2.784	0.34

D_{10} = effective grain diameter (mm), D_{50} = median grain diameter (mm), D_{60} = grain diameter at 60% passing (mm)

Table 5 Velocity of solute/pore-water (V , cm h⁻¹), dispersion coefficient (D , cm h⁻²), dispersivity (λ , cm) and retardation factor (R) of ten solutes in eight agricultural soils of Bangladesh.

Locations	Para- meters	Solutes									
		Ca	As	Pb	Cd	Ni	Zn	Cu	Co	Cartap	Carben.
Mymensingh (LS)	V	0.94	0.73	0.77	0.80	0.82	0.86	0.81	0.74	0.88	0.80
Mymensingh (SL)	V	0.71	0.57	0.61	0.60	0.65	0.63	0.63	0.59	0.65	0.60
Dinajpur	V	0.83	0.65	0.68	0.70	0.73	0.76	0.72	0.66	0.76	0.71
Bogra	V	0.76	0.60	0.64	0.64	0.69	0.69	0.67	0.62	0.70	0.64
Gazipur	V	0.66	0.52	0.56	0.55	0.60	0.59	0.59	0.55	0.60	0.56
Rajshahi	V	0.66	0.50	0.53	0.52	0.57	0.56	0.56	0.52	0.56	0.53
Comilla	V	0.59	0.45	0.48	0.48	0.53	0.52	0.51	0.48	0.51	0.48
Satkhira	V	0.54	0.41	0.44	0.44	0.49	0.48	0.47	0.44	0.47	0.44
Mymensingh (LS)	D	0.24	0.24	0.18	0.16	0.13	0.16	0.14	0.26	0.16	0.13
Mymensingh (SL)	D	0.19	0.24	0.16	0.14	0.12	0.14	0.13	0.24	0.14	0.12
Dinajpur	D	0.23	0.24	0.17	0.14	0.13	0.15	0.14	0.25	0.15	0.12
Bogra	D	0.19	0.23	0.17	0.14	0.12	0.15	0.13	0.24	0.15	0.12
Gazipur	D	0.19	0.23	0.16	0.14	0.12	0.15	0.12	0.24	0.14	0.12
Rajshahi	D	0.18	0.22	0.15	0.14	0.11	0.14	0.12	0.23	0.14	0.12
Comilla	D	0.17	0.22	0.15	0.14	0.11	0.15	0.12	0.22	0.14	0.12
Satkhira	D	0.16	0.20	0.14	0.13	0.10	0.14	0.11	0.20	0.13	0.11
Mymensingh (LS)	λ	0.26	0.26	0.19	0.17	0.14	0.17	0.15	0.28	0.17	0.14
Mymensingh (SL)	λ	0.25	0.31	0.21	0.18	0.16	0.19	0.16	0.31	0.19	0.16
Dinajpur	λ	0.27	0.28	0.20	0.17	0.15	0.18	0.16	0.29	0.18	0.14
Bogra	λ	0.24	0.30	0.20	0.18	0.15	0.18	0.16	0.30	0.18	0.15
Gazipur	λ	0.26	0.32	0.22	0.19	0.16	0.20	0.17	0.32	0.20	0.16
Rajshahi	λ	0.26	0.32	0.22	0.20	0.16	0.21	0.18	0.33	0.20	0.17
Comilla	λ	0.27	0.34	0.24	0.22	0.18	0.23	0.19	0.35	0.22	0.18
Satkhira	λ	0.27	0.34	0.24	0.22	0.17	0.24	0.19	0.35	0.22	0.19
Mymensingh (LS)	R	1.01	1.30	1.24	1.19	1.16	1.11	1.17	1.28	1.08	1.18
Mymensingh (SL)	R	1.09	1.37	1.27	1.30	1.19	1.22	1.22	1.32	1.19	1.28
Dinajpur	R	1.03	1.31	1.25	1.23	1.18	1.12	1.18	1.30	1.11	1.20
Bogra	R	1.07	1.35	1.27	1.28	1.18	1.18	1.21	1.31	1.17	1.27
Gazipur	R	1.09	1.39	1.30	1.31	1.20	1.23	1.23	1.33	1.21	1.30
Rajshahi	R	1.04	1.39	1.31	1.33	1.21	1.23	1.24	1.34	1.23	1.31
Comilla	R	1.07	1.41	1.33	1.33	1.20	1.23	1.24	1.34	1.24	1.33
Satkhira	R	1.10	1.44	1.35	1.34	1.22	1.24	1.25	1.35	1.26	1.35

Table 6 Relationship of dispersion coefficient (**D**), dispersivity (λ) and retardation factor (**R**) with length of travel path (L') for different solutes along with coefficient of determination (r^2) and significance level (p).

Metal in solution	Depth (cm) vs. D (cm ² /h)	Depth (cm) vs. λ (cm)	Depth (cm) vs. R (cm)
Ca	$D = 0.2039\ln(L') - 0.2028$ ($r^2 = 0.97$, p = 1%)	$\lambda = 0.1523\ln(L') - 0.1562$ ($r^2 = 0.97$, p = 1%)	$R = 0.9056L'^{0.0547}$ ($r^2 = 0.59$, p = ns)
As	$D = 0.107\ln(L') - 0.0091$ ($r^2 = 0.98$, p = 5%)	$\lambda = 0.0807\ln(L') - 0.0075$ ($r^2 = 0.96$, p = 5%)	$R = 0.2654\ln(L') + 1.4297$ ($r^2 = 0.98$, p = 5%)
Pb	$D = 0.0855L'^{0.2943}$ ($r^2 = 0.97$, p = 1%)	$\lambda = 0.068L'^{0.2636}$ ($r^2 = 0.98$, p = 1%)	$R = 2.1107L'^{0.0374}$ ($r^2 = 0.98$, p = 5%)
Cd	$D = 0.0111L' + 0.0686$ ($r^2 = 0.99$, p = 1%)	$\lambda = 0.0086L' + 0.0494$ ($r^2 = 0.99$, p = 1%)	$R = 0.0272L' + 1.8202$ ($r^2 = 0.85$, p = 5%)
Ni	$D = 0.0125L' + 0.1229$ ($r^2 = 0.98$, p = 1%)	$\lambda = 0.0086L' + 0.1008$ ($r^2 = 0.95$, p = 1%)	$R = 2.2861L'^{0.0203}$ ($r^2 = 0.96$, p = 5%)
Zn	$D = 0.1031\ln(L') - 0.0109$ ($r^2 = 0.99$, p = 5%)	$\lambda = 0.074\ln(L') - 0.0035$ ($r^2 = 0.98$, p = 5%)	$R = 0.2094\ln(L') + 1.7822$ ($r^2 = 0.97$, p = 5%)
Cu	$D = 0.234e^{0.0384L'}$ ($r^2 = 0.99$, p = 1%)	$\lambda = 0.1778e^{0.0382L'}$ ($r^2 = 0.99$, p = 1%)	$R = 2.1601e^{0.0035L'}$ ($r^2 = 0.96$, p = 1%)
Co	$D = 0.0026L' + 0.1799$ ($r^2 = 0.99$, p = 1%)	$\lambda = 0.0013L' + 0.1557$ ($r^2 = 0.98$, p = 1%)	$R = 2.833e^{0.0011L'}$ ($r^2 = 0.97$, p = 1%)
Pesticide solution			
Cartap	$D = 0.1196e^{0.0247L'}$ ($r^2 = 0.92$, p = 5%)	$\lambda = 0.0912e^{0.0239L'}$ ($r^2 = 0.84$, p = 5%)	$R = 1.7994e^{0.0047L'}$ ($r^2 = 0.76$, p = ns)
Carbendazim	$D = 0.1024L'^{0.1517}$ ($r^2 = 0.97$, p = 1%)	$\lambda = 0.0784L'^{0.1368}$ ($r^2 = 0.95$, p = 1%)	$R = 1.7573L'^{0.0713}$ ($r^2 = 0.93$, p = 5%)

Table 7 Pollution potentiality of solutes in soils and groundwater based on retardation factors of the solutes

Soil	Selectivity sequence of solute transport	High potential for accumulation in soil	High potential for transportation through soils
Mymensingh loamy sand	As>Co>Pb>Cd>carbendazim>Cu>Ni>Zn>cartap>Ca	As, Co, Pb, Cd, carbendazim	Ca, Cu, Ni, Zn, cartap
Mymensingh silt loam	As>Co>Cd>carbendazim>Pb>Zn>Cu>Ni>cartap>Ca	As, Co, Cd, carbendazim, Pb	Ca, Zn, Cu, Ni, cartap
Dinajpur sandy loam	As>Co>Pb>Cd>carbendazim>Cu>Ni>Zn>cartap>Ca	As, Co, Pb, Cd, carbendazim	Ca, Cu, Ni, Zn, cartap
Bogra silt loam	As>Co>Cd>carbendazim>Pb>Cu>Zn>Ni>cartap>Ca	As, Co, Cd, carbendazim, Pb	Ca, Cu, Zn, Ni, cartap
Gazipur silt loam	As>Co>Cd>carbendazim>Pb>Cu>Zn>cartap>Ni>Ca	As, Co, Cd, carbendazim, Pb	Ca, Cu, Zn, cartap, Ni
Rajshahi silt	As>Co>Cd>carbendazim>Pb>Cu>cartap>Zn>Ni>Ca	As, Co, Cd, carbendazim, Pb	Ca, Cu, cartap, Zn, Ni
Comilla silt loam	As>Co>carbendazim>Cd>Pb>Cu>cartap>Zn>Ni>Ca	As, Co, carbendazim, Cd, Pb	Ca, Cu, cartap, Zn, Ni
Satkhira silt loam	As>carbendazim>Pb>Co>Cd>cartap>Cu>Zn>Ni>Ca	As, carbendazim, Pb, Co, Cd	Ca, cartap, Cu, Zn, Ni

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7