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A Study on Vertical Transport of Zinc and Cadmium in Some Alluvial Soils of West Bengal, India

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Abstract

A study on vertical transport of aqueous Zinc (Zn) and Cadmium (Cd) in soil system has been carried out at the soil science laboratory of Uttar Banga Krishi Viswavidyalaya, Pundibari, Cooch Behar, West Bengal, India. Aqueous solution of Zn and Cd are vertically leached down through the soils collected from Pundibari (Agroecological zone 15.1, climate: sub-humid) and Malda (Agroecoloogical zone 15.1, climate: sub-tropical humid) in a double-chambered glass column. The similar procedure has been repeated for the soils collected from both places separately mixing with farm yard manure. The formation of the Breakthrough Curves (BTCs) for Zinc in Pundibari soils at 0.97 pore volume (Pv), while at 0.85 (Pv) in soil treated with FYM. The BTCs for Malda was at 0.49 (Pv), and that in soils treated with FYM was at 0.36 (Pv), while the BTCs for Cadmium at 0.96 (Pv) for Pundibari soil and that at 0.83 (Pv) for soil treated with FYM were observed. The order of time of dilution in both the cases using Zinc and Cadmium solution in the leachate followed as: Malda (Soil+FYM) > Pundibari (Soil+FYM) > Malda (Soil) > Pundibari (Soil) respectively. The capacity of soil mixed with FYM was found to be an effective sink for metals like Zinc and Cadmium and thus moderating the toxic effects of Zn and Cd in soils.

Keywords: Zinc, Cadmium, Transport, Breakthrough Curve, Soil Pollution, Metal sink, Metal Toxicity

I. INTRODUCTION

Contamination from soil-borne heavy metals, i.e., Nickel (Ni), lead (Pb), cadmium (Cd), chromium (Cr), copper (Cu), cobalt (Co), zinc (Zn), manganese (Mn), aluminium (Al), and mercury are heavy metal(loid)s that are typically found in soils has grown to be a major issue in many parts of the world in recent years. Due to heavy metals produced by both natural and anthropogenic sources, investigations linked to agricultural and urban soil contamination garnered particular attention (Song *et al.*, 2018; Stevanovi*et al.*, 2018). Heavy metal pollution has worsened due to industrial effluents, residential trash, extensive fertiliser use, and automotive exhaust emissions as a result of the world's rapid expansion of agriculture and industry (Song *et al.*, 2018; Zheng *et al.*, 2018; Adimalla, 2019). The studies on heavy metals in agricultural soil are therefore extremely concerning for two main reasons: (i) The main source of consumption directly through the various food products, such as vegetables, fruits, rice, and wheat, which may pose health risks, is the polluted agricultural food chain. (ii) Heavily accumulated heavy metals leak into the groundwater system through the pore spaces, degrading the quality of the water, which has an immediate negative impact on human health when consumed (Adimalla, 2018; Adimallaand Wang, 2018; Keshavarziet *al*., 2018).

According to Goldschmidt (1954), the lithosphere has an average zinc level of around 80 ppm. It was reported that (Swaine, 1955; Jensen and Lamm, 1959), soil zinc concentrations typically vary from 10 to 300 ppm. As per the standard set up by Environmental Protection Agency (EPA), drinking water should contain no more than 5 mg/L of Zinc. Due to its concentration, zinc may undoubtedly be categorised as a trace element in soil, because zinc only exhibits the single valence state of Zn^{2+} in natural surroundings, with lesser complexity than that of many other heavy metals. Zn^{2+}often exhibits 4-coordination in mineral formations, while 6-coordination with oxygen can occur in some minerals (Krauskopf, 1972).

A non-essential trace element that is abundantly present in the environment is cadmium (Cd). Cadmium concentrations in soils and groundwater, which are crucial for ensuring wholesome food supply and safe drinking water, can be increased by both geogenic and anthropogenic causes. High Cadmium dosages can cause human cancer. A recommended guideline value of 3 g/L for Cadmium is provided by the World Health Organisation (WHO) for Drinking-Water Quality. The usage of Cadmium-containing fertilisers, atmospheric deposition of combustion emissions, and mining are a few significant anthropogenic sources of Cadmium. In addition to anthropogenic sources of Cadmium, it is also incorporated into sulphides, carbonates, and phosphorites, causing elevated Cadmium concentrations in related rock types.

When heavy metals accumulate in soils as a result of human activity, they may seep out of the soil and contaminate surface and groundwater, endangering aquatic ecosystems, drinking water supplies, and people (Hoodaand Alloway, 1993).In order to evaluate the fate of heavy metals in soil profiles and also to make predictions about how much heavy metal will leach when applied to soil, research on the leaching of heavy metals from soils is crucial. The majority of the knowledge about heavy metal transport comes from research that used single heavy metal solutions (Ramrez-Perez *et al.*, 2013). Ions in solution and those adsorbed onto the soil surface compete for space during the sorption of heavy metals. Single heavy metal solutions have limited applications in this context (Garrido-Rodriguez *et al.*, 2014).

Agricultural soils are treated with organic materials like FYM, compost, sludge, and crop residues to improve soil fertility, boost crop yield, and lessen soil salinity (Westermanand Bicudo, 2005;Jalaliand Ranjbar, 2009). However, adding organic amendments could change the mobility and toxicity of heavy metals. Jalaliand Jalali(2011), Jalaliand Rostaei(2012), and Jalaliand Aboulghazi(2013) reported on the utilisation of organic amendments as adsorbents for the removal of heavy metals.

The interaction between metals and soil, which primarily involves complexation, surface adsorption, exchange reactions, chelation, and precipitation of metal ions in the soil particle surface of diffusion into the mesopores and macropores, causes the transformation of highly soluble forms into less soluble ones (Hoodaand Alloway, 1993; Jalaliand Khanlari, 2007; Ma *et al.*, 2006). There is very little information on the release kinetics of metals like cadmium and zinc in soil, especially when it comes to rice soil. In many cases, metal contaminants are first held in the soil's top layer before being transported to the lower layer by untimely leaching water (particularly large volumes of rainwater, irrigation water, etc.). West Bengal (India) is the leading producer of rice and is known as the rice bowl of the country. It is an essential staple food for the people living in this state. Boro rice has a considerable contribution to the percentage share of total rice production in the state. But the areas of Pundibari of Coochbehar and Malda is deficient in some plant nutrients viz, P, B, Zn, Cd and Mo etc. The soils of Pundibari are mostly acidic in reaction, sandy to sandy - loam in texture and contains Fe and Al oxides and hydroxides, whereas, the soils of Malda are mostly alkaline, clayey loam in texture. The native Zinc and Cadmium content in these soils are low. The relative availability of these metals depends upon the physical and chemical properties of soils as well as the interaction mechanism of these metals with soil. In order to appropriately assess their contamination risk and to develop effective remediation techniques, it is crucial to comprehend the heavy metals' transformation and transport mechanisms in soil. Now-a-days, organic matter in the form of FYM, compost, crop residues etc. are being widely used for maintaining soil quality and health and due to their ability to combine with metals to produce chelates and insoluble complexes, organic substances play an essential role in the interactions of heavy metals in soil environments, in retarding their mobility and thus helping to mitigate contaminated soils.Based on the above perspectives, the present study was conducted to find out the effect of organic matter on retention of Zinc and Cadmium in soils having different textures.

II. METHODOLOGY

Preparation of Soil sample:

Two sample sitesnamely Pundibari(Hill and Terai Zone) (26.3927º N latitude, 89.3824º E longitude, elevation 43 m above Mean Sea Level) and Malda(Old Alluvial Zone) (25° 13' 0.48" N latitude, 87° 55' 28.56" E longitude, elevation 25 m above Mean Sea Level)of West Bengal (India) were selected (**Figure1**) and approximately 10 kg soil from each site was collected from the surface layer (0–20 cm). Each soil sample was carefully broken up by hand using a hammer, and then air-dried in the laboratory at room temperature to a constant weight. While removing the coarse litter and plant detritus, care was taken to prevent soil loss. A 2-mm brass sieve was then used to prepare the soil sample. The composite soil samples were then placed in polybags with the appropriate labelling for further analysis in the laboratory.

Analysis of physico-chemical properties of soil:

During this experiment, the analysis of various soil parameters like texture, pH, EC, oxidizable organic carbon, N, P, K of soil samples were done following standard methods mentioned below:

Soil pH: A glass electrode-pH metre was used to measure the pH of soil samples in suspensions (soil: water: 1.2.5). (Jackson, 1967).
Electrical Conductivity (EC): A digital conductivity metre made by was used to test electrical conductivity in soil water suspensions (soil: water 1:2.5) (Jackson, 1967).
Oxidizable Organic Carbon (OC): The Walkley and Black (1934) titration method was used to quantify the amount of oxidizable organic carbon in soils (Nelson and Sommers, 1982).

Available Nitrogen (N): The alkaline $KMnO_4$ method devised by Subbiah and Asija (1956) was used to measure the amount of available nitrogen (Saha, 2008).

Available Phosphorus (P): Available P content was determined by two methods. By extracting the soil with a mixture of 0.03 M NH_4F and 0.025 M HCl (Bray and Kurtz, 1945) and by extracting the soil with 0.5N $NaHCO_3$ at pH 8.5 (Olsen and Sommers, 1982), followed by colorimetric measurement using spectrophotometer (Black,1965).

Available Potassium (K): A neutral normal ammonium acetate extractant was used to extract the soils, and the concentration of available K of soil was estimated by flame photometer (Black, 1965).

Extractable zinc (Zn) and cadmium (Cd): Ten gram of air dried soil and 20 ml of 0.005 M DTPA solution adjusted at pH 7.3 (Soil: extractant: 1:2) were taken in 125 ml plastic bottle and shaken for 2 hours (Lindsay and Norvel,1978) in a reciprocating shaker. The suspension was filtered through Whatman No. 42 filter paper and the filtrate was analyzed for Zn and Cd using Atomic Absorption Spectrophotometer (AAS).

Mechanical Analysis of soils: The Bouyoucos (1962) hydrometer method was used to determine the clay content of soils (Dewis and Freitas, 1984). The distribution of sand, silt, and clay particle sizes provided additional information about the soil textures.

Soil column Experiment: According to Balseiro-Romeroa*et al.*, (2016), Hattab*et al.*, (2015), and Jordan *et al.*, (2017), laboratory soil column leaching experiments can mimic natural conditions and are frequently used to provide information about the risk of leaching of potential pollutants and nutrients from soils and technosols into surface water and groundwater. The Soil column experiment was conducted using glass columns of 27.03 mm diameter, and 50 cm in length. The columns were set up for each soil sample (Pundibari and Malda) having two replications each. The upper column was fitted into the lower column through a B-34/35 standard joint. The bottom of the lower column was closed by a G-4 sintered glass disc and on the top of that a Whatman No. 42 filter paper was placed forming the base of the soil column. The air-dried soil samples were weighed and filled into the column, simultaneously another column was filled with air-dried soil mixed with decomposed Farm yard Manure (composition N:P:K:Zn:Cd :: 0.56% : 0.3% : 0.75% : 0.65 mg/kg : 0.05mg/kg) at 10% by weight of soil maintaining their natural bulk density of 1.31 g/cc. Zinc and Cadmium solutions of 100 mg/L prepared from the salt of $ZnSO_4$ and $CdCl_2$ respectively were added to each of the soil columns from the top by means of a Marriot arrangement which was attached to the upper column by a standard joint and the solutions were allowed to leach after getting fully saturated and 10 leaching events were carried out. Following the leaching experiment, the soil columns were allowed to air dry at room temperature before dismantling them. Leachate from each leaching events were collected in bottles for analysis of Zn and Cd concentrations using Atomic absorption spectrophotometer.

Statistical and graphical Interpretations;

The necessary statistical computations were performed using SPSS version 21.0 (SPSS, Inc., Chicago, IL, USA), OP STAT and R software. Necessary graphical representations were done using Microsoft Excel 2019.

III. RESULTSAND DISCUSSION

The results obtained from the column study were plotted *via* Break through Curve (BTC), with the ratio (C/C_0) against the number of pore volumes, P_V, of the leachate collected, obtained from Eq. A.1 which is as;

$$P_V = \frac{V}{V_0} \qquad \text{...... } \mathbf{Eq.\ (A.1)}$$

Where C_0 is the initial concentration of the solution and C is the concentration of the leachate at the specific interval and 'V' is the volume of the leachate collected in a given time 't' and $V_{0,}$ is the volume of the voids, which was obtained from the Eq. A.2;

$$V_0 = nV_1\mathrm{V_0} \qquad \text{....... } \mathbf{Eq.\ (A.2)}$$

Where 'n' is the water filled porosity at the given time and V_1 is the total volume of the soil column.

Initial physico-chemical properties of soils:

The soil samples were collected from two experimental sites Pundibari of Coochbehar district and from Malda district of West Bengal (India). The soils from the sampling site Pundibari were found to be acidic in reaction with the pH value 5.48 (**Table 1**), whereas for Malda soils it was found to be alkaline in nature with a pH value of 7.51 (**Table 1**). The organic carbon and electrical conductivity value were found to be 4.1 g/kg, 3.7 g/kg and 0.81 dSm^{-1} and 0.38 dsm^{-1} (**Table 1**)for samples collected from Pundibari and Malda respectively. The available Nitrogen, Phosphorus and Potassium content of the soils were 272.83 kg/ha, 174.05 kg/ha; 24.24 kg/ha, 59.54 kg/ha and 102.56 kg/ha, 240.03 kg/ha respectively in the soils of Pundibari and Malda while the CEC [(cmolp+kg^{-1}] were 6.5 and 11.6 in the soils of Pundibari and Malda respectively (**Table 1**). For soil samples collected from Pundibari the percent sand, silt and clay were recorded to be 55.03, 32.12 and 12.85 % respectively, suggesting a Sandy loam texture (**Table 1**) and for samples collected from Malda, the sand, silt and clay % were found to be 35.60%, 25.24% and 39.16% respectively, thus falling into the textural class Clayey loam (**Table 1**). The pore volume of the soils collected from Pundibari and Malda were recorded 160.0 and 130.5 respectively (**Table 2**). The experiment was conducted with an initial concentration of 100 mg/lit., of Zn and Cd maintaining a bulk density of 1.31 g/cc for the soils collected from both the sampling sites inside the column.

Table 1. Initial physico-chemical properties of soil sample

Physico-chemical Properties	**Pundibari**	**Malda**
Sand (%)	55.03	35.60
Silt (%)	32.12	25.24
Clay (%)	12.85	39.16
Textural class	Sandy loam	Clayey loam
pH (Soil:Water::1:2.5)	5.48	7.51
EC (dSm^{-1})	0.81	0.38

Organic carbon (g/kg)	4.1	3.7
Available N (kg/ha)	272.83	174.05
Available P (kg/ha)	24.24	59.54
Available K (kg/ha)	102.56	240.03
CEC [cmol(p+)kg^{-1}]	6.1	11.6
DTPA extractable Zn (mg/kg)	1.04	0.26
DTPA extractable Cd (mg/kg)	0.46	0.14

Table 2. Transport parameters under column experiment

Sampling site	**Initial concentration of metals (mg/lt)**	**Length of the column (cm)**	**Bulk density of soil in the column (g/cc)**	**Pore Volume**
Pundibari	100	50	1.31	160.0
Malda	100	50	1.31	130.5

DTPA- Extractable metal concentrations of the studied soil:

The DTPA-Extractable metal concentration of Zinc for the soils of Pundibari and Malda were found to be 1.04 mg/kg and 0.26 mg/kg (**Table 1**) suggesting the soils were having low concentration of Zinc. The extractable-Cadmium was recorded 0.26 mg/kg and 0.14 mg/kg respectively for samples collected from Pundibari and Malda, suggesting the presence of low concentration of the metal in both the sites.

Table 3. Cumulative Effect of Duration (Days) and FYM application on Zn and Cd adsorption in Soils collected from Pundibari

Treatment	**Initial Zn conc. (mg/l)**	**Conc. of Zn in lechate (mg/l)**	**C/C° (Zn)**	**Times of dilution**	**Initial Cd conc. (mg/l)**	**Conc. of Cd in lechate (mg/l)**	**C/C° (Cd)**	**Times of dilution**
S1-1	100	56.29^{a}	0.562^{a}	1.78	100	37.07^{a}	0.370^{a}	2.70
S1-2		55.28^{ab}	0.552^{ab}	1.81		36.04^{ab}	0.360^{ab}	2.77
S1-3		52.26^{b}	0.5226^{b}	1.91		35.99^{ab}	0.359^{ab}	2.78
S1-4		49.84^{bc}	0.498^{bc}	2.01		35.89^{ab}	0.358^{ab}	2.79
S1-5		45.62^{c}	0.456^{c}	2.19		32.82^{b}	0.328^{b}	3.05
S1-6		43.50^{cd}	0.435^{cd}	2.30		26.62^{c}	0.266^{c}	3.76
S1-7		39.15^{d}	0.391^{d}	2.55		24.30^{cd}	0.243^{cd}	4.12
S1-8		38.10^{d}	0.380^{d}	2.62		22.07^{d}	0.220^{d}	4.53
S1-9		37.04^{d}	0.370^{d}	2.70		21.02^{e}	0.210^{e}	4.76

S1-10		36.04^{d}	0.360^{d}	2.77		19.90^{de}	0.199^{de}	5.03
Mean	-	**45.31**	**0.453**	**2.26**	-	**29.17**	**0.292**	**3.63**
Sd	-	**7.72**	**0.08**	**0.38**	-	**7.05**	**0.07**	**0.88**
SE(m) ±	-	**2.441**	**0.024**	**0.120**	-	**2.230**	**0.022**	**0.277**
S1+F-1	100	24.04^{e}	0.240^{e}	4.16	100	19.56^{e}	0.195 e	5.11
S1+F-2		23.99^{ef}	0.239^{ef}	4.17		18.54^{ef}	0.185^{ef}	5.39
S1+F-3		22.96^{f}	0.229^{f}	4.36		15.50^{f}	0.155^{f}	6.45
S1+F-4		21.89^{fg}	0.218^{fg}	4.57		14.49^{f}	0.1449^{f}	6.90
S1+F-5		20.94^{g}	0.209^{g}	4.78		12.44^{fg}	0.124^{fg}	8.04
S1+F-6		19.75^{gh}	0.197^{gh}	5.06		11.25^{g}	0.112^{g}	8.89
S1+F-7		19.35^{h}	0.193^{h}	5.17		9.95^{h}	0.099^{h}	10.05
S1+F-8		19.16^{h}	0.191^{h}	5.22		9.94^{h}	0.099^{h}	10.06
S1+F-9		18.95^{h}	0.189^{h}	5.28		8.80^{hi}	0.088^{hi}	11.36
S1+F-10		18.21^{h}	0.182^{h}	5.49		8.76^{hi}	0.087^{hi}	11.42
Mean	-	**20.92**	**0.209**	**4.82**	-	**12.92**	**0.129**	**8.37**
Sd	-	**2.17**	**0.02**	**0.49**	-	**3.94**	**0.04**	**2.35**
SE(m) ±	-	**0.687**	**0.007**	**0.154**	-	**1.246**	**0.012**	**0.742**

[S1 = Pundibari soil; S1-1,…,S1-10 = 1st day,…,10th day after leaching the untreated soil with metal solutions; S1+F1,…S1+F10 = 1st day,…,10th day after leaching the FYM treated soil with metal solutions. C_0 = Initial conc. of metals in solution, C = conc. of metals at the collected lechates at respective days; Values with different superscripted alphabets are significantly different from each other according to the Duncan Multiple Range Test (DMRT) ($P < 0.05$). Each value is a mean value. Conc. = Concentration.]

Table 4. Cumulative Effect of Duration (Days) and FYM application on Zn and Cd adsorption in Soils collected from Malda

Treatment	Initial Zn conc. (mg/l)	Conc. of Zn in lechate (mg/l)	C/C_0 (Zn)	Times of dilution	Initial Cd conc. (mg/l)	Conc. of Cd in lechate (mg/l)	C/C° (Cd)	Times of dilution
S2-1	100	39.98^{a}	0.399^{a}	2.50^{a}	100	25.85^{a}	0.258^{a}	3.87
S2-2		38.88^{ab}	0.388^{ab}	2.57^{ab}		25.85^{a}	0.258^{a}	3.87
S2-3		37.84^{b}	0.378^{b}	2.64^{b}		25.65^{a}	0.256^{a}	3.90
S2-4		36.65^{bc}	0.366^{bc}	2.73^{bc}		25.24^{ab}	0.252^{ab}	3.96
S2-5		36.60^{bc}	0.366^{bc}	2.73^{c}		25.03^{ab}	0.250^{ab}	4.00
S2-6		35.49^{c}	0.354^{c}	2.82^{d}		24.94^{ab}	0.249^{ab}	4.01
S2-7		30.87^{d}	0.308^{d}	3.24^{de}		24.64^{ab}	0.246^{ab}	4.06
S2-8		29.80^{de}	0.298^{de}	3.36^{e}		20.50^{b}	0.205^{b}	4.88
S2-9		28.70^{e}	0.287^{e}	3.48^{e}		19.99^{bc}	0.199^{bc}	5.00
S2-10		28.03^{e}	0.280^{e}	3.57^{f}		19.44^{c}	0.194^{c}	5.14
Mean	-	**34.28**	**0.342**	**2.96**	-	**23.71**	**0.237**	**4.27**
Sd	-	**4.48**	**0.045**	**0.40**	-	**2.62**	**0.02**	**0.49**

SE(m) ±	-	**1.417**	**0.014**	**0.128**	-	**0.828**	**0.008**	**0.155**
S2+F-1	100	23.66^{f}	0.236^{f}	4.23^{f}	100	12.49^{d}	0.124^{d}	8.01
S2+F-2		23.05^{fg}	0.230^{fg}	4.34^{fg}		12.49^{d}	0.124^{d}	8.01
S2+F-3		22.99^{fg}	0.229^{fg}	4.35^{fg}		12.85^{d}	0.124^{d}	7.78
S2+F-4		22.63^{fg}	0.226^{fg}	4.42^{fg}		11.99^{de}	0.119^{de}	8.34
S2+F-5		21.92^{g}	0.219^{g}	4.56^{g}		11.87^{de}	0.118^{de}	8.42
S2+F-6		21.92^{g}	0.219^{g}	4.56^{g}		11.72^{de}	0.117^{de}	8.53
S2+F-7		20.95^{gh}	0.209^{gh}	4.77^{gh}		10.97^{e}	0.109^{e}	9.12
S2+F-8		16.88^{h}	0.168^{h}	5.92^{h}		10.80^{e}	0.108^{e}	9.26
S2+F-9		16.22^{h}	0.162^{h}	6.17^{h}		8.37^{f}	0.083^{f}	11.95
S2+F-10		16.09^{h}	0.160^{h}	6.22^{h}		8.12^{f}	0.081^{f}	12.32
Mean	-	**20.63**	**0.206**	**4.95**	-	**11.17**	**0.111**	**9.17**
Sd	-	**3.02**	**0.03**	**0.81**	-	**1.67**	**0.02**	**1.63**
SE(m) ±	-	**0.955**	**0.010**	**0.256**	-	**0.528**	**0.005**	**0.515**

[S2 = Malda soil; S2-1,…,S2-10 = 1st day,…,10th day after leaching the untreated soil with metal solutions; S2+F1,…S2+F10 = 1st day,…,10th day after leaching the FYM treated soil with metal solutions. C_0 = Initial conc. of metals in solution, C = conc. of metals at the collected lechates at respective days; Values with different superscripted alphabets are significantly different from each other according to the Duncan Multiple Range Test (DMRT) ($P < 0.05$). Each value is a mean value. Conc. = Concentration.]

Table 5. Comparison between Zn and Cd adsorption by Soil and (Soil+FYM) in Pundibari and Malda

	Avg. values					
Soil	**Leachate concentration of Zn (mg/l)**	**C/C_0 (Zn)**	**Times of Dilution (Zn solution)**	**Leachate concentration of Cd (mg/l)**	**C/C_0 (Cd)**	**Times of Dilution (Cd solution)**
Pundibari (S1)	45.31^{a}	0.453^{a}	2.26^{d}	29.17^{a}	0.292^{a}	3.63^{d}
Pundibari (S1+F)	20.92^{c}	0.209^{c}	4.82^{b}	12.92^{c}	0.129^{c}	8.37^{b}
Malda (S2)	34.28^{b}	0.342^{b}	2.96^{c}	23.71^{b}	0.237^{b}	4.27^{c}
Malda (S2+F)	20.63^{d}	0.206^{d}	4.95^{a}	11.17^{d}	0.111^{d}	9.17^{a}
LSD (P=0.05)	**7.488**	**0.075**	**0.857**	**6.648**	**0.066**	**2.303**
SE(m) ±	**2.476**	**0.025**	**0.284**	**2.199**	**0.022**	**0.761**

[Values with different superscripted alphabets are significantly different from each other according to the Duncan Multiple Range Test (DMRT) ($P < 0.05$). Each value is a mean value. S1 and S2 = Untreated soils collected from Pundibari and Malda respectively; S1+F or S2+F = Respective soils Soils treated with FYM; (S2+F)= Soil treated with FYM.]

Experimental Breakthrough curve of Pundibari (Soil; Soil+FYM) and Malda (Soil; Soil+FYM) using Zn and Cadmium Solution:

The nature of shapes of BTC (Break Through Curve) were similiar for both the heavy metals and for both the treatments i.e, soil and soil along with FYM. The apparently sigmoid shaped breakthrough curves for Zinc and Cadmium solution in the given soils indicated the hydrodynamic dispersion of the solute between the soil and the flowing medium. A shift in the breakthrough curve towards the left of the inflexion point (at $P_V = 1$) was observed in soils experimenting elsewhere , suggesting a degree of retention by the soils (Mukhopadhyay and Sanyal, 2002).

In case of soils of Pundibari, the breakthrough for Zinc occurred at 0.97 pore volume (**Figure2a**) whereas in Pundibari soil treated with FYM, the breakthrough occurred at 0.85 pore volume (**Figure2b**) indicating more retention of Zinc by soil treated with FYM as compared to control soil. While in case of soils collected from Malda the breakthrough was observed at 0.49 pore volume (**Figure2c**) and for the soils treated with FYM the breakthrough occurred at 0.36 pore volume (**Figure2d**) indicating more retention of metal Zinc by the later.

In case of leaching using Cadmium solution, for soil of Pundibari , the breakthrough was at 0.96 pore volume (**Figure3a**), and for soil treated with FYM, it occurred at 0.83 pore volume (**Figure3b**) where, adsorption being more in case of former. For Malda situation, the breakthrough was observed at 0.48 pore volume (**Figure3c**), and for soil treated with FYM it was detected at 0.34 pore volume (**Figure3d**), thus more adsorption of Cadmium in soils treated with FYM. This opinion also can be justified by observing the datas given in **Table 3**, **Table 4 and also Table 5.** The lechate concentration of Zn has been found significantly lower in FYM treated soils than the untreated soils for both Pundibari (**Table 3** and **Table 5**) and Malda region (**Table 4**and **Table 5**). Simular result also occurred incase of leachate concentration of Cd for both the soils (**Table 3, Table 4** and **Table 5)**. Incase of Pundibari region,the mean C/C_0 ratio of Znand Cd for untreated soil are 0.453 and 0.292 respectively which are significantly higher than those for the FYM treated soil (0.209 and 0.129 respectively) (**Table 5**). Incase of Malda region, similar results occurred, where the mean C/C_0 ratio of Zn and Cd for untreated soil are 0.342 and 0.237 respectively which are significantly higher than those for the FYM treated soil (0.206 and 0.111 respectively) (**Table 5**). The change in C/C_0 ratio in the lechates of the soilcolumn experiment can predict the metal retentionability of soil.

The above observationspredictthat, in case of Malda soil , the retention was more as compared to Pundibari soil as the soils collected from Malda, exhibits more shifting of the breakthrough curve towards the left of the inflexion point compared to that of the soils collected from Pundibari for both untreated and FYM- treated conditions. The reason may be due to the high clay content in soils collected from Malda compared to soils of Pundibari. In both the cases,addition of FYM enhanced the heavy metal retention, and the leaching decreased markedly. This suggests that with the addition of organic matter to soil, there is an increase in retention of heavy metals. This might be due to the complexation between organic matter and metals,restricting the mobility of metalsfor exibiting more sorption sites (Igloria, *et.al.*,1996) of reaction.

Status of ion concentration (Zn^{2+} and Cd^{2+}) in the leachates collected from the soils ofPundibari and Malda at different time intervals:

From the results of leaching experiment it has been observed that concentrations of heavy metals as well as C/C_0 ratio in the collected leachate from both the untreated and FYM treated soilsof Pundibari and Malda have showed a significantly decreasing tendency with duration (Days) at the beginning **(Figure4 and Figure5)** and at the later stages, the decrease is not always statistically significant (**Table 3** and **Table 4**). The maximum concentrations as well as C/C_0 ratio of the metal ions (Zn and Cd) in the leachates were obtained at the beginning of the leaching process in both the cases of Pundibari and Malda for the both untreated and FYM treated soils**(Figure4 and Figure5)**.

The leachate concentration of Znin the untreated soils of Pundibari and Malda has been found 56.29 mg/l **(Table 3)**and 39.98 **(Table 4)** respectively at the first day. Next the trend has followed a decreasing order which is 55.28 mg/l, mg/l, 52.26 mg/l, 49.84 mg/l, 45.62 mg/l, 43.50 mg/l, 39.15 mg/l, 38.10 mg/l, 37.04 mg/l and 36.04 for the untreated soils of Pundibari**(Table 3)**and 38.88 mg/l, 37.84 mg/l, 36.65 mg/l, 36.60 mg/l, 35.49 mg/l, 30.87 mg/l, 29.80 mg/l, 28.70 mg/l and 28.03 mg/l for the untreated soils of Malda **(Table 4)** at subsequent days (Day 2nd to day 10th) respectively.The lechate concentration of Zn have been shown a significantly lower value incase of FYM treated soils as compared to untreated soil for the both places at the similar levels of duration (Day) which are 24.04 mg/l, 23.99 mg/l, 22.96 mg/l, 21.89 mg/l, 20.94 mg/l, 19.75 mg/l, 19.35 mg/l, 19.16 mg/l, 18.95 mg/l and 18.21 mg/l for the soils of Pundibari**(Table 3)** and 23.66 mg/l, 23.05 mg/l, 22.99 mg/l, 22.63 mg/l, 21.92 mg/l, 21.92 mg/l, 20.95 mg/l, 16.88 mg/l, 16.22 mg/l and 16.09 mg/l for the soils of Malda**(Table 4)**. It can also be further confirmed from the **Figure4** that the C/C_0 ratio of Zn has attained a lesser value incase of FYM treated soils than the untreated for both the places Pundibari and malda.

Similar trend also has been observed in case of the Cadmium. The leachate concentration of Cd in the untreated soils of Pundibari and Malda has been found 37.07 mg/l**(Table 3)** and 25.85**(Table 4)** respectively at the first day. Next the trend has followed a decreasing order which is 36.04 mg/l, mg/l, 35.99 mg/l, 35.89 mg/l, 32.82 mg/l, 26.62 mg/l, 24.30 mg/l, 22.07 mg/l, 21.02 mg/l and 19.90 for the untreated soils of Pundibari**(Table 3)** and 25.85 mg/l, 25.65 mg/l, 25.24 mg/l, 25.03 mg/l, 24.94 mg/l, 24.64 mg/l, 20.50 mg/l, 19.99 mg/l and 19.44 mg/l for the untreated soils of Malda**(Table 4)** at subsequent days (Day 2nd to day 10th)respectively. The lechate concentration of Cd have been shown a significantly lower value incase of FYM treated soils as compared to untreated soil for the both places at the similar levels of duration (Day) which are 19.56mg/l, 18.54 mg/l, 15.50 mg/l, 14.49 mg/l, 12.44 mg/l, 11.25 mg/l, 9.95 mg/l, 9.94 mg/l. 8.80 mg/l and 8.76 mg/l for the soils of Pundibari **(Table 3)** and 12.49 mg/l, 12.49 mg/l, 12.85 mg/l, 11.99 mg/l, 11.87 mg/l, 11.72 mg/l, 10.97 mg/l, 10.80 mg/l, 8.37 mg/l and 8.12 mg/l for the soils of Malda**(Table 4)**. It can also be further confirmed from the **Figure5** that the C/C_0 ratio of Cd has attained a lesser value incase of FYM treated soils than the untreated for both the places Pundibari and malda.

Most of the metals (Zn and Cd) were leached out from the soil in the first half of the experimental stage and the concentrations were comparatively low at the end of leaching **(Figure6 and Figure7)**.

The average leaching concentration of Zinc was more than Cadmium for both the soils of Pindibari **(Table 3)** and Malda **(Table 4)**and so the average Times of Dilution of Cd was more than that of the Zn in case of both the places Pundibari and Malda **(Figure9)**. Concentration is one of the important factors that influences the mobility of metals in soil. Metals in soils are adsorbed more readily when concentration is low and this might be the reason for getting lower leaching amount of Cadmium (Huang *et al*, 2015).

The time of dilution in both the cases using Zinc solution in the leachate followed the order Malda (Soil+FYM) > Pundibari (Soil+FYM) > Malda (Soil) > Pundibari (Soil) which are statistically significant from each other as per Duncan's Multiple Range Test (**Table 5**) **(Figure9)** and the similar trend was also observed using Cadmium solution for leaching **(Table 5) (Figure9)**indicating more accumulation of Zn and Cd by the Malda soils treated with FYM. Comparing the results of time of dilution of Zinc and Cadmium in both the sampling sites, the time of dilution was observed more in case of Cadmium as compared to Zinc suggesting more retention of Cd^{2+}.

Comparison between Zn and Cd adsorption by soil and (soil+FYM) in Pundibari and Malda:

From the findings of leaching experiment, we can predict how much amount of the metal ions get adsorbed or retained by the soil. The C/C_0 ratio of any metal ion in the collected leachates is inversely proportional to the the Times of dilution**(Figure8)**. More Times of dilution value indicates less C/C_0 ratio of ion in leachate which means more adsorption of metal ions have been occurred. Times of dilution was recorded statistically more in case Malda sampling site as compared to Pundibari in case of using Zn as leaching solution both with soil and (Soil+FYM)**(Figure9)(Table 5)**. Similarily, using Cd as leaching solution, the times of dilution was recorded to be statistically more in case of Malda sampling site compared to Pundibari**(Figure9)(Table 5)**. So, the trend of permeability was ascertained, i.e, Pundibari > Malda and the reasons might be due to the sandy texture of Pundibari soil having comparatively more sand content than Malda soil (**Table 1**).It suggests a better degree of retention in case of Malda soil, and the reason may be attributed to the texture of Malda soil i.e, clayey loam. The retention of Cadmium by both the sampling site was recorded to be more as compared to Zinc, might be due to the presence of low initial concentration of Cadmium in soils .

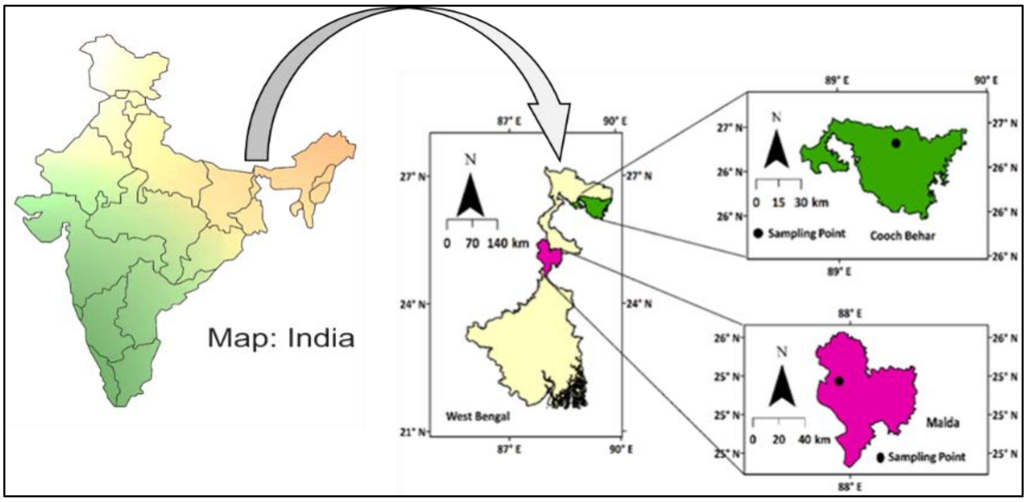
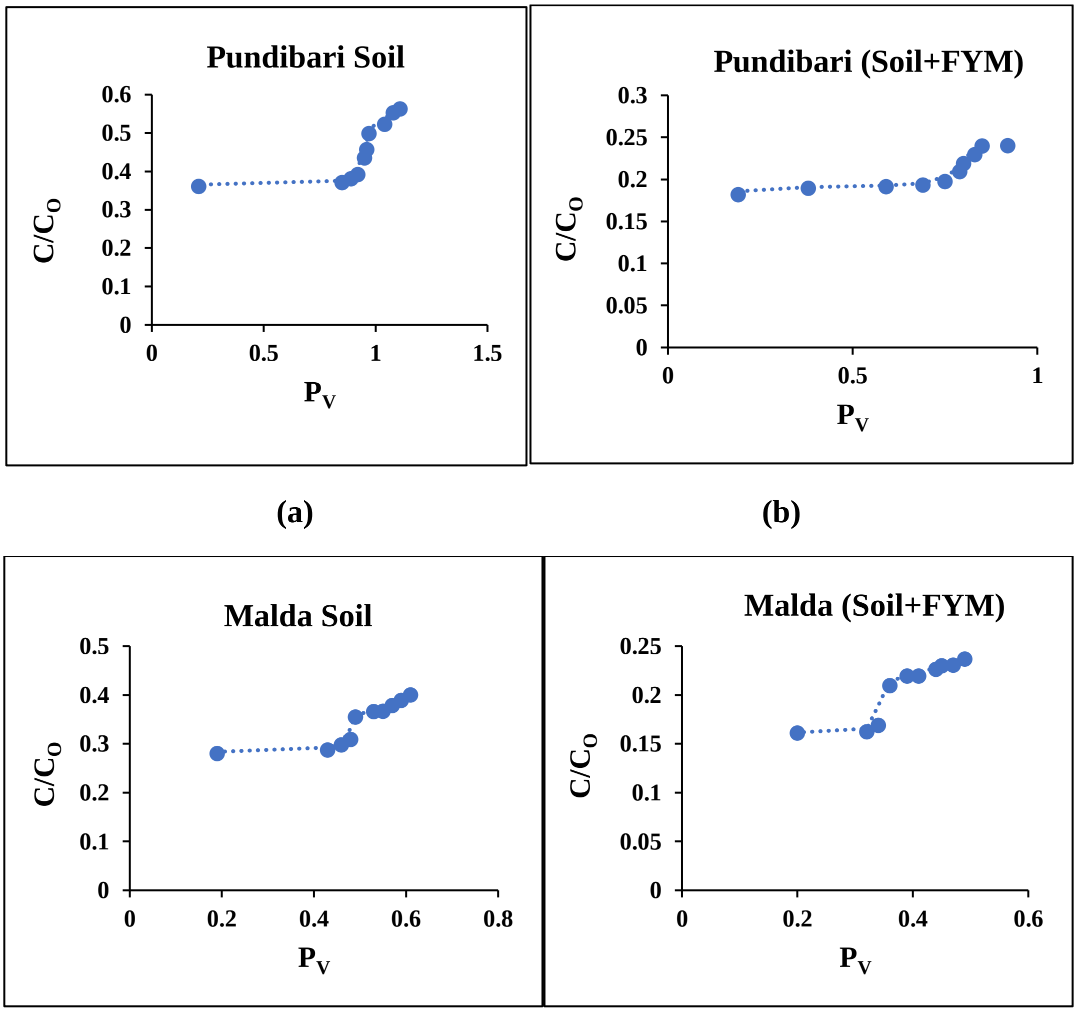


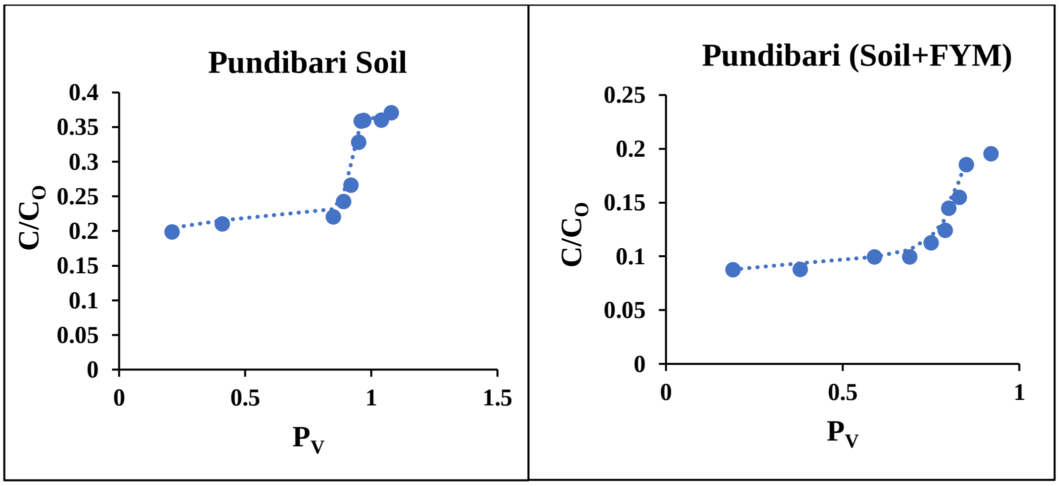
Fig.1 Geographical map of India and the experimental sites



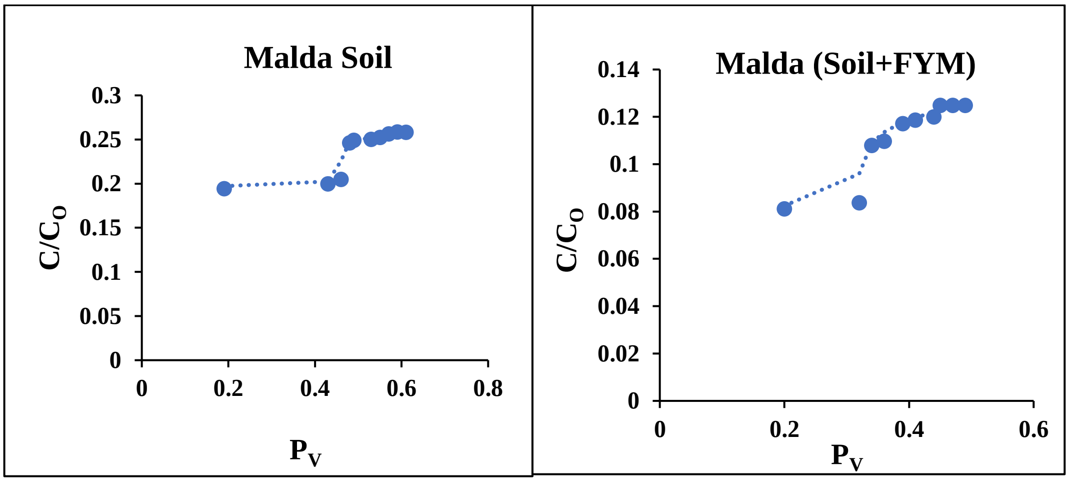
(a) (b)

(c) (d)

Fig.2 Experimental Breakthrough curve in soils of Pundibari (a,b) and Malda (c,d) using Zn Solution

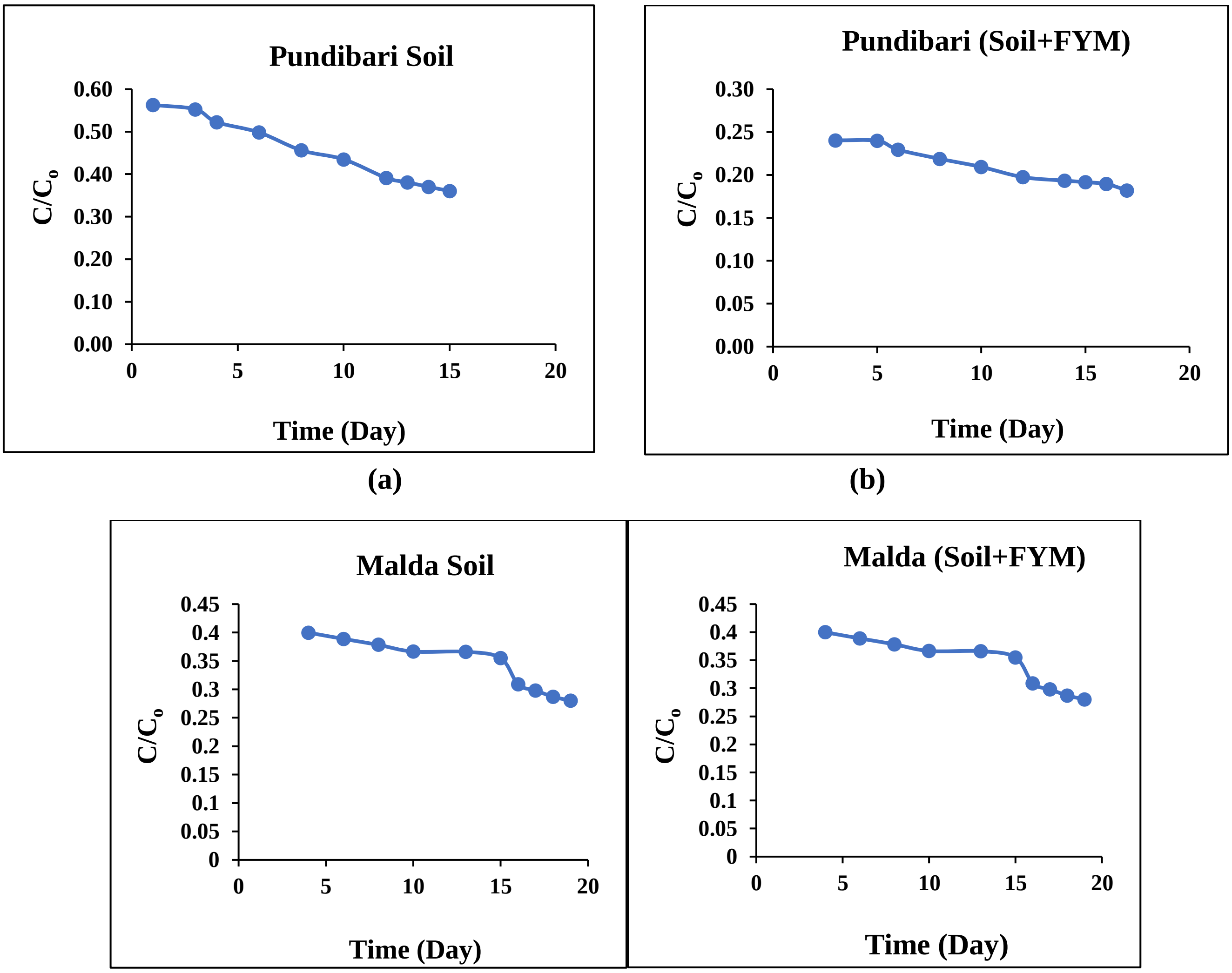


(a) (b)



(c) (d)

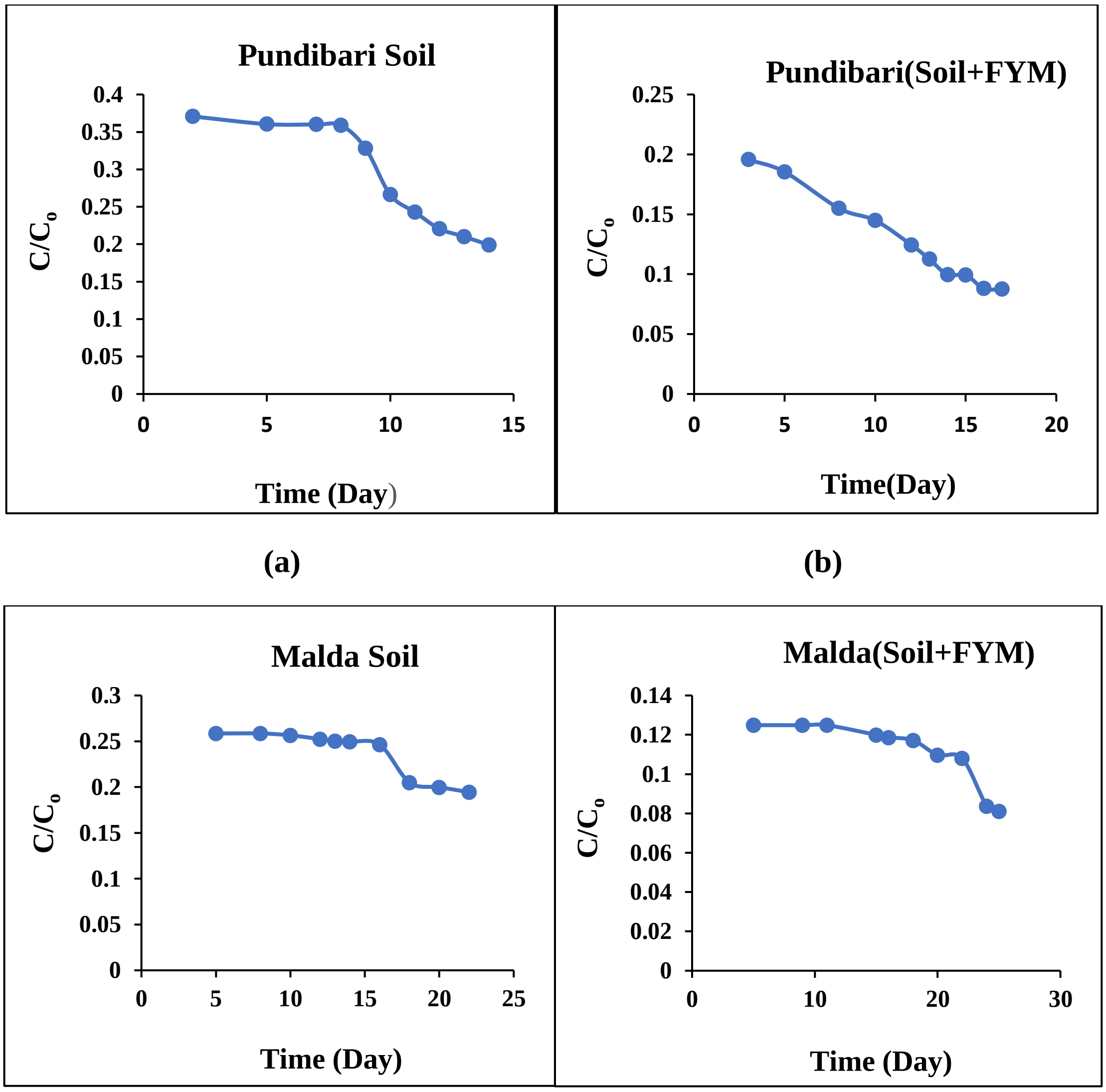
Fig.3 Experimental Breakthrough curve in soils of Pundibari (a,b) and Malda (c,d) using Cd Solution



(a) (b)

(c) (d)

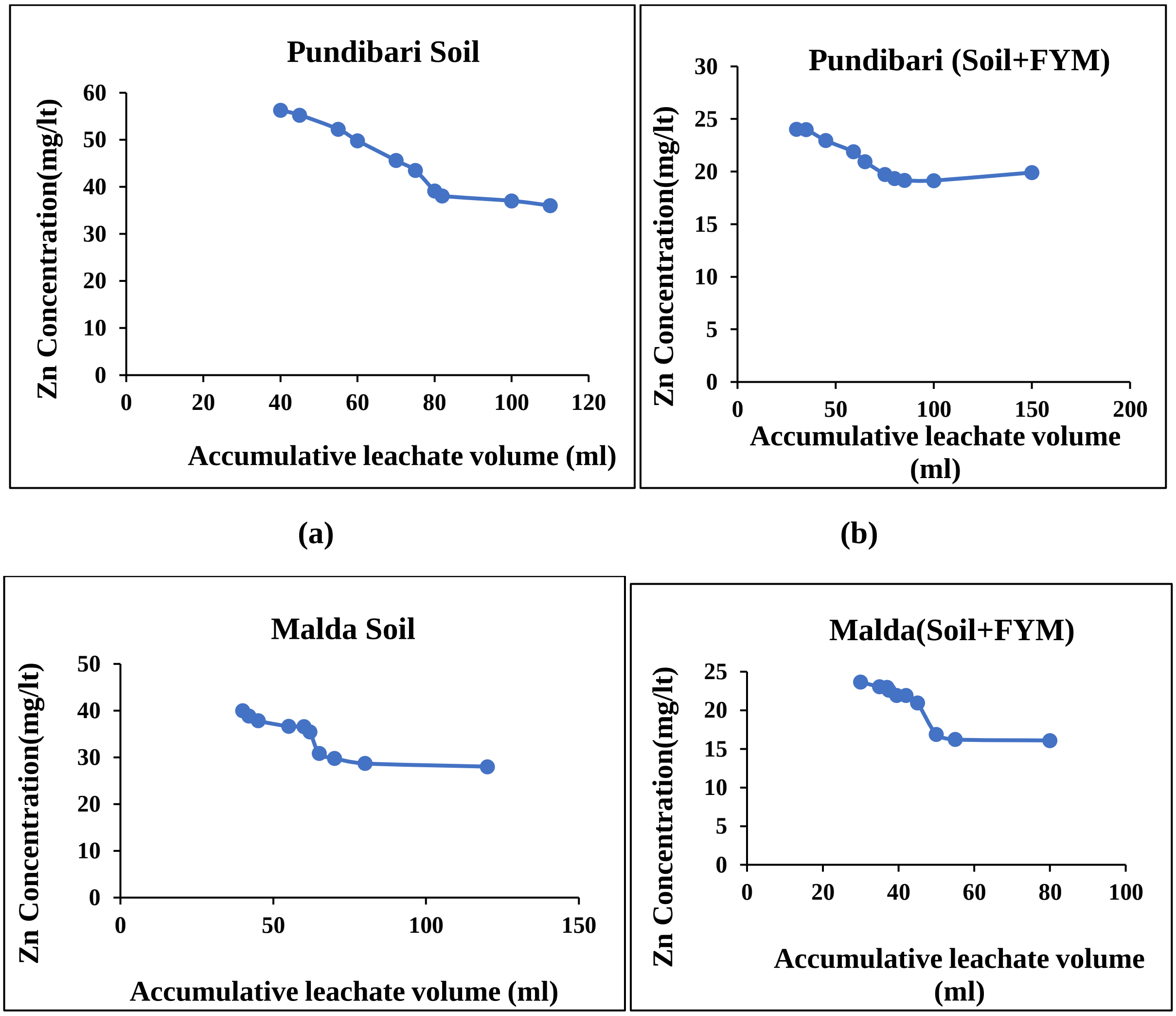
Fig.4 Change in concentration of Zn in leachates passing through the soils of Pundibari (a,b) and Malda (c,d) with respect to time



(a) (b)

(c) (d)

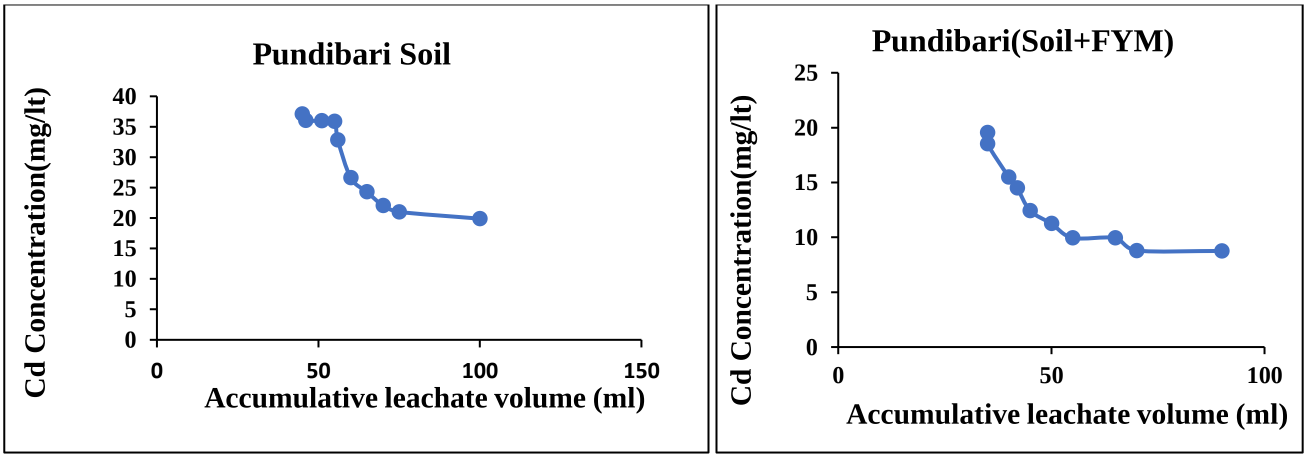
Fig.5Change in concentration of Cd in leachates passing through the soils of Pundibari (a,b) and Malda (c,d) with respect to time



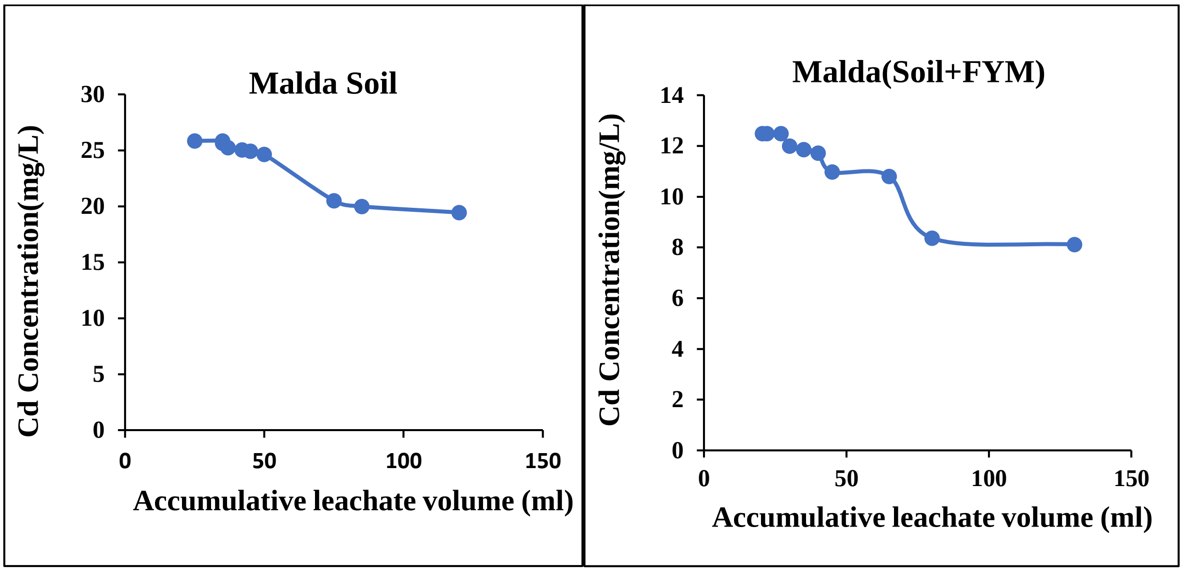
(a) **(b)**

(c) **(d)**

Fig.6Concentration of Zn in leachate released from soils of Pundibari (a,b) and Malda (c,d)



(a) **(b)**



(c) (d)

Fig.7Concentration of Cd in leachate released from soils of Pundibari (a,b) and Malda (c,d)

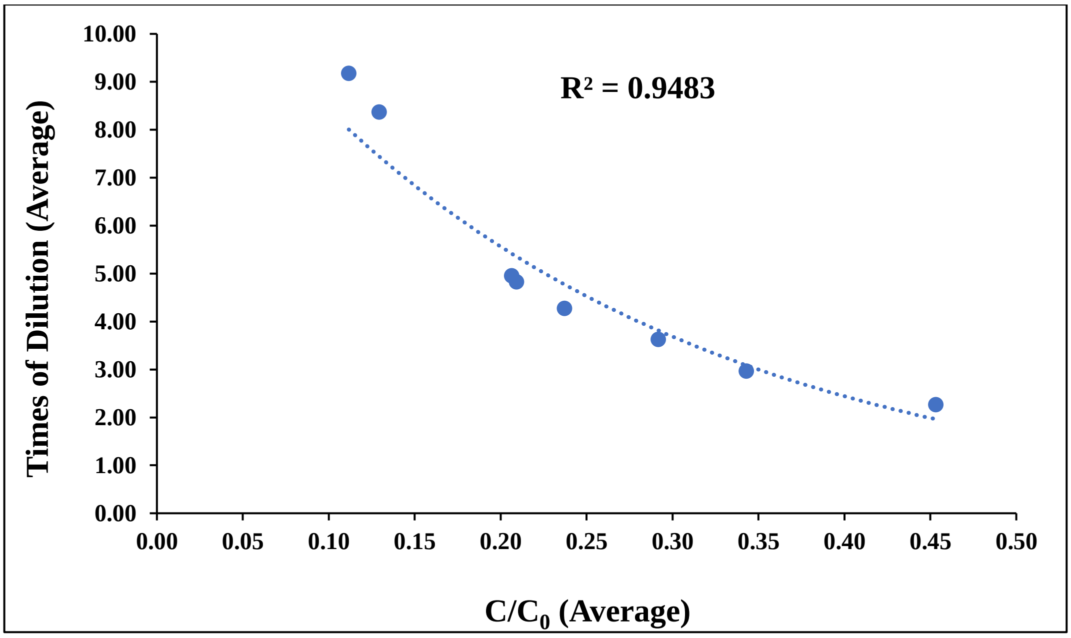


Fig. 8 Relationship between Times of Dilution and C/C_0 ratio

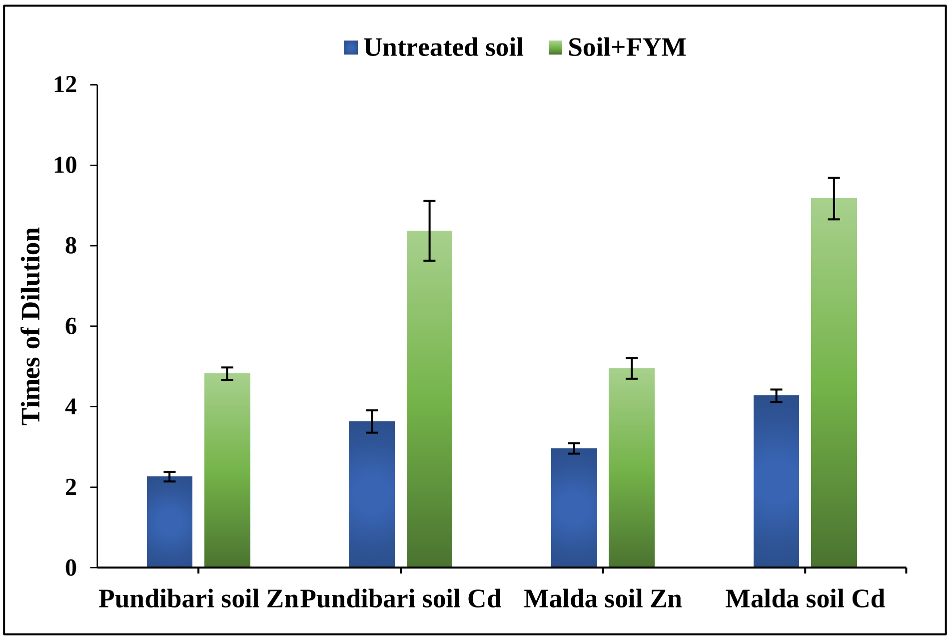


Fig.9Comparison between Zn and Cd adsorption by Soil and (Soil+FYM) in soils of Pundibari and Malda (The line bars signifies the Standard Error of Mean)

IV. CONCLUSION

Thus, from the present study conducted on soils collected from two different sites, it can be concluded that, soil treated with FYM served as an effective sink for Zinc and Cadmium, thereby retaining it better in comparison to soil in their matrix. Such kind of retention was highly influenced by the interactions of Zinc and Cadmium in soil with organic matter. Hence, it can be said that, Zinc and Cadmium retentions in soil could be augmented by applications of farm yard manure, which helped bind these metals into soil matrix by forming complexes with them, thereby preventing their rapid transport to crop rhizospheric zone, and consequently the uptake of these metals by growing crops in the given soil. This is expected to moderate the hazards due to the toxicity of heavy metals like Zinc and Cadmium in the soil-crop systems.

Conflict of Interest:

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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