Assessment of The Dioxins Leaching Potentials In Selected Soils Through Breakthrough Curves (BTCs) Model

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Abstract

The current study was to investigate the leaching and groundwater contamination potential of selected Dioxins, in local soil series. Solute transport was modelled through Breakthrough curve (BTC) plots, based on distribution coefficient (K_d), Retardation factor and Dispersivity, under normal velocity (20 cm day⁻¹) and preferential or steady flow (50 cm day⁻¹). In case of Dibenzo *p*-Dioxin (DD), distribution coefficient values were found in order of Charsadda > Peshawar > Sultanpur series, while for 2 Chloro- *p*-Dioxin (2Cl-DD), the order was Charsadda > Sultanpur > Peshawar. However, the overall sorption was low. Under the normal velocity both of selected Dioxins (DD & 2Cl-DD), BTC plots relatively took longer time to reach the point of saturation as compared to high seepage velocity. However, the overall solute transport was found to be rapid. This behaviour showed that sorption of the Dioxins selected soil series is low and there is potential for leaching and groundwater contamination.

1. Introduction

Among the various components of Environment, soil forms the most complex system, being comprised of different chemical and biological species (Turner, 2021). Soils perform both as provisionary as well as regulatory roles; they provide food and other resources as well as regulate various processes (nutrients recycling, waste assimilation and degradation etc), (Schröder and Schulte, 2016). However, these capacities can be greatly affected by the addition of numerous contaminants such as heavy metals (HMs), biological pathogens and persistent organics which are released through multiple sources including natural inputs as well anthropogenic sources. Major activities responsible for soil degradation may include intensive use of agro chemicals, mining, solid waste burning, fossil fuel burning, oil spillages and industrial growth multifold increase and accumulation of contaminants in soil strata has been reported (Sharma et al. 2021; Holík et al. 2019). Contaminants from these degraded soils can either entered the human body directly through ingestion, or may become the part of food and water we consume.

One of such contaminants are Dioxins, which is a group of 75 members with similar chemical and structural properties (USEPA, 2017). Persistence, toxicity and strong sorption in the soil matrixes form Dioxins as notorious contaminants and have been included in dirty dozen. Dioxins have been reported to be carcinogenic; while the non-carcinogenic health implications include hepatic, neurological, immunological, reproductive, endocrine, and developmental effects through binding to the Ah receptor (Hulin et al. 2020; Loganathan and Masunaga, 2020).

Another important aspect about Dioxins is their unintentional generation as by product during various activities like land filling, waste burning and bleaching as well during burning process of forest (Pan et al. 2021; Gul et al. 2018; Akele and Tarekegn, 2017). After generation, Dioxins may get deposit in the soil matrixes through absorption by clay and Organic matter (OM), from where there is possibility of Dioxins leaching under preferential flow through macro pores or through movement along loosely bound sediments and fly ash (Tao et al. 2021; Müller, 2017; Xu et al. 2017; Ghafoor et al. 2013). Various transport models have been suggested to monitor the transport and leaching of Dioxins from soils, sediments and fly ash solute transport, based on soil properties such as bulk density, texture, porosity, OM content, and distribution coefficient (K_d), (Freire et al. 2015; Badea et al. 2013; Yasuhara and Katami, 2007; Frankki et al. 2006). One of such study was conducted by Gul et al. (2018), where the local soils series from Pakistan were selected and assessed for Dioxin leaching through Breakthrough curves (BTCs). BTCs were modeled at normal and fast seepage velocities. Rapid solute transport was predicted from the obtained BTCs under preferential flow conditions. The general assumptions for BTCs calculation were 1) Steady solute flow through column 2) continuous injection of solute and 3) measurement of injecting a chemical solution of a known solute concentration (C_i) into the column inlet as a function of time. Based on the findings of Gul et al. (2018), the current study was designed for other three major soil series (Charsadda, Peshawar and Sultanpur series) collected from the respective districts (Charsadda,

Peshawar and Swabi). The basic aim was to assess Dioxins leaching and transport potential under normal and preferential flow with respect to groundwater contamination risk. Selected Dioxins for the current study include Dibenzo-*p*-Dioxin (DD) and 2-Chloro Dibenzo-*p*-Dioxin (2 Cl-DD). The K_d values measured from batch sorption experiments were used to calculate soil retardation factor (R) and to model the solute transport in selected soils.

2. Material And Methods

2.1. Sample collection

The major soil series selected for this study were Charsadda series, Peshawar series, and Sultanpur series; each series representing a specific textural and physical properties. Representative soil series were collected respectively from three districts, Charsadda, Peshawar and Swabi, of Khyber Pakhtunkhwa (KP), Province of Pakistan. Each sample was collected at a depth of 30 cm, as a single sample and stored in polyethylene bag. Charsadda series belongs to Swat river alluvium, silty loam, non-calcareous, being dark grey in color with well drained drainage (Table 1). Peshawar series is brown/dark brown, coarse granular, silty clay loam and strongly calcareous in nature and falls in Udic Haplustalfs category under USDA classification. Peshawar series belongs to Piedmont alluvium deposits and possess well drainage. Similarly, Sultanpur series is strongly calcareous, silty loam alluvium deposited soils (Table 1).

Soil texture was determined using a hydrometer method of Ryan et al. (2001), and OM was determined by loss on ignition (Schulte and Hopkins, 1996); organic carbon (OC) was further calculated from OM values by dividing OM with 1.7 (Heaton et al. 2016). pH meter of Consort Electrochemical Analyzer (C931) was used for pH measurement in soil water solution (1 g: 25 mL). Bulk density (ρ) and porosity (θ) were determined using methods of Blake and Hartge (1986) and Schoper (1982), respectively. Soil properties are summarized in Table 1.

2.2. Chemicals

All the chemicals used were of analytical grade. Dioxins were purchased from AccuStandard, Inc. (New Haven, CT, USA). Hexane was purchased from Sigma-Aldrich with 99.9% purity.

2.3. Batch Sorption

Distribution coefficient values (K_d) for the selected soil series were taken from batch sorption data of Gul et al. (2018). During their batch sorption analysis, mass to volume (M/V) ratio of soil and solution was kept 1g: 25 mL. Sorbate and sorbent in tubes were then mixed end-over-end for 72 hr to attain equilibrium. After shaking, the tubes were centrifuged for 30 mins at 3000 rpm. After centrifuge 20 mL of solution was extracted with 2 mL hexane for dioxin. Final 1 mL of Hexane extract was stored in GC vials. Desorption phase was carried out by decent and refill method. Glass tubes containing soil and solutions were weighted at different points. For desorption the same background solution of 0.005M CaCl_2 was used. Rest of the procedure was same as for sorption phase. Details of the method are also being given by Li et al. (2003).

The analysis of Dioxins was performed on Agilent 6890 GC, connected to an Agilent 5975B Mass Selective Detector. Column used was an Agilent VF-5 ms 30 m $\times$ 0.25 mm $\times$ 0.25 μm film thickness with 10-m EZ-guard (part no. CP9013). Initial oven temperature was 40°C and rose up to 350°C, with sample run time of 9.75 min. The injection temperature was 270°C, and helium was used as a carrier gas at the flow rate of 1 min^{-1} .

Soil water distribution coefficient, K_d (L Kg^{-1}), was calculated from measured sorbed concentration C_s (mg Kg^{-1}) and the concentration remaining in solution after equilibration C_e (mg L^{-1}) according to the following relationship:

$$K_d = C_s C_e^{-1}$$

2.4. Retardation factor and dispersion coefficient

Retardation factor describes the attenuation capacity of soils and is dependent on sorption of solutes and their nature. Besides that, soil properties such as porosity, bulk density and soil textures also determine the retardation capacity. Retardation factor for the BTCs were calculated as;

$$R = 1 + (\rho / \theta) \times K_d$$

Where “ ρ ” denotes bulk density, “ θ ” represents porosity, and K_d (L Kg^{-1}) is the distribution coefficient value obtained from the batch sorption analysis. Dispersion coefficient “ D ” ($\text{cm}^2 \text{day}^{-1}$) was calculated using the following equation:

$$D = \alpha_L v$$

Where “ α_L ” is the longitudinal dispersivity (cm) of the porous media in the direction of transport, and “ v ” denotes to average linear velocity (cm day^{-1}). Longitudinal dispersivity values for different textures were taken from literature (Kang et al. 2008) and used to calculate dispersion coefficient for selected soil series.

2.5. Estimation of BTCs

Convection dispersion solute transport was modeled through in CXTFIT 2.1 in the STANMOD software package to simulate solute transport (Simunek et al., 2003). Time and solute concentration was assumed to be dimensionless.

3. Results And Discussion

3.1. Physical properties of selected soil series

Table 1. Summarizes the physical properties of the three soil series, which shows vary little variation among data values. All the three soil series were of well drained drainage with porosity ranging between 52 to 60 %. Organic Matter content varied from 1.4 to 2.5 %, highest content being found for Charsadda series. pH of the series ranged from 7.6-8.0, bulk density varied from $1.36\text{--}1.50 \text{ g cm}^{-3}$. Highest clay (20 %) and sand (39%) contents were found for Charsadda and Sultanpur series, respectively.

Table.1 Physical characteristics of selected soil series										
Soil Series	District	Drainage	USDA classification	Sand (%)	Clay (%)	Silt (%)	OM (%)	Porosity (%)	Bulk density	pH
Charsadda	Charsadda	Well drained	Typic Haplustepts	36.4	53.9	9.7	2.5	60	1.36	7.6
Peshawar	Peshawar	Well drained	Udic Haplustalfs	22.5	65.5	20	1.4	52	1.49	8.0
Sultanpur	Swabi	Well drained	Haplocambids	39	60	1.0	2.0	55	1.50	8.0

3.2. Soil portioning DD and 2Cl-DD on selected soils

Details about the batch sorption, dispersion and retardation factor for studied soil series have been summarized in table.2. As mentioned earlier, distribution coefficient values were taken from the study of Gul et al. (2018). Distribution coefficient values were found in order of Charsadda > Peshawar > Sultanpur series. Charsadda series, was observed with high K_d value (1583 LKg^{-1}), for DD in comparison with other two series (Table 2). This behaviour could be attributed to high OM (2.5%) content of the Charsadda series. Another possible reason behind the high distribution value could be the neutral pH of the soil series, as highly alkaline soils are reported to have low sorption tendency for Dioxins. Peshawar and Sultanpur showed little variations among them in case of DD, due to similar physical properties like clay content and OM (Table 1).

Table 2
Distribution coefficients (K_d) and retardation factor (R) values for selected soil series

Soil Series	Dibenzo- <i>p</i> -Dioxin				2-Chlorodibenzo- <i>p</i> -Dioxin	
	$D^a \text{ (cm}^2 \text{ day}^{-1}\text{)}$	$D^b \text{ (cm}^2 \text{ day}^{-1}\text{)}$	$K_d \text{ (LKg}^{-1}\text{)}$	R	$K_d \text{ (LKg}^{-1}\text{)}$	R
Charsadda	112	280	1583	3589	1057	2396
Peshawar	192	480	78	224	219	628
Sultanpur	112	280	58	159	558	1522
$D^{a,b}$ Dispersion coefficient at pore water velocity at 20 & 50 cm day ⁻¹ , respectively						
K_d values taken from the batch sorption data of Gul et al., 2018						

In case of 2Cl-DD, distribution coefficient values were found in order of Charsadda > Sultanpur > Peshawar. Charsadda series again found with high value of K_d values among the three series, but the overall sorption was low in comparison with DD. The possible reason for this behaviour could be the higher molecular size of chlorinated Dioxins molecules, due to which interlayer sorption is hindered. Sultanpur series showed significant sorption towards 2Cl-DD, in comparison with the DD.

Low sorption affinities in the two soil series (Peshawar and Sultanpur series) could be due to the clay minerals, as hydration of exchangeable cations is a major determinant of sorption affinities of the clay. Large hydration sphere (Ca^+ , Na^+), have been reported to prohibit the interlayer interactions and absorption of the Dioxins (Liu et al., 2015). From the sorption affinities of the studied series indicate the SOM is generally the dominant partitioning phase in soils for hydrophobic compounds as expected, while soil clay fractions may also contribute significantly in sorption (Chiou, 2003). According to Li et al. (2003), high Ca^{+2} content hinders the sorption of non-polar compounds such as Dioxins and PCBs.

3.3. Breakthrough curves for selected dioxins at 20 cm day⁻¹ seepage velocity through soil profile

Figure 1a and b show the BTCs for DD and 2 Cl-DD, under 20 cm day⁻¹ linear velocity. For DD, among the three soil series, BTC for Charsadda series originated at concentration around 0.2 and took relatively longer timer to reach the equilibrium (Fig. 1a). Peshawar series BTC reached the end point earlier than the rest of two due to low K_d and R values and high dispersivity ($480 \text{ cm}^2 \text{ day}^{-1}$). Curve for the Sultanpur reached equilibrium point slowly. The solute

transport behavior via BTCs was identical to the plots obtained by Gul et al. (2018), for Dioxins, but different than that of Chowdhury et al. (2013).

In case of 2Cl-DD, BTC for Charsadda series was recorded to start above concentration of 0.4, with no plot at low concentrations and reaching the equilibrium point quickly. It can be concluded from the Both, Peshawar and Sultanpur series showed similar BCTs. Again the plots obtained were similar to the BTCs, reported by Gul et al. (2013), but were different from the plots of other studies. For example, BTCs obtained for pharmaceuticals by Kiecak et al. (2019), were some projectile shaped. Similarly in another study conducted by Imbrie and Park (1995), curve obtained were “S” shaped, indicating gradual raise in the solute concentration towards the saturation point. It can be concluded that due to little variations in the physical properties of the soil series, collected during the both studies, BCTs obtained were identical for selected Dioxins.

3.4. Breakthrough curves for selected dioxins at 50 cm day⁻¹ seepage velocity through soil profile

Figure 2a and b, show the plots of BTCs under high seepage velocity of 50 cm day⁻¹. For DD, all the plots obtained were identical. All the curves originating at lowest concentration and reaching the point of exhaustion quickly. The same behaviour of the series was also observed for the 2Cl-DD, under the same velocity. It can be concluded from such behavior that under steady flow conditions like preferential flow, rapid solute transport could take place leaving the sorption bed earlier with minimum interaction with soil media (Chowdhury et al. 2013), irrespective of their distribution coefficient and retardation factors. Such behaviour of the rapid solute transport and low sorption indicate groundwater contamination chances, along with severe health implications.

4. Conclusion

Breakthrough curves obtained in the study showed little variations among the plots of three selected series, despite of difference in their K_d , retardation factor and dispersivity. This behaviour indicates that the local series due to their low OM content, and calcareous nature have low Dioxins sorption potential for both DD and 2Cl-DD. From the results it is also concluded that clay can also be the controlling factor along with soil OM. Leaching potential and transport of both DD and 2Cl-DD were predicted in all soil series under both seepage velocities (20 & 50 cm day⁻¹), which indicates that risk of groundwater resources contamination with Dioxins. Such contamination could bring severe health implications such as Cancer. Therefore, there is need of further research and resource management to minimize severe consequences.

Declarations

Disclosure Statement

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Ethical Approval

No ethical approval is required by the authors for this manuscript.

Consent to Participate

All the authors agreed upon their participation.

Consent to Publish

Authors declare that they have no objection on publishing the data.

Authors Contributions

All the authors have equally contributed in the study and manuscript writing. Nida Gul (Analysis and manuscript writing), Bushra Khan (Breakthrough curve modelling), Ishaq Ahmad Mian Kakakhel (manuscript writing), Syed Muhammad Mukarram Shah (data interpretation), Muhammad Saeed (data interpretation), Fayaz Ali (Analysis)

Availability of data and materials

Relevant data and material will be available whenever requested.

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Figures

Figure 1

a, b Breakthrough curves for DD and 2 Cl-DD in selected soil series at 20 cm day⁻¹

Figure 2

a, b Breakthrough curves for DD and 2 CI-DD in selected soil series at 50 cm day⁻¹