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Dioxins Leaching Prediction in Selected Soils Series through Breakthrough Curves (BTCs) Model

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Abstract

This study investigated the possibility of selected dioxins leaching and causes of groundwater contamination. For this purpose, soil samples were taken from the KP districts of Peshawar, Charsadda, and Swabi. Soil desorption analysis was used to assess the sorption capacity of these particular soil series. Breakthrough Curve (BTC) plots were used to describe the transportation of solutes. The distribution coefficient (K_d), retardation factor, and dispersivity are used to determine the K_d values during sorption and desorption. Dioxin transportation was expected to occur at two different velocities: steady or preferential flow (50 cm day $^{-1}$) and normal velocity (20 cm day $^{-1}$). Regarding Dibenzo-p-Dioxin (DD), the K_d values for three series were found to be in ascending order: Charsadda > Peshawar > Sultanpur series; however, the order for 2 Chloro-*p*-Dioxin (2Cl-DD) was determined to be Charsadda > Sultanpur > Peshawar. Comparing the results with those from other studies, the total sorption was observed to be low. In contrast to high seepage velocity, BTC graphs took comparatively longer to reach the point of saturation under the usual velocity for both of the selected Dioxins (DD and 2Cl-DD). The investigation found that the chosen dioxins significantly leached and had low sorption.

Keywords: Groundwater pollution, leaching potential, preferential flow, sorption, dioxins, and BTCs.

1. Introduction

Due to its diversity of chemical and biological species, soil is the most complicated element of the environment (Turner, 2021). Soil provides food as well as regulates so many other ecological processes, such as nutrient recycling and degradation of waste (Schröder and Schulte, 2016). Nevertheless, a multitude of human activities have a significant impact on these functions. Agrochemical usage, mining, burning solid waste, burning fossil fuels, oil spills, industrial growth, have resulted in the accumulation of pollutants in soil strata and its degradation (Qu et al., 2019; Sunitha et al., 2019). Numerous contaminants, including biological pathogens, heavy metals (HMs), and persistent organic pollutants (POPs), are discharged into soils. Among such chemical contaminants, Dioxins are the most notorious and toxic. Dioxins is a class of 75 chemicals with comparable structural and chemical characteristics is one such contaminant (USEPA, 2017).

Dioxins have been classified as one of the "dirty dozen" pollutants because of their infamous status and significant sorption in soil matrixes, toxicity, and persistence. Dioxins have been linked to cancer, but they can also have non-cancerous health consequences by binding to the Ah receptor and affecting the liver, brain, immune system, reproductive system, endocrine system, and development (Marinkovic et al., 2010). Dioxins' accidental creation as byproducts of a variety of processes, including land filling, garbage burning, bleaching, and forest fire burning, is another significant feature which make them more noticeable (Liu et al., 2023; Gul et al., 2018a;

Mudhoo et al., 2013). Dioxins may be released and then get adsorbed into clay and organic matter (OM) in the soil matrixes. From there they may leach through macropores with preferential flow or travel along loose soil and ash particles (Tao et al., 2022; Ghafoor et al., 2013; Xu et al., 2017). Based on soil characteristics like bulk density, texture, porosity, OM content, and distribution coefficient (K_d), several solute and media interaction models have been proposed to track the movement and leaching of Dioxins through fly ash samples, sediments and soils solute transport (Yasuhara and Katami, 2007; Freire et al., 2015; Frankki et al., 2006; Badea et al., 2013). Gul et al. (2018a) carried out one such study in which they picked local soil series from Pakistan and used Breakthrough curves (BTCs) to measure the amount of dioxin leaching. Both typical and rapid seepage velocities were used to represent BTCs. Based on the obtained BTCs, rapid solute transfer under steady flow conditions was projected. The following general hypotheses were used to calculate BTCs; Consistent solute movement down the soil column with a solute of known concentration (Ci) is continuously injected into the column inlet, and its time-dependent injection is measured. The current research was designed to assess the sorption and leaching potential for other soil series such as Peshawar, Charsadda, and Sultanpur series which were gathered from the corresponding districts of Charsadda, Swabi, and Peshawar) based on the findings of Gul et al. (2018a). The main objective was to evaluate the risk of groundwater contamination due to Dioxins leaching under regular and preferential flow. Dibenzo-*p*-Dioxin (DD) and 2-Chloro Dibenzo-*p*-Dioxin (2Cl-DD) are the dioxins that have been chosen for the current investigation. The solute transport and Retardation factor (R) in particular soils were computed using the K_d values obtained from batch sorption tests.

2. Materials and Methods

2.1. Sampling

Charsadda, Peshawar, and Sultanpur soil series were the main ones chosen for this investigation; each series represented a particular set of textural and physical characteristics. The districts of Peshawar, Charsadda, and Swabi were the sources of the series of Peshawar, Charsadda, and Sultanpur respectively. At a depth of 30 cm, each sample was taken as a composite sample and stored in a polyethylene bags. The pH of soil solution (1 g: 25 mL) was measured using the Consort Electrochemical Analyzer's pH meter (C931). The organic matter (OM) was calculated using the loss on ignition method.

2.2. Batch Sorption

The K_d values were obtained using the same batch sorption method as Gul et al. (2018b) used for their batch sorption analysis. Each sample was repeated twice, and the ratio of the soil and water was maintained at 1 g: 25 mL (m/v). To achieve equilibrium, sorbent and sorbate were mixed end over end in tubes for duration of 72 hours. The tubes were shaken and then centrifuged for 30 minutes at 3000 rpm. Following the centrifugation, 2 mL of hexane was used to extract the Dioxins from each tube. GC vials held the last 1 mL of extract.

Dioxin quantification was done through using an Agilent 6890 GC that was attached to a Mass Selective Detector (5975). A 30-m × 0.25 mm x 0.25 μm film thickness Agilent VF-5 ms column with 10-m EZ-guard (part no. CP9013) was utilized. A flow rate of one minute was maintained while the temperature in the oven and gradually increased from 40 °C to 350 °C.

The following relationship was used to compute the distribution coefficient, K_d (LKg^{-1}), given the measured sorbed concentration Cs ($mgKg^{-1}$) and the concentration that remained in solution after equilibration Ce (mgL^{-1}):

$$K_d = Cs\, Ce^{-1} \qquad (1)$$

2.3. The dispersion coefficient and Retardation factor

The resistance offered by soils during transport was described by the retardation factor, which is reliant on the kind and sorption of solutes. Aside from that, the retardation capacity is also determined by the characteristics of the soil, including bulk density, porosity, and texture. The following equation was used to get the retardation factor for the Bitcoins:

$$R = 1 + (\rho/\theta) \times K_d \qquad (2)$$

Where, K_d (LKg^{-1}) is the distribution coefficient value derived from the batch sorption analysis, "ρ" stands for bulk density, and "θ" for porosity. To obtain the dispersion coefficient "D" (cm^2day^{-1}), the following equation was utilized;

$$D = \alpha L\, v \qquad (3)$$

Where "ν" is the average linear velocity ($cmday^{-1}$) and "αL" represents the dispersivity (cm) of the soil or porous media. The dispersion coefficient for particular soil series was computed using longitudinal dispersivity values for various textures that were obtained from the literature (Kang et al., 2008).

2.4. Estimation of BTCs

The STANMOD software package's CXTFIT 2.1 was used to model BTCs.

2.5. Chemicals

Analytical grade compounds were all that were used. Selected Dioxins were purchased from Accu Standard Incorporation, USA. While pure Hexane with 99.9% purity was acquired from Sigma-Aldrich in the United States.

3. Results and discussion

3.1. Physical characteristics of selected soil series

The physical characteristics of the three selected series are compiled in Table 1, which displays minimal fluctuation in the data values. Charsadda series was dark grey in color, non-calcareous, and part of the Swat River alluvium. The Peshawar series is classified by the USDA as Udic Haplustalfs, which is a silty clay loam with coarse granules, brown/dark brown color, and strong calcareous character. The Peshawar series has been reported excellent drainage and is a part of the Piedmont alluvium deposits. Similarly, the silty loam alluvium deposited Sultanpur series of soils is very calcareous. It was discovered that all three-soil series had porosities ranging from 52% to 60% and were well-drained. The percentage of Organic Matter ranged from 1.4 to 2.6%, with the Charsadda series having the greatest percentage. The series' bulk density varied from 1.36 to 1.50 gcm^{-3}, while its pH ranged from 7.6 to 8.0. The Peshawar and Sultanpur series had the highest percentages of sand (40%) and clay (65.5%), respectively.

Table.1 Physical characteristics of representative soil series

Series	District	Coordinates	Drainage	USDA classification	Sand (%)	Clay (%)	Silt (%)	OM (%)	Porosity (%)	Bulk density	pH
Charsadda	Charsadda	34.15° N 71.74° E	Well drained	Typic Haplustepts	37.5	53.9	9.7	2.7	60	1.36	7.6
Peshawar	Peshawar	34.02° N 71.62° E	Well drained	Udic Haplustalfs	22.5	65.5	20	1.4	52	1.49	8.0
Sultanpur	Swabi	34.12° N 72.47°E	Well drained	Haplocambids	40	60	1.0	1.8	55	1.50	8.0

3.2. *Soil Partitioning of DD and 2Cl-DD on selected soils*

Table 2 provides an overview of the values of dispersion coefficient, batch sorption, and factor of retardation for the soil series under investigation. K_d values were discovered in the Charsadda > Peshawar > Sultanpur sequence, in ascending order. Compared to the other two series, the Charsadda series was shown to have a higher K_d value (1657 LKg^{-1}) for DD (Table 2). This tendency might be explained by the Charsadda series' comparatively greater OM (2.7%) content. The neutral pH of the Charsadda series can be attributed towards the high K_d value in respect to other two soil series with alkaline pH ranges. Because Peshawar and Sultanpur have comparable physical characteristics, such as clay content and OM, they did not differ much in the case of DD (Table 1).

Table 2. Values of Distribution coefficients (K_d) and retardation factor (R) values for representative soil series.

Soil Series	D^a (cm^2 day^{-1})	D^b (cm^2 day^{-1})	Dibenzo-*p*-Dioxin		2-Chlorodibenzo-*p*-Dioxin	
			K_d (LKg^{-1})	R	K_d (LKg^{-1})	R
Charsadda	113	281	1657	3590	1206	2397
Peshawar	193	481	111	225	234	629
Sultanpur	113	281	69	160	606	1523

$D^{a,b}$ Dispersion coefficients at 20 and 50 cm per day, respectively

The distribution coefficient values for 2Cl-DD were discovered to be in the following order: Charsadda > Sultanpur > Peshawar. Among the three series, the Charsadda series was once more shown to have a high K_d value; nonetheless, total sorption was lower than that of DD. The larger size of chlorinated Dioxins molecules, which prevents the Dioxins sorption into interlayer spaces, may be the cause of this phenomenon. When compared to DD, the Sultanpur series demonstrated a notable amount of sorption towards 2Cl-DD.

Given that one of the main factors influencing the sorption affinities of clay is the hydration of exchangeable cations, the low sorption tendencies in the Sultanpur and Peshawar series may be caused by the clay minerals. It has been found that large hydration spheres (Ca^+, Na^+) prevent Dioxin absorption and interlayer interactions (Liu et al., 2015). As would be expected, the sorption affinities of the investigated series show that SOM is typically the predominant phase in soils for the partitioning of hydrophobic contaminants; however, clay content of the soils may also play a substantial role in sorption (Chiou, 2003). Li et al. (2003) stated that the elevated Ca^{+2} content might prevent the adsorption of non-polar chemicals like PCBs and Dioxins from sorbing.

3.3. *BTCs obtained at 20 cm day−1 seepage velocity*

The BTCs for DD and 2Cl-DD are displayed in Figures 1a and 1b under a linear velocity of 20 cm per day. In terms of DD, the BTCs for the Charsadda series began at a concentration of about 0.2 and needed a comparatively longer time to reach the equilibrium point than the other two soil series (Fig. 1a). Due to high dispersivity of 481cm^2 day^{-1}) and low R and K_d values, BTCs of Peshawar series arrived at the end point sooner than the other two. Sultanpur's curve took a while to attain equilibrium. The solute transport behavior measured through BTCs differed from that reported by Chowdhury et al. (2013) but were in similar pattern to the BTCs obtained by Gul et al. (2018a) in their recent study.

Regarding 2Cl-DD, the BTCs for the Charsadda series were observed to begin above at a concentration around 0.4, showing no discernible pattern at low concentrations and swiftly approaching the equilibrium point.

Conclusion: The BTCs from the Sultanpur and Peshawar series were comparable. Once again, the plots obtained differed from the plots of other investigations but were comparable to Gul et al. (2018a). For instance, several of the BTCs that Kiecak et al. (2019) obtained for medicines had a projectile-like morphology. Similar results were found in a different study by Imbrie and Park (1995), where the curve was "S" shaped and showed a slow increase in solute concentration towards the equilibrium. It can be inferred that the BCTs obtained for specific Dioxins were the same because of minor differences in the physical characteristics of the soil series under the investigation.

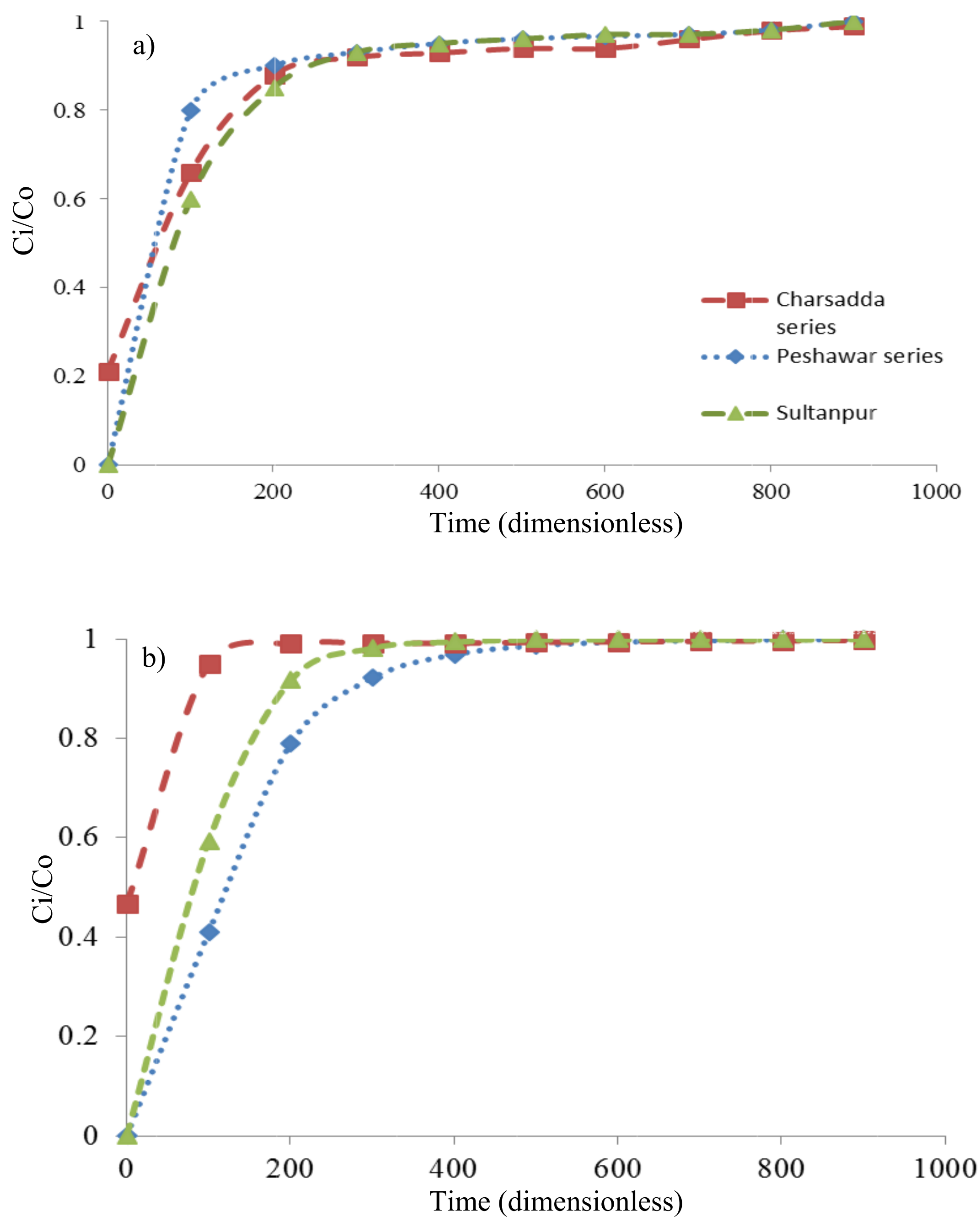

Fig. 1. BTCs for a) DD and b) 2Cl-DD in soil series at 20 cm day^{-1}

3.4. BTCs obtained at 50 cm day−1 seepage velocity

Plots of BTCs under high seepage velocity conditions (50 cm day^{-1}) are displayed in Figures 2a and 2b. Every plan that was obtained for DD was the same. Every curve started at the lowest concentration and rapidly approached the exhaustion point. Under the same velocity, the 2Cl-DD showed the same behavior of the series. Such behavior suggests that, regardless of their distribution coefficient and retardation factors, rapid solute transport could occur under rapid flow conditions such as preferential flow by exiting the sorption bed quickly with least interaction with sorbent (Chowdhury et al., 2013). Such low sorption and quick solute transport behavior point to the possibility of groundwater pollution and serious health risks.

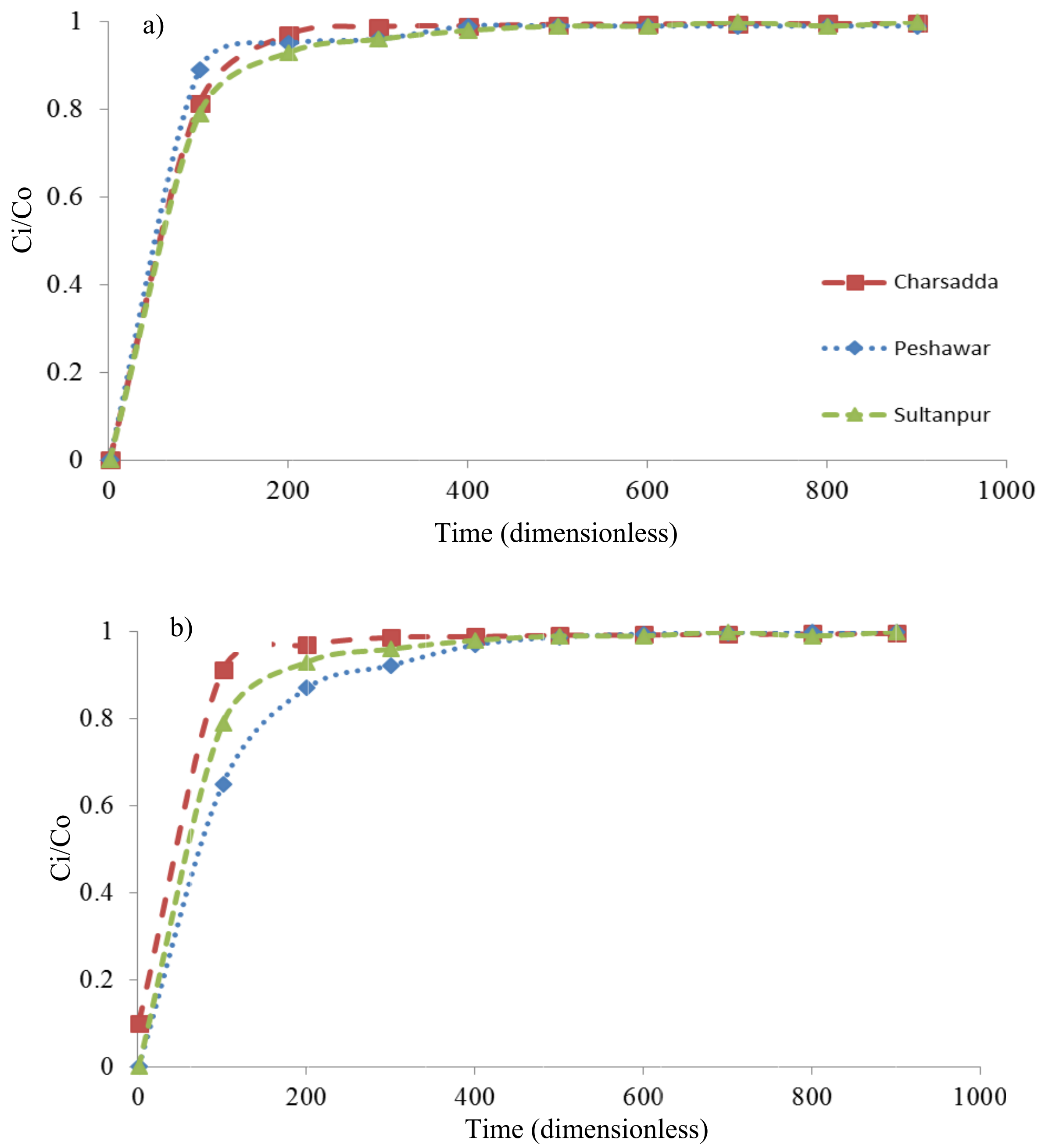

Fig. 2. BTCs obtained for a) DD and b) 2Cl-DD in the soil series at 50 cm day^{-1}

4. Conclusion

Despite the variances in the K_d, retardation factor, and dispersivity values of the three selected series, the breakthrough curves derived from the investigation demonstrated little variations among their plots. This trend suggests that the local series have limited dioxin sorption capacity for both DD and 2Cl-DD due to their calcareous composition and comparatively low OM content. The findings further suggest that, in addition to soil OM, clay may also be a determining factor in the local soils. In all three-soil series, leaching and transport potential can be predicted for both DD and 2Cl-DD under both preferred and normal flow conditions. Current research clearly indicates that there is a risk of dioxin contamination in groundwater, which could have detrimental effects on human health. In-depth investigation is required to learn more about the destiny of dioxins in the local soils and how they build up in the food chain.

Authors' Contribution

Nida Gul did all Lab analysis and research. Bushra Khan proposed the main concept and guidance. Syed Muhammad Mukaram Shah and Ishaq Ahmad Mian Kakakhel assisted in computer based modeling. Muhammad Saeed and Muhammad Farooq provided assistance in manuscript writing. Fayaz Ali helped in the field survey and interpretation of results. Faiza Tawab did technical review before submission and proof read of the manuscript.

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References

Badea, S. L., Lundstedt, S., Liljelind, P., Tysklind, M., 2013. The influence of soil composition on the leachability of selected hydrophobic organic compounds (HOCs) from soils using a batch leaching test. Journal of Hazardous Materials, 254, 26-35.

Chiou, C.T., 2003. Partition and adsorption of organic contaminants in environmental systems. John Wiley & Sons.

Chowdhury, Z.Z., Zain, S.M., Rashid, A.K., Rafique, R.F., Khalid, K., 2013. Breakthrough curve analysis for column dynamics sorption of Mn (II) ions from wastewater by using Mangostana garcinia peel-based granular-activated carbon. Journal of Chemistry, 1-8; http://dx.doi.org/10.1155/2013/959761.

Frankki, S., Persson, Y., Tysklind, M., Skyllberg, U., 2006. Partitioning of CPs, PCDEs, and PCDD/Fs between particulate and experimentally enhanced dissolved natural organic matter in a contaminated soil. Environmental Science & Technology, 40(21), 6668-6673.

Freire, M., Lopes, H., Tarelho, L. A. 2015. Critical aspects of biomass ashes utilization in soils: Composition, leachability, PAH and PCDD/F. Waste Management, 46, 304-315.

Ghafoor, A., Koestel, J., Larsbo, M., Moeys, J., Jarvis, N., 2013. Soil properties and susceptibility to preferential solute transport in tilled topsoil at the catchment scale. Journal of Hydrology, 492, 190-199.

Gul, N., Khan, B., Khan, H. and Ahmad, I., 2018a. Assessment of dioxin risk in the selected soils through sorption/desorption. Journal of Himalayan Earth Science, 51(2).

Gul, N., Khan, B., Khan, H., Israr, M., 2018b. Dioxin leaching risk assessment through selected soils by estimating distribution coefficient and breakthrough curves. Environmental Monitoring and Assessment, 190(11), 1-7.

Holík, L., Hlisnikovský, L., Honzík, R., Trögl, J., Burdová, H., Popelka, J., 2019. Soil microbial communities and enzyme activities after long-term application of inorganic and organic fertilizers at different depths of the soil profile. Sustainability, 11(12), 3251.

Imbrie, J., Park, J.K., 1995. Prediction of Organic Chemical Leachate from soil samples. Department of civil and environmental engineering, University of

Wisconsin, Madison, pp 1-124.
Kang, D. H., Yang, S. I., Kim, T. Y., Kim, S. S., Chung, S. Y., 2008. Hydrodynamic dispersion characteristics of multi-soil layer from a field tracer test and laboratory column experiments. Journal of Soil and Groundwater Environment, 13(4), 1-7.
Kiecak, A., Breuer, F., Stumpp, C., 2019. Column experiments on sorption coefficients and biodegradation rates of selected pharmaceuticals in three aquifer sediments. Water, 12(1), 14.
Li, H., Sheng, G., Teppen, B. J., Johnston, C. T., Boyd, S. A., 2003. Sorption and desorption of pesticides by clay minerals and humic acid-clay complexes. Soil Science Society of America Journal, 67(1), 122-131.
Liu, C., Gu, C., Yu, K., Li, H., Teppen, B. J., Johnston, C. T., ... Zhou, D., 2015. Integrating structural and thermodynamic mechanisms for sorption of PCBs by montmorillonite. Environmental Science & Technology, 49(5), 2796-2805.
Liu, X., Liu, G., Wang, M., Wu, J., Yang, Q., Liu, S., ... Zheng, M., 2023. Formation and Inventory of Polychlorinated Dibenzo-p-dioxins and Dibenzofurans and Other Byproducts along Manufacturing Processes of Chlorobenzene and Chloroethylene. Environmental Science & Technology, 57(4), 1646-1657.
Marinkovic, N., Pasalic, D., Ferencak, G., Grskovic, B., Rukavina, A. S., 2010. Dioxins and human toxicity. Arhiv za higijenu rada i toksikologiju, 61(4), 445.
Mudhoo, A., Thayalan, G., Muthoora, N. J., Muthoora, M. N., Oozeer, B. Z., Rago, Y. P., Kumar, S., 2013. Dioxins and furans: sources, impacts and remediation. Pollutant diseases, remediation and recycling, 479-541.
Qu, C., Albanese, S., Lima, A., Hope, D., Pond, P., Fortelli, A., De Vivo, B., 2019. The occurrence of OCPs, PCBs, and PAHs in the soil, air, and bulk deposition of the Naples metropolitan area, southern Italy: Implications for sources and environmental processes. Environment International, 124, 89-97.
Schröder, J. J., Schulte, R. P. O., Creamer, R. E., Delgado, A., Van Leeuwen, J., Lehtinen, T., Wall, D. P., 2016. The elusive role of soil quality in nutrient cycling: a review. Soil Use and Management, 32(4), 476-486.
Schulte, E.E., Hopkins, B.G., 1996. Estimation of soil organic matter by weight loss on ignition. pp 21–31.
Sunitha, V., Reddy, B. M., Reddy, M. R., 2012. Groundwater contamination from agro-chemicals in irrigated environment: Field trials. Advances in Applied Science Research, 3(5), 3382-3386.
Tao, Z. H. U., Zeyu, X. U. E., Ruonan, W. A. N. G., Xuyang, C. H. O. N. G., 2021. Leaching toxicity and dioxin distribution characteristics of MSW fly ash by thermal plasma melting. Chinese Journal of Environmental Engineering, 15(6), 2072-2079.
Turner, B. L., 2021. Soil as an archetype of complexity: A systems approach to improve insights, learning, and management of coupled biogeochemical processes and environmental externalities. Soil Systems, 5(3), 39.
U.S. Environmental Protection Agency (EPA), 2017. Learn about dioxin. https://www.epa.gov/dioxin/learn-aboutdioxin.
Xu, P., Tao, B., Zhou, Z., Fan, S., Zhang, T., Liu, A., Huang, Y., 2017. Occurrence, composition, source, and regional distribution of halogenated flame retardants and polybrominated dibenzo-p-dioxin/dibenzofuran in the soils of Guiyu, China. Environmental Pollution, 228, 61-71.
Yasuhara, A., Katami, T., 2007. Leaching behavior of polychlorinated dibenzo-p-dioxins and furans from the fly ash and bottom ash of a municipal solid waste incinerator. Waste Management, 27(3), 439-447.