Assessment of dioxin risk in the selected soils through sorption/desorption

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Abstract

Dioxins are deposited in soils from both natural and anthropogenic sources. Sorption and desorption capacity of six different soils representing a specific soil series were analyzed for 2 Chloro dibenzo- p-dioxin (2 Cl-DD) and dibenzo- p-dioxin (DD). Calculated Kd values for 2 Cl-DD and DD were in the range of 219-2623 L/Kg and 58-1583 L/Kg respectively. Sorption was reported high for the soil series of Burhan, Charsadda and Warsak having samples SS1, SS2 and SS3, respectively. Minor variations were observed among the distribution coefficient (Kd) values of chlorinated and non-chlorinated dioxins. Application of Freundlich and Langmuir Isotherms showed that most of the samples fitted the Freundlich isotherm. This study revealed low sorption capacity of the selected soils towards 2 Cl-DD and DD and hence a risk of potential release to the environment.

Keywords: Sorption; Desorption, Dioxins; Soil series; Environmental risk.

1. Introduction

Dioxins offers a classical example of persistent organic pollutants (POP) comprise of 75 poly halogenated organic compounds (Bretthauer et al.,1991). Poor handling of the municipal and industrial waste; including combustor emission, cigarette smoke, herbicides, alkali plants, wastewater effluents, compost and pulp bleaching are some of the sources responsible for the entry of Dioxins to environment (Fiedler, 1999; Behnisch et al., 2001; Holt et al., 2008). In addition to lead added fuels used in the automobiles the famous process of chlorine-alkali is a leading source of dioxins. Accumulation of dioxins in sediments and soils from atmosphere, erosion, runoff and leaching are concerns of significant nature (Laegdsmand et al., 2005; Seike et al., 2007). Exposure of humans to dioxins i.e. 90% is via intake of contaminated food, sea food, dairy products, poultry and ingestion of polluted soil (Liem et al., 2000; Pemberthy et al., 2016). Dioxins enter human body through inhalation of dust and direct ingestion of soil; accumulation in plant tissues and vegetables contamination (Domingo et al., 2000; Jou et al., 2007). In soils, the bioavailability and transport of dioxins are regulated by the processes of sorption and desorption in addition to certain others (Kukkonen et al., 2004; Koelman et al., 2006). Some of the key factors responsible for the dioxins sorption/desorption in soil are solution and solid phase portioning, clay content and organic matter (Gevao et al., 2000; Gevao et al., 2000; Breus and Mishchenko, 2006).

Van der Waals forces and hydrogen bonding are responsible for the speedy sorption process in the start that later on slow down due to sorbent swelling, complexes formation and particle structure breakage (Hance, 1967; Gevao et al., 2000). The mobility and retention of sorbate is shown through sorption isotherms; commonly used are Freundlich and Langmuir isotherms in sorption studies (Limousin et al., 2007). Multilayer and reversible adsorption is shown through Freundlich isotherms and Langmuir is used for monolayer sorption on equally available sited (Adamson and Gast, 1997; Kundu and Gupta, 2006).

In Pakistan the province of Khyber Pakhtunkhwa (KP) has brick kilns, cement industries and burning of waste in open in several locations. These anthropogenic sources can potentially contribute to the release and accumulation of dioxins in local soils. This study was carried with the objective to assess local soils for the potential of sorption and desorption of PCDDs. Therefore, two dioxins i.e. 2-Chlorodibenzo-p-dioxin (2 Cl-DD) and dibenzo-p-dioxin (DD) representing

chlorinated and non-chlorinated dioxins were investigated accordingly. Results of this study are equally important for researchers and local policy making. Details regarding key characteristics of these compounds are shown in Table 1.

2. Materials and methods

2.1. Sample collection

Composite soil samples were collected from three districts of the KP province of Pakistan i.e. Swabi, Charsadda and Peshawar (Fig.1). These samples were representing six major soil series prevailing in the study area; where SS1, SS2, SS3, SS4, SS5 and SS6 represented Burhan, Charsadda, Warsak, Kunda, Sultanpur and Peshawar series respectively as shown in Table 2. Soil samples of 1 kg weight were collected from surface to a depth of the 30 cm in polyethylene bags. Air

dried soil samples were sieved with a 200 mm size mesh.

Soil series of Burhan is mainly re-deposited loess, moderately drained, fine silty in texture, yellowish brown and deep dark. Soils of this series are massive and strongly calcareous. Soil series of Charsadda being of alluvial nature, grayish brown, coarse to medium sub-angular blocky, slightly calcareous and silt loam texture. Soils of Warsak series are well drained, semi-arid, coarse loam texture, calcareous and alkaline pH around 8 (SSP, 2008). The soil series of Kunda is made from the deposits of Indus river, massive, grayish brown dark, loamy sand of coarse texture. Sultanpur is a river alluvium, well drained, silt loam texture and moderately calcareous. Peshawar series is like Kufi series, soils are mainly of Piedmont alluvium, strongly calcareous, well drained, sub-angular blocky with silty clay loam texture (SSP, 2008).

Table 1. Selected Dioxin Congeners and their basic Properties.

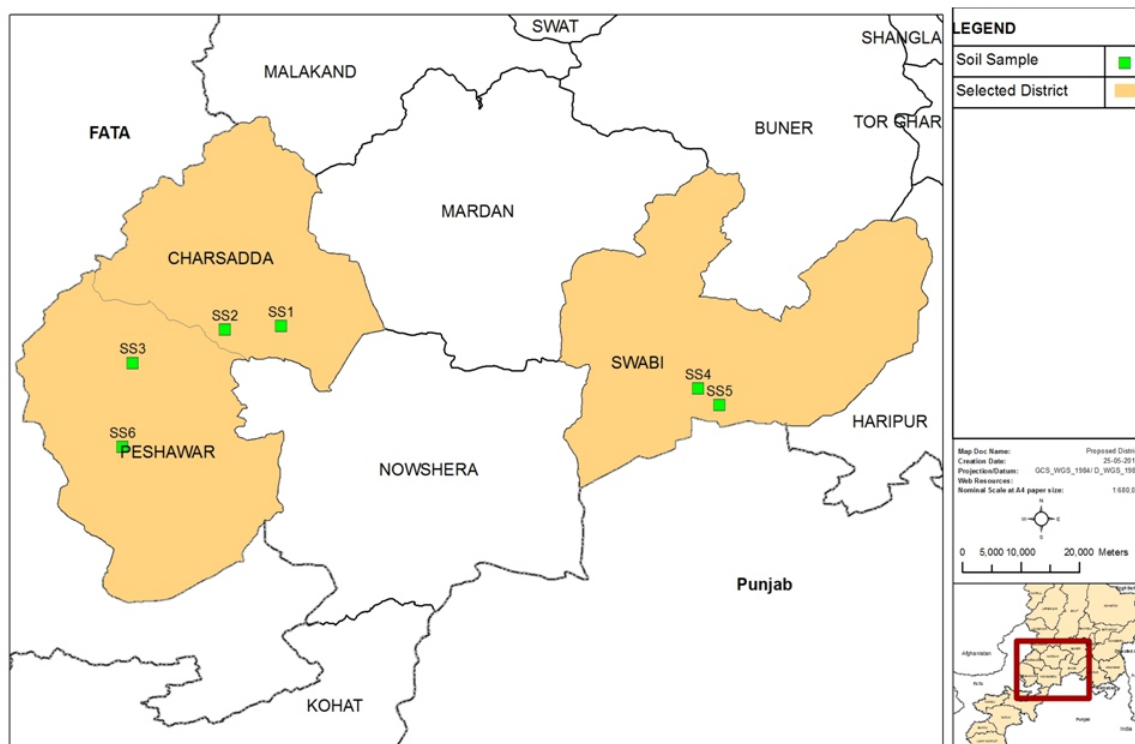| Compound	Formula	Mol. Wt	Aqu solubility (μgL^{-1})	Log K_{ow}
Dibenzo *p* dioxin	$C_{12}H_8O_2$	184.19	900	4.40
2 chloro dibenzo *p* dioxin	$C_{12}H_7ClO_2$	218.62	278	5.00

Fig. 1. Location map for Soil Sampling.

2.2. Physio-chemical parameters

Standard methods were used for the determination of various physical and chemical properties of the soil samples. Texture of the soil samples was determined via Hydrometer method (Ryan et al., 2001) and Organic Matter (OM) was determined through method of loss on ignition (Schulte et al., 1991). Electric conductivity (EC) and pH of the soil samples were measured in soil and distilled water solution of 1:5. Porosity and Bulk Density were determined through the methods reported by Schopper, 1982, and Blake and Hartge, 1986, respectively.

2.3. Chemicals

Analytical grade PCDDs were purchased from AccuStandard Inc. New Haven, CT 06513 USA. Stock solutions with 1000 mg/L and 1079 mg/L were prepared where methanol was used as a solvent for 2 Cl-DD and DD respectively. Background solutions of CaCl2 with 0.005M were used for the preparation of working solutions having different concentrations. The ranges of working solutions concentration were from 0.04-0.24 mg/L and 0.05-0.5 mg/L 2 Cl-DD and DD respectively. Co-solvent effect was minimized by using 0.1% methanol in all aqueous solutions of the study.

2.4. Sorption/desorption experiment

Sorption/desorption analysis was carried through static batch sorption method. Ratio of mass to volume (M/V) for soil and solution was 1 g: 25 mL. Each time the concentration of the solute was taken in one blank with two replicates in glass centrifuge tubes. Sorbent and sorbate in the tubes was shacked end over end for 72 hours to attain equilibrium. Shaking of the tubes was followed by centrifugation for 30 minutes at 3000 rpm. After centrifugation 20 ml of solution was extracted with 2 mL Hexane for dioxin and a final 1 mL of Hexane extract was stored in GC vials. Desorption part was carried out by the method of refill and being weighted. Background solution of 0.005M CaCl2 was used for desorption. Rest of procedure was same as followed in sorption phase (Li et al. 2003).

It was assumed that the amount of dioxin sorbed on the soil is equal to the difference of the initial concentration of dioxin in solution and the concentration of dioxin after equilibration. The coefficient of sorption Kd (L/Kg) was calculated from sorbed Cs (mg/Kg) concentration and the remaining concentration in solution after equilibration Ce (mg/L) as per the following equation:

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

2.3. Instrumental analysis

Agilent 6890 GC, connected to an Agilent 5975B Mass Selective Detector was used for the analysis of dioxins, connected with a VF-5ms 30m x 0.25mm x 0.25 μm film thickness with 10 m EZ-guard (part #CP9013) column. Initial temperature of the oven was 40 °C that increased to 350 °C and the run time for sample was 9.5 minutes. The temperature during injection was 270 °C and Helium was used as a carrier with 1 ml/minute flow rate.

3. Results and discussion

3.1. Physical properties of samples

Physico-chemical properties of the selected soil samples are provided in Table 2. Draining of the soil samples varied from moderate to well drained, range of the porosity was from 30-60 %, OM was in the range of 0.6-2.9 % and pH in the range of 7.6-8.0. Soil samples of Burhan Series were high for OM, Charsadda Series was high for porosity, while Warsak, Sultanpur and Peshawar series showed high pH values. Range of the bulk density varied from 1.31 to 1.6 g/cm3 as shown in Table 2.

3.2. Sorption results

Sorption related parameters for various selected dioxins are summarized in Table 3. Sorption on the soils is given through isotherms as shown in figure 1 and figure 2. Data were analyzed via Langmuir and Freundlich models. Equation 1 and 2 describe Freundlich and Langmuir respectively.

$$C_s = K_f C_e^{1/n} \ [1]$$

Where "K_f" is Freundlich sorption coefficient and describer of isotherm slope is denoted by "n".

$$qe = \frac{Qmax.KL.Ce}{1+KL.Ce} \qquad [2]$$

Equation 2 denotes Langmuir isotherm, where "qe" denotes the amount of adsorbate adsorbed at the equilibrium (mg/Kg), "Qmax" the maximum adsorption capacity of the adsorbent (mg/Kg). Ce is the equilibrium concentration and "KL" Langmuir equilibrium constant (L/Kg).

3.3. Sorption of DD

Values of Kd for the sorption of DD were in the range of 58 to 1583 L/Kg. These values of Kd were lower than the expected values which were calculated on the basis of the OC content present in soil samples. Lowest and highest values of Kd were calculated for SS5 and SS2 respectively. Sorption magnitude of dioxins (mg/Kg) on soil (Cs) were in the order of SS5<SS6<SS4<SS2<SS3<SS1 (Fig. 2). Burhan series (SS1) showed a relatively high Cs value (23.34 mg/Kg). High sorption rate can be associated with the amount of organic content present in the samples (SS1, SS2 and SS3) and value of low Cs can be linked to low content of OC in SS4 as shown in figure 2 and Table 3.

Most of the data fitted the Freundlich isotherm very well except, SS3 and SS5 as shown in figure 2. Such type of best fitting indicates adsorption of multilayered heterogeneous and reversible nature for dioxins in soil samples (Haghseresht and Lu, 1998).

Table 2. Various properties of the selected soil series

Sample	Series	Drainage	USDA Classification	Particles distribution (%)			OM (%)	Porosity (%)	Bulk density (gcm⁻³)	pH
				Sand	Silt	Clay				
SS1	Burhan	Moderate	Typic Haplustepts	33.3	53.4	13.3	2.9	43	1.32	7.6
SS2	Charsadda	Well	Typic Haplustepts	36.4	53.9	9.7	2.5	60	1.36	7.6
SS3	Warsak	Well	Typic Haplustepts	39	46	14.9	2.8	30	1.31	8.0
SS4	Kunda	Excessive	Ustipsamments	55.8	44	0.2	0.6	40	1.6	7.9
SS5	Sultanpur	Well	Haplocambids	39	60	1	2	55	1.5	8.0
SS6	Peshawar	Well	Udic Haplustalfs	22.5	65.5	20	1.4	52	1.49	8.0

Table 3. Sorption, Freundlich and Langmuir parameters

Sample Id	OC (%)	E_{st} Kd	E_{xp} K_d (Sorp)	Freundlich	Langmuir	Avg Desorption (%)
				R^2	R^2	
		dibenzo *p* dioxin				
SS1	1.71	634.433	950	0.85	0.03	1
SS2	1.47	546.925	1583	0.96	0.85	4
SS3	1.65	612.556	479	0.85	0.98	2
SS4	0.35	131.262	94	0.96	0.95	4
SS5	1.18	437.54	58	0.95	0.98	0
SS6	0.82	306.278	78	0.91	0.89	6
		2 Chloro dibenzo *p* dioxin				
SS1	1.71	2833.987	2516	0.90	0.79	30
SS2	1.47	2443.093	1057	0.91	0.85	2
SS3	1.65	2736.264	1290	1.00	0.76	2
SS4	0.35	1368.132	2623	0.86	0.20	0
SS5	1.18	1954.474	558	0.82	0.91	3
SS6	0.82	586.3422	219	0.83	0.93	5

E_{st} = estimated from K_{oc} $\qquad$ E_{xp} = experimentally obtained
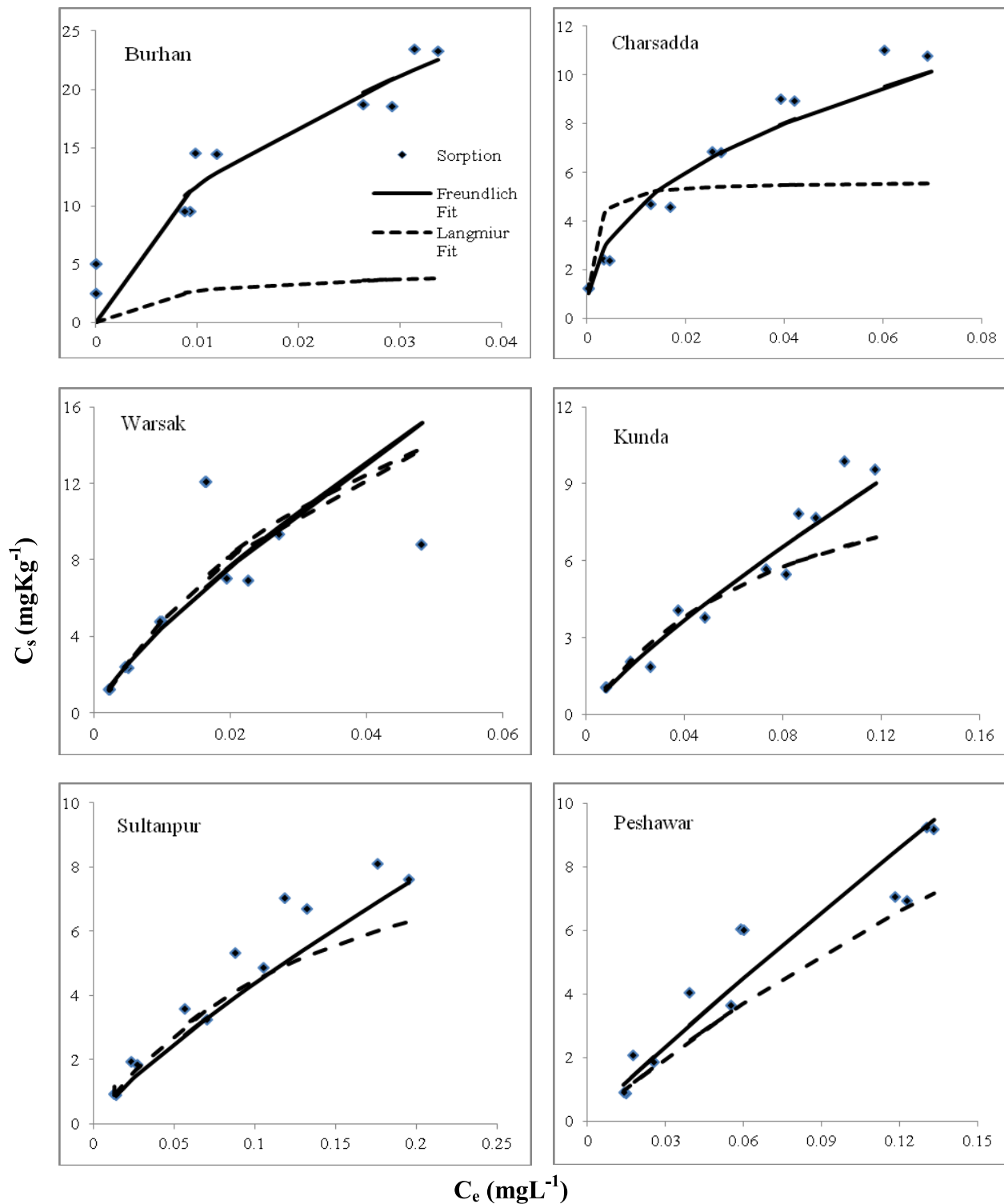
Fig. 2. Sorption, Freundlich and Langmiur Isotherms for DD.

3.4. Sorption of 2 Cl-DD

Like DD the values of Kd for 2 Cl-DD were also lower 219-2623 L/Kg than the expected Kd values. Sorption concentration (Cs) of dioxin to soil followed the order of SS6<SS5<SS4<SS3<SS2<SS1with minor capacity of sorption among these soils. A relatively high Cs value of 11.78 mg/Kg was

measured than the rest of the soil samples as shown in figure 3. Soil samples of SS1 and SS3 showed high affinity of sorption for Cl-DD due to relatively higher amount of clay and organic matter contents. Likewise, SS6 showed low capacity of sorption irrespective of high clay and organic matter contents. Comparatively, the values of Kd for 2 Cl-DD were higher than the Kd values for DD that is indicating more

binding capacity on chlorination. Measured sorption capacity in this study was found to be lower than other research studies where different geosorbents were used for dioxins and organic contaminants (Johnston et al., 2001; Li et al., 2003; Liu et al., 2009; Liu et al., 2015). Strong calcareous nature of the soil and organic film formation around the clay content of the soil attribute to such behavior i.e. rendering sorption (Li et al., 2003). High amounts of Ca+2 content can also hinders sorption i.e. through high density of charge and by reducing the attractions of the functional groups; therefore dioxins compete for interlayer sites during sorption (Liu et al., 2009). Values of Kd were higher for chlorinated dioxins.

Majority of the data in case of 2 Cl-DD fitted well Freundlich model except SS5 and SS6 which well fitted the Langmuir model, as shown in Figure 3 and Table 3. Sultanpur Series was represented by SS5 also fitted the Langmuir for DD. This indicates an adsorption of homogeneous nature by the soil where are sites are equally available for sorption (Kundu and Gupta, 2006).
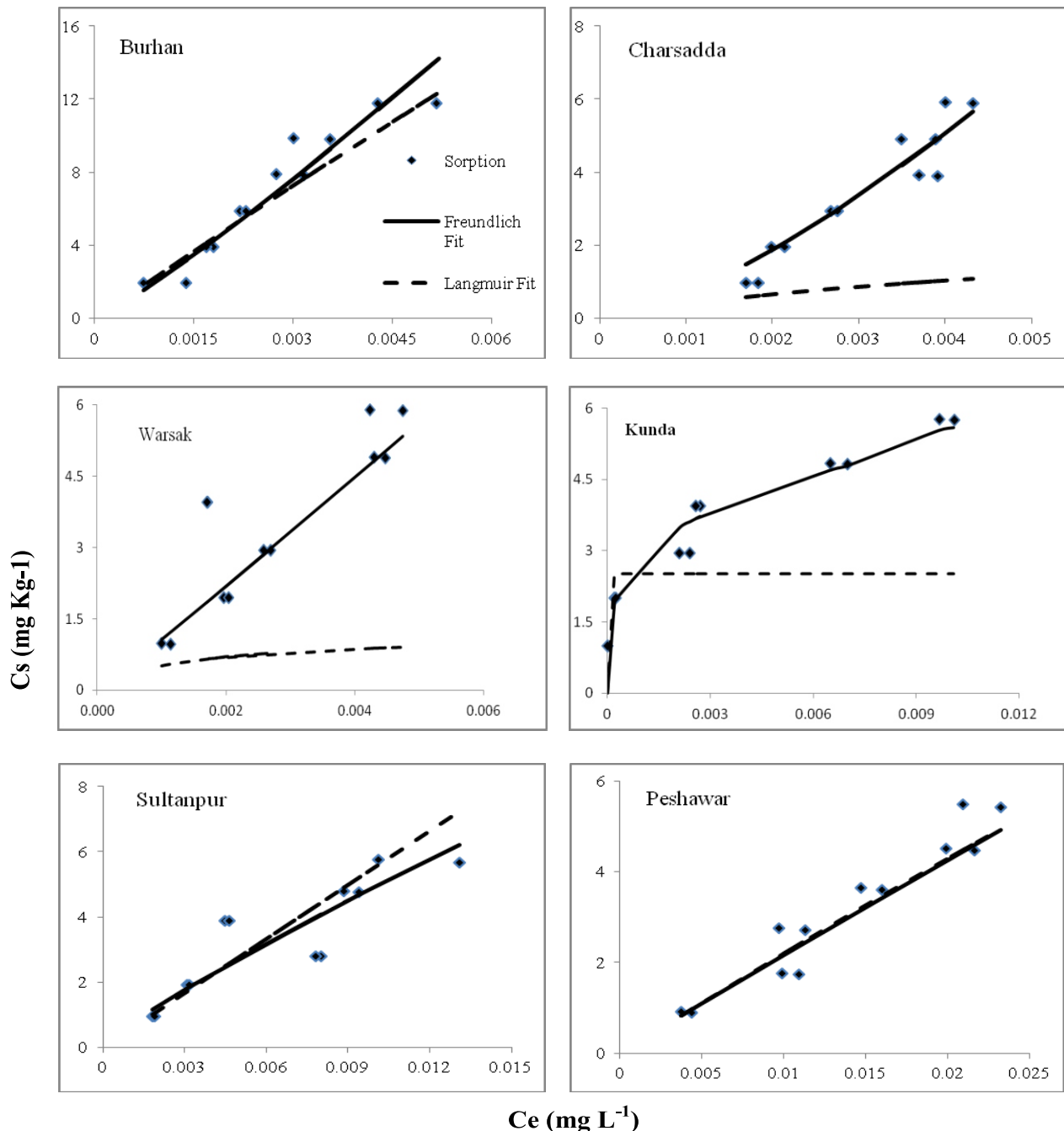

Fig. 2. Rainfall trends at different weather stations of the study area.

3.5. Desorption results

Generally, a very slow and low desorption was observed from the soil samples. Desorption ranged from 0 to 6 % for DD and 0 to 30 % for 2 Cl-DD as shown in Table 3. Lowest deposition values for DD can be attributed to organic content that is high for SS5. On the other hand, 2 Cl-DD with relatively high Kd values (SS1) showed more deposition than the rest of the samples indicating low retention of 2 Cl-DD by soil surfaces (Li et al., 2003).

Figure 4a & 4b; 5a & 5b also show the desorption data. For DD, it ranged from 0.6153-1.665 mgKg-1, relatively high value was found for SS5. For 2 Cl-DD, values of desorption ranged from 0.0763-3.702 mgKg-1, highest value found for Ss1.

Conclusion

Sorption behavior of six soil series was assessed for selected dioxins. Generally sorption was low as measured Kd was lower than the expected values of Kd on the basis of OC in soil samples; indicating that the content of Carbon is not the only controlling factor. Calcareous nature can be attributed to the hindering of dioxins sorption to the local soils. In the same manner the behavior of local soils was alike to both the chlorinated and non-chlorinated dioxins. In contrast, measured values of Kd were high chlorinated dioxin than the non-chlorinated; showing that chlorine substitution can significantly affect the sorption capacities of the soils. Charsadda, Burhan and Warsak series showed relatively high sorption tendencies than the rest of three series i.e. Kunda, Peshawar and Sultanpur series. Data was linear for most of the samples and fitted well with Freundlich sorption Isotherm.
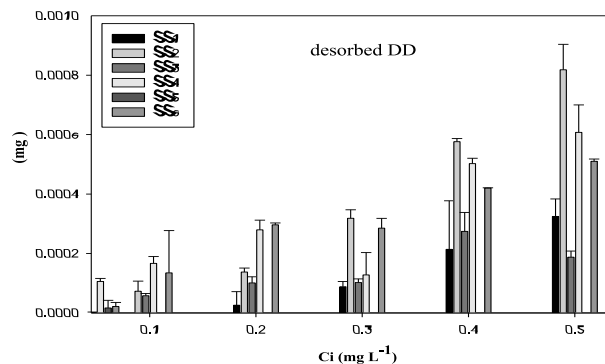
Acknowledgments
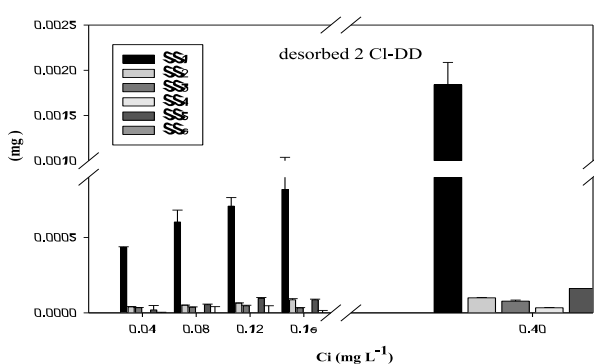
Fig. 4a. Amount of desorbed DD (mg).

Fig. 4b. Amount of desorbed 2 Cl-DD (mg).

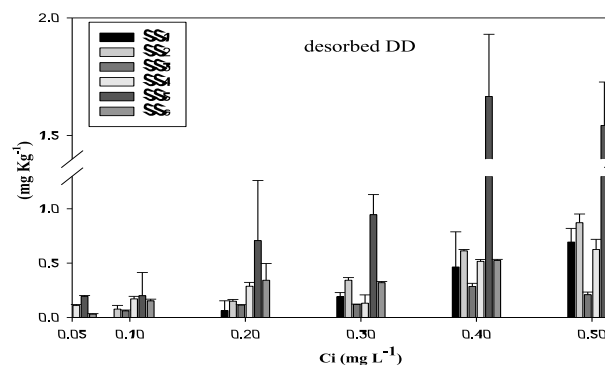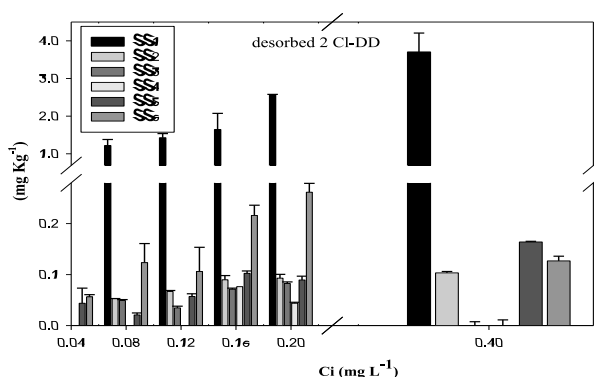
Fig. 5a. Amount of desorbed DD (mgKg-1).

Fig. 5b. Amount of desorbed 2 Cl-DD (mgKg-1).

References

Adamson, A.W., Gast, A.P., 1997. Physical Chemistry of Surfaces, sixth ed., Wiley-Interscience, New York.

Behnisch, P.A., Kazunori, H., Shin-ichi, S., 2001. Combinatorial bio/chemical analysis of dioxin and dioxin-like compounds in waste recycling, feed/food, humans/wildlife and the environment. Environment International, 27, 495-519.

Blake, G.R., Hartge, K.H., 1986. Bulk Density. Methods of Soil Analysis, Part 1. Soil Science Society of America Madison, Wisconsin, USA, 363-376.

Bretthauer, E.W., Kraus, H.W., Domenico, A.A., 1991. Pilot study on International Information Exchange on Dioxins and Related Compounds. Springer Science Business media, LLC, 400-534.

Breus, P., Mishchenk, A.A., 2006. Sorption of Volatile Organic Contaminants by Soils: Review. Eurasian Journal of Soil Science, 39, 1271-1283.

Domingo, J.L., Schuhmacher, M., Muller, L., Rivera, J., Granero, S., Llobet, J.M., 2000. Evaluating the environmental impact of an old municipal waste incinerator: PCDD/Flevels in soil and vegetation samples. Journal of Hazardous Materials, 76, 1–12.

Fiedler, H., 1999. Dioxin and furan inventories-national and regional emissions of PCDD/PCDF. UNEP, Geneva Switzerland, 1-15.

Gevao, B., Semple, K.T., Jones, K.C., 2000. Bound pesticide residues in soils: a review. Environmental Pollution, 108 (1), 3-14.

Haghseresht, F., Lu, G., 1998. Adsorption characteristics of phenolic compounds onto coal-reject-derived adsorbents. Energy Fuels, 12, 1100-1107.

Hance, R.J., 1967. The speed of attainment of sorption equlibria in some systems involving herbicides. Weed Research, 7, 29-36.

Holt, E., Von der, R.R., Walter, V., Caroline, G., 2008. Assessing dioxin precursors in pesticide formulations and environmental samples as a source of octachlorodibenzo-p-dioxin in soil and sediment. Environmental Science and Technology, 42, 1472-1478.

Johnston, C.T., De Oliveira, M.F., Teppen, B.J., 2001. Spectroscopic study of nitroaromatic-smectite sorption mechanisms. Environmental Science and Technology, 35, 4767-4772.

Jou, J.J., Chung, J.C., Weng, Y.M., 2007. Identification of dioxin and dioxin-like polychlorbiphenyls in plant tissues and contaminated soils. Journal of Hazardous Materials, 149, 174-179.

Koelmans, A.A, Jonker, M.T., Cornelissen, G., 2006. Black carbon: the reverse of its dark side. Chemosphere, 63, 2343-2351.

Kukkonen, J.V.K., Landrum, P.F., Mitra, S., 2004. The role of desorption for describing the bioavailability of selected polycyclic aromatic hydrocarbon and polychlorinated biphenyl congeners for seven laboratory-spiked sediments. Environmental Toxicology and Chemistry, 23, 1842-1851.

Kundu, S., Gupta, A.K., 2006. Arsenic adsorption onto iron oxide-coated cement (IOCC): regression analysis of equilibrium data with several isotherm models and their optimization. Chemical Engineering Journal, 122, 93-106.

Laegdsmand, M., de Jonge, L.W., Moldrup, P., 2005. Leaching of colloids and dissolved organic matter from columns packed with natural soil aggregates. Soil Science, 170, 13-27.

Li, H., Sheng, G., Brian, J.T., Johnston, C.T., Boyd, S.A., 2003. Sorption and desorption of pesticides by clay minerals and humic acid-clay complexes. Soil Science Society of American Journals, 67, 122-31.

Liem, A.K.D., Fürst, P., Rappe, C., 2000. Exposure of populations to dioxins and related compounds. Food Additives Contamination, 17, 241-259.

Limousin, G., Gaudet, J.P., Charlet, L., Szenknect, S., Barthes, V., Krimissa, M., 2007. Sorption isotherms: a review on physical bases, modeling and measurement, Applied Geochemistry, 22, 249-275.

Liu, C., Gu, C., Yu, K., Li, H., Teppen, B.J., Johnston, C.T., Boyd, S.A., Zhou, D., 2015. Integrating structural and thermodynamic mechanisms for sorption

of PCBs by montmorillonite. Environmental Science and Technology, 49, 2796- 2805.

Liu, C., Li, H., Teppen, B.J., Johnston, C.T., Boyd, S.A., 2009. Mechanisms associated with the high adsorption of dibenzo-p-dioxin from water by smectite clays. Environmental Science and Technology, 43, 2777-2783.

Pemberthy, D.A., Quintero, M.G., Martrat, J.P., Ábalos, M., Abad, E., Villa, A.L., 2016. Polychlorinated dibenzo-p-dioxins, dibenzofurans and dioxin-like PCBs in commercialized food products from Colombia. Science of the Total Environment, 568, 1185-1191.

Pennell, K.D., 2002. Specific Surface Area, in Methods of Soils Analysis: Part 4, Physical Methods., edited by Dane, J.H., Topp, G.C., SSSA, Madison, WI, 295-315.

Ryan, J., Estexen, G., Rashid, A., 2001. Soil and plant analysis. Lab Manual 2nd Edition, ICARDA.

Schopper, J., 1982. Porosität und Permeabilität, in Landolt- Bomstein: Physikalische eigenschaften der gesteine, Springer, V/1a, 184.

Schulte, E.E., Hopkins, B.G., 1996. Estimation of soil organic matter by weight loss-on-ignition, 21-31.

Seike, N., Kashiwagi, N., Otani, T., 2007. PCDD/F contamination over time in Japanese paddy soils. Environmental Science and Technology, 41, 2210-2215.

Shlu, W.N., Doucette, W., Gobas, F., Andren, A., Mackay, D., 1988. Physical-Chemical Properties of Chlorinated Dibenzo-p-dioxins. Environmental Science and Technology, 22, 651- 658.

Soil Survey of Pakistan (SSP), 2008. Ministry of Food, Agriculture & Livestock, Government of Pakistan.