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RESEARCH ARTICLE

Aggregation-dependent phosphorus adsorption under different land uses of district Kupwara of Kashmir Valley

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Abstract

Background: Phosphorus (P) is among the essential elements for plant growth and one of the main elements of fertilizers. Decreased availability of P may limit agricultural production in the coming years. The magnitude of soil aggregation influences phosphorus access to mineral surfaces.

Aim: The present study aims to determine phosphorus adsorption processes affected by soil aggregation under different land-use systems.

Methods: The distribution of soil aggregates was determined in representative soil samples in the district Kupwara of Kashmir Valley in India. To predict the phosphorus fertilizer requirement of a particular soil, we used the Freundlich adsorption equation and Langmuir equation and drew a clear comparison between these two models.

Results and discussion: Maximum phosphorus (P) adsorption was recorded at the smallest aggregate size, 0.5–0.1 mm. However, soil aggregates >2.0 mm (the largest category) adsorbed the least amount of P. Our results revealed that increasing the addition of P to the soil decreased the percentage of adsorbed P regardless of aggregate size. The maximum P adsorption of different size aggregates varied between 1869–1924, 1872–1900, 1718–1739, and 1800–1890 mg P kg^{-1} in irrigated agriculture, forest, orchard and rainfed agriculture soils, respectively. The variation in P adsorption parameters across the different land uses was attributed to their mean weight diameter difference. The maximum bonding energy in the forest resulted in higher P adsorption. Langmuir and Freundlich's adsorption equations were fitted to each soil aggregate size and land-use system.

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Conclusion: Our results revealed that for all soil aggregate sizes and land use systems, the Freundlich adsorption equation performs better than the Langmuir equation.

KEYWORDS
Freundlich adsorption equation, Langmuir equation, mean weight diameter, phosphorus adsorption isotherms, soil aggregation

1 | INTRODUCTION

Phosphorus (P) is among the essential elements for plant growth and the most important component of fertilizers for crop nutrition (Liu et al., 2017). Natural resources for P are limited, so the availability of sufficient P is a global environmental challenge for the 21st century (Fink et al., 2016). Decreased availability of P may limit agricultural production in the coming years. Phosphorus accumulates in soil due to the unnecessary use of fertilizers in crop production systems and is gradually released into water bodies, leading to eutrophication (Van der Salm et al., 2017). Elucidation of the adsorption processes is the key to understanding the behavior of P in soil. Excessive adsorption can limit the phytoavailability of P (Wang et al., 2014).

Soil aggregate stability influences its productivity by altering various soil characteristics, including carbon stabilization by protecting it from depletion and soil porosity by improving structure, hydraulic properties, and resistance to erosion by keeping the soil intact. Therefore, maintaining the stability of aggregates is essential for preserving soil productivity, reducing erosion and degradation, and consequently minimizing environmental pollution (Hussain et al., 2021).

Land use modifies soil characteristics; the modification depends on the management practices and the soil characteristics themselves (Borrelli et al., 2020). Farmers can achieve improved availability of applied P through soil management that encourages aggregate formation. As a result, it is appropriate to consider the distribution of soil aggregates when making P management decisions (Q. Zhang et al., 2020).

The present work aimed to (1) characterize the soil physicochemical properties and P adsorption processes and (2) examine the effect of soil aggregation on P adsorption behavior under a variety of land-use systems.

2 | MATERIALS AND METHODS

2.1 | Study area

Kupwara district is located in the Jammu and Kashmir regions of northern India (Figure 1). The district lies in the geographical coordinates of 74015"19" eastern longitude and 34031"33" north latitude, at an altitude of 5371 feet (1652 m) above mean sea level, at a distance of 55.92 miles (90 km) from the main town of Srinagar. It covers an area of 66,594 ha, with cultivable areas of 46,651 and 340 ha of forest area. The landscape also consists of the land of 5166 ha for nonagricultural use, permanent pastures of 5191 ha, 3338 ha for barren and uncultivable land, 2572 ha for cultivable land, 2467 ha for current fallows, and 189 ha for miscellaneous tree crops and groves.

2.2 | Climate and Soil

The Mediterranean temperate-type climate prevails in the district, while the temperature remains low all year round at higher ranges. The average minimum and maximum temperatures vary from –5 to 32°C. For approximately 2 months, the district receives an average annual rainfall of approximately 869 mm in rain and snow. Kupwara district is hilly and mountainous in the north, west, and east regions of the Pir-Panjal Range of the Lesser Himalayas with a wide intermountain valley. Soils in the hilly areas are poor, while soils in the plains are fertile. Higher range productivity is poor while fertile in the central regions. Medium- to fine-textured soils developed on the tops of Karewa and upland areas known as Hapludalf. The soils found in plains are clay loam and dark brown (CGWB, 2013).

2.3 | Collection and preparation of soil samples

Ten field moist composite soil surface samples (0–15 cm) were collected from all selected sites of four land uses, namely, irrigated agriculture, rainfed agriculture, orchard, and forest, in 2019–2020. Before aggregate analysis, the samples were allowed to air-dry for 72 h. For aggregate analysis, samples were sieved through 4.0 mm but retained on 2.0 mm. In addition, some air-dried samples were ground

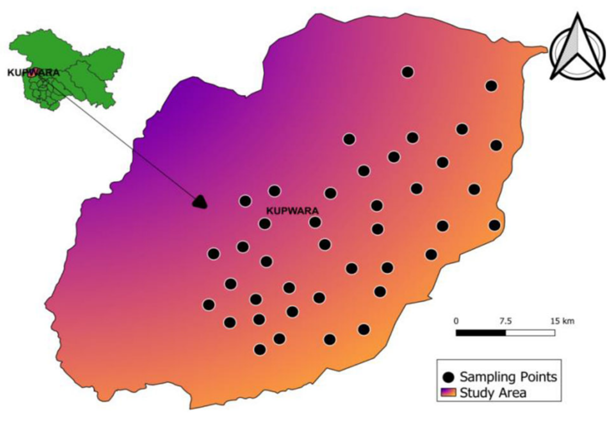

FIGURE 1 Map of the study area in Kupwara, India, depicting the soil sampling distribution

with a mortar and pestle, passed through a 2.0-mm sieve, and kept for various physicochemical analyses. Processed soil samples (<2 mm) were analyzed for particle size distribution by the Bouyoucos hydrometer method (Bouyoucos, 1962), organic carbon (Walkley & Black, 1934), pH (pH meter; Jackson, 2005), and aggregate analysis (wet sieving; Yoder, 1936). The distribution of soil aggregates obtained from the wet sieving method was expressed as the mean weight diameter (MWD) soil aggregate index:

$$\mathrm{MWD} = \frac{\sum_{i=1}^{n} W_i X_i}{\sum_{i=1}^{n} W_i}, \tag{1}$$

where n is the number of fractions, W_i is the weight (g) of aggregated particles—sand content in the i^{th} sieve, and X_i is the mean diameter (mm) of each sieve class.

2.4 | Adsorption study of phosphorus by soils

Soil samples (3 g) were balanced for 6 days at 25°C in a centrifuge tube with 30 mL of 0.01 M $CaCl_2$ solution containing 5, 10, 20, 30 50, and 100 mg P L^{-1} (i.e., 50, 100, 200, 300, 500, and 1000 mg kg^{-1} soil) as KH_2PO_4 with one drop of toluene for microbial activity inhibition. The soil was shaken twice daily for 30 min. The tube content was centrifuged at 5000 rpm for 20 min at the end of the required incubation period and filtered through Whatman No. 42 filter paper. Phosphorus (P) in the filtrate was estimated colorimetrically using a spectrophotometer. The difference was adsorbed P between the amount added and that recovered in the solution (Kuo, 1996).

2.5 | Adsorption equations

2.5.1 | Langmuir equation

$$Q_e = \frac{Q_{\max} \times b \times C_e}{1 + (b \times C_e)}, \tag{2}$$

where Q_e is the amount of P adsorbed, $Q_{\max}$ is the adsorption maxima, b is the bonding energy, and C_e is the equilibrium concentration.

2.5.2 | Freundlich equation

$$Q_e = K' \mathrm{x} C_e^{1/n}, \tag{3}$$

where Q_e is the amount of P adsorbed, K' is the measure of relative P adsorption capacity, C_e is the equilibrium concentration, and n is the relative affinity.

2.6 | Statistical analysis

Data were analyzed using the Sigmastat 3.1 SPSS Inc. software (SPSS Inc., Chicago, IL, USA) and were subjected to one-way analysis of variance. Means between control and treatments were statistically analyzed by Fisher's LSD test at $p \leq 0.05$. The number of replicates (n) for each measured parameter is specified in the figure captions. To determine the goodness of fit (R^2) of adsorption data to Langmuir and Freundlich adsorption isotherms, model fitting was performed using regression analysis.

3 | RESULTS

3.1 | Particle size distribution

The mean sand content ranged from 14.48% to 44.16%, with the lowest level in irrigated agriculture and the highest in forest land use. The silt content ranged from 39.09% to 46.45% under the studied land-use-systems (LUSs), with the lowest values in forest soils and the highest values in soils of rainfed agricultural land use, with mean values of 46.14, 42.53, 46.45, and 39.09.

The percentage of clay in soils under different LUSs ranged from 16.75 to 39.36, with the lowest in forest soils and the highest value in irrigated soils in agriculture, with mean values of 16.75, 18.61, 20.51, and 39.36 in the forest, irrigated agriculture, orchard, and rainfed agriculture soils, respectively (Table 1, Figure 2A,B).

3.2 | Mean weight diameter

The MWD under different land uses ranged from 0.51 to 0.71, 0.42 to 0.64, 0.34 to 0.53, and 0.27 to 0.47 mm under forest, orchard, irrigated agriculture, and rainfed agriculture land use, respectively (Table 1, Figure 2B).

3.3 | Soil reaction and organic carbon

Soil pH varied between different land uses. Under the forest land-use system, the lowest pH (6.31) was observed, and the highest average pH of 6.8 was reported under rainfed agriculture soils. The highest variation in pH was found in irrigated agriculture (5.30–7.15), and the minimum (6.12–6.53) was found in the forest land-use system. Organic carbon varied considerably in the various land uses. The maximum organic carbon content was recorded in soils under forest land-use at 1.41% and a minimum of 0.72% under the rainfed agriculture land-use system. The organic carbon content varied from 0.58% to 1.02%, 0.38% to 1.50%, 0.66% to 2.04%, and 1.23% to 1.71% under irrigated agriculture, orchard, rainfed agriculture, and forest land-use systems, respectively (Table 1, Figure 3).

Means with different superscripts differ significantly ($p < 0.05$)

3.4 | Adsorption of phosphorus under different land uses

A decrease in aggregate size resulted in higher phosphorus adsorption (P) regardless of land use pattern. However, the amount of

TABLE 1 Particle size distribution, mean weight diameter, pH, and organic contents in different land uses

Land–use	Sand (%)	Silt (%)	Clay (%)	MWD (mm)	OC (%)	pH
Irrigated agriculture	$14.48^c \pm 1.11$	$46.14^a \pm 1.37$	$39.36^a \pm 1.59$	$0.43^c \pm 0.02$	$1.08^b \pm 0.11$	$6.55^a \pm 0.20$
Rainfed agriculture	$34.93^b \pm 1.71$	$46.45^a \pm 1.39$	$18.61^b \pm 1.06$	$0.38^c \pm 0.01$	$0.72^c \pm 0.04$	$6.80^a \pm 0.10$
Forest	$44.16^a \pm 1.73$	$39.09^b \pm 1.77$	$16.75^b \pm 0.91$	$0.61^a \pm 0.01$	$1.41^a \pm 0.05$	$5.66^b \pm 0.13$
Orchard	$36.36^b \pm 2.19$	$42.53^{ab} \pm 1.32$	$20.51^b \pm 2.00$	$0.54^b \pm 0.02$	$1.12^b \pm 0.14$	$6.75^a \pm 0.10$
Mean	32.48 ± 0.30	43.55 ± 0.13	23.80 ± 0.25	0.49 ± 0.002	1.08 ± 0.009	6.44 ± 0.132
CD ($p < 0.05$)	4.95	4.23	4.19	0.05	0.28	0.42

Note: Different letters represent significant differences at $p < 0.05$.
Abbreviation: MWD, mean weight diameter; OC, orgain carbon; CD, critical difference.

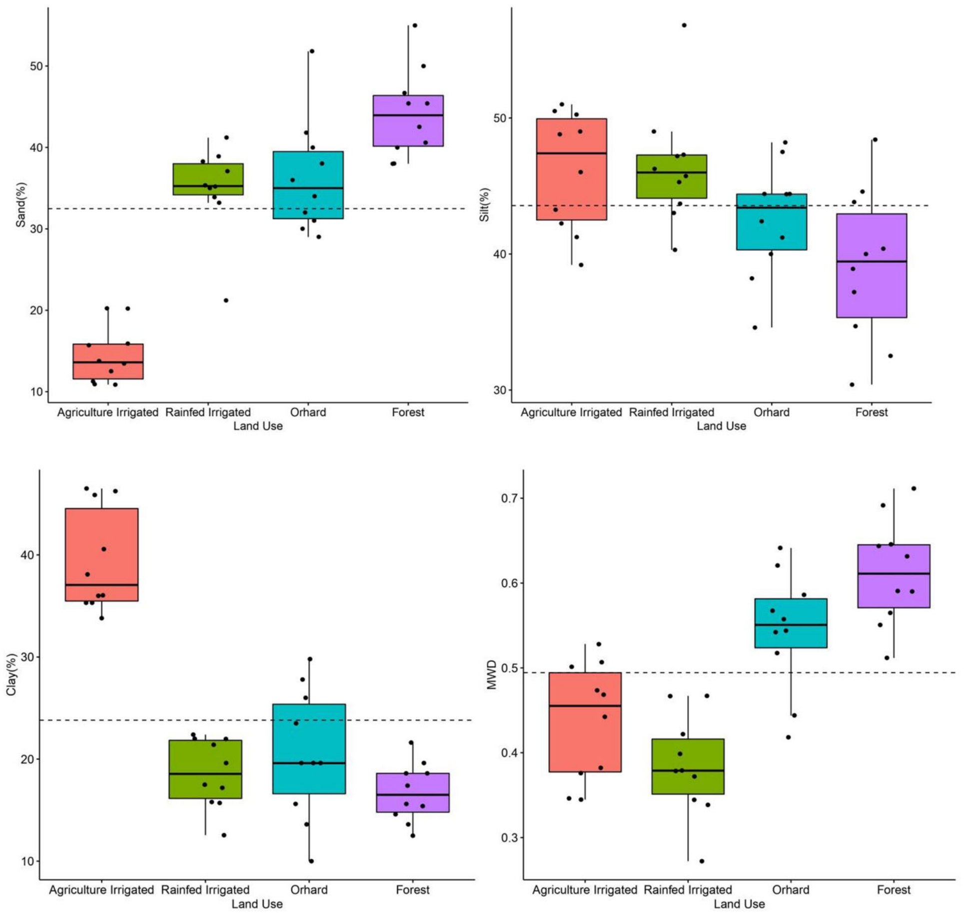

FIGURE 2 (A) Sand and silt (%) under different land uses. (B) Clay and mean weight diameter under different land uses

P adsorbed increased at any size fraction with the addition of P. Regardless of land use or aggregate size fraction, the percentage of added P adsorbed decreased linearly from the lowest (5 mg L^{-1}) to the highest level of P addition (100 mg L^{-1}). Among the four land uses, the amount of P adsorbed at any level of added P increased at lower aggregate sizes. Maximum P adsorption was noted under soils of the forest, followed by an orchard, irrigated agriculture, and rainfed agriculture among the different land uses (Table 2).

3.5 | Adsorption parameters of various aggregate sizes under four land-use types

The adsorption data for each aggregate size were fitted to Langmuir and Freundlich adsorption equations under each land use pattern. Adsorption maxima (Q_{max}) of different size aggregates varied between 1869–1924 , 1872–1900 , 1454–1890, and between 1718 and 1739 mg P kg^{-1} in irrigated agriculture, forest land use, orchard, and rainfed agriculture, respectively. Adsorption maxima decreased

TABLE 2 Amount of phosphorus adsorbed (mg kg^{-1}) by soil aggregate size of soils under different land uses

P added (mg kg^{-1})	Agriculture Irrigated				Rainfed agriculture				Orchard				Forest			
	>2 mm	2–1 mm	1–0.5 mm	0.5- 0.1 mm	>2 mm	2–1 mm	1–0.5 mm	0.5- 0.1 mm	>2 mm	2–1 mm	1–0.5 mm	0.5- 0.1 mm	>2 mm	2–1 mm	1–0.5 mm	0.5- 0.1 mm
50	38.51 (77.0)	40.42 (77.6)	40.76 (78.2)	41.06 (79.0)	34.68 (69.35)	34.98 (69.95)	35.31 (70.62)	35.64 (71.28)	40.09 (80.18)	40.42 (80.84)	40.76 (81.53)	41.06 (82.12)	43.20 (86.39)	43.44 (86.89)	43.73 (87.47)	44.12 (88.23)
100	73.52 (73.5)	77.45 (73.8)	77.77 (74.2)	78.11 (74.8)	65.77 (65.77)	66.06 (66.06)	66.36 (66.36)	66.78 (66.78)	77.14 (77.14)	77.45 (77.45)	77.77 (77.77)	78.11 (78.11)	83.31 (83.31)	83.60 (83.60)	83.90 (83.90)	84.31 (84.31)
200	141.03 (70.5)	148.22 (70.5)	148.79 (71.8)	149.33 (72.3)	125.37 (62.69)	125.87 (62.94)	126.37 (63.18)	127.13 (63.57)	147.71 (73.85)	148.22 (74.11)	148.79 (74.40)	149.33 (74.66)	160.57 (80.28)	161.14 (80.57)	161.68 (80.84)	162.32 (81.16)
300	203.19 (67.7)	212.72 (67.7)	213.59 (68.2)	214.45 (68.6)	178.99 (59.66)	179.9 (59.97)	180.73 (60.24)	181.84 (60.61)	212.01 (70.67)	212.72 (70.91)	213.59 (71.20)	214.45 (71.48)	231.86 (77.29)	232.68 (77.56)	233.42 (77.81)	234.35 (78.12)
500	323.34 (64.6)	340.40 (64.6)	341.85 (65.2)	343.01 (65.6)	282.45 (56.49)	283.61 (56.72)	285.06 (57.01)	286.96 (57.39)	339.10 (67.82)	340.40 (68.08)	341.85 (68.37)	343.01 (68.60)	370.22 (74.04)	371.30 (74.26)	372.36 (74.47)	373.77 (74.75)
1000	615.81 (61.5)	647.19 (61.5)	649.65 (61.1)	631.67 (62.5)	533.24 (53.32)	536.24 (53.62)	538.97 (53.90)	542.46 (54.25)	644.96 (64.50)	647.19 (64.72)	648.4 (64.84)	649.65 (64.97)	709.35 (70.93)	711.80 (71.18)	714.13 (71.41)	716.61 (71.66)

Adsorption parameters	Agriculture irrigated				Rainfed agriculture				Orchard				Forest			
	>2 mm	2–1 mm	1–0.5 mm	0.5- 0.1 mm	>2 mm	2–1 mm	1–0.5 mm	0.5- 0.1 mm	>2 mm	2–1 mm	1–0.5 mm	0.5–0.1 mm	>2 mm	2–1 mm	1–0.5 mm	0.5–0.1 mm
Adsorption maxima (Q_{max})	1924	1909	1885	1869	1718	1733	1734	1739	1890	1882	1870	1454	1900	1892	1891	1872
Bonding energy (*b*)	0.00123	0.00124	0.00128	0.00132	0.00097	0.00098	0.00099	0.00100	0.00144	0.00147	0.001502	0.00206	0.00202	0.00205	0.00209	0.00215
Buffering capacity ($Q_{max}b$)	2.34	2.37	2.42	2.47	1.68	1.71	1.71	1.75	2.72	2.77	2.81	2.99	3.84	4.0	4.0	4.03
K'	5.46	5.49	6.20	5.63	3.67	3.70	3.73	3.8	6.34	6.41	6.71	8.12	8.98	9.06	9.16	10.29
N	1.26	1.26	1.23	1.26	1.22	1.22	1.22	1.22	1.27	1.27	1.28	1.30	1.31	1.31	1.31	1.33

Note: Figures in parentheses are the percent P adsorbed of added P. The R^2 values of the Freundlich adsorption equation for various aggregate sizes varied from 0.9994 to 0.9998 for irrigated agriculture, 0.9998 for unirrigated agriculture, 0.9997 to 0.9998 for orchard, and 0.999 to 0.9994 for forest land use. The corresponding values for Langmuir adsorption equations varied from 0.7992 to 0.7984, 0.7993 to 0.7992, 0.8741 to 0.7994, and 0.7976 to 0.7971 in agriculture irrigated, rainfed agriculture, orchard and forest land-use, respectively.

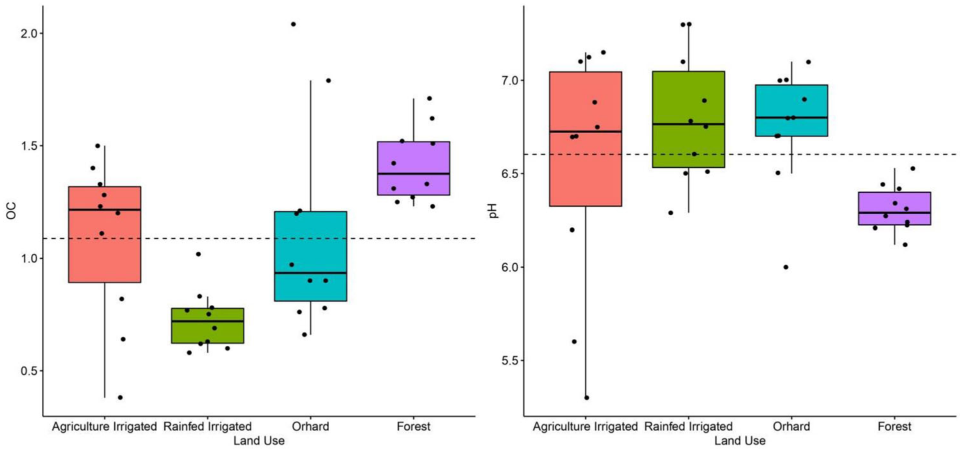

FIGURE 3 Organic carbon and pH under different land uses

lower aggregate sizes, barring a few exceptions in rainfed agriculture. The constant relating to bonding energy (*b*) or the affinity of the aggregates for P increased at smaller sizes of aggregates. Among the four land uses, the bonding energy was highest in forest land use (0.002021–0.002153 L mg^{-1}), followed by an orchard (0.001444–0.00206 L mg^{-1}), irrigated agriculture (0.001213–0.001324 L mg^{-1}), and rainfed agriculture (0.000979–0.0001005 L mg^{-1}). The buffering capacity (Q_{max} *b*) of the aggregates of various land uses followed almost the same trend as the P-binding energy. Among the land uses, the maximum buffering capacity (Q_{max} *b*) was found in the forest (3.84–4.03 L mg^{-1}), followed by orchards (2.72–2.99 L mg^{-1}), irrigated agriculture (2.34–2.47 L mg^{-1}), and rainfed agriculture (1.68–1.75 L mg^{-1}). The Freundlich constant *K′* (a measure of adsorbability) increased at the smaller size of aggregates except for irrigated agriculture. Among the land uses, the highest adsorption capacity was observed in forests (8.98–10.29 mg P kg^{-1}), followed by orchards (6.34–8.12 mg P kg^{-1}), rainfed agriculture (3.67–3.8 mg P kg^{-1}), and irrigated agriculture (5.46–5.63 mg P kg^{-1}). Freundlich's other constant, *n* (a measure of bonding energy), increased with a decrease in the aggregate, while it remained constant in some land uses, such as in irrigated agriculture and rainfed agriculture, while in forest and orchard, it varied from 1.27 to 1.30 l mg^{-1} and 1.31 to 1.33 l mg^{-1}, respectively (Table 1).

3.6 | Evaluation of adsorption isotherms

The Freundlich adsorption equation was fitted better in all aggregate sizes irrespective of land use among the two adsorption isotherms. Based on model evaluation criteria, viz. R^2, root mean square error (RMSE), mean absolute error (MAE), Akaike information criteria (AIC), and Bayesian information criteria (BIC), a comparison of both models was made. The applied Freundlich model was found to best fit all the land uses in all aggregate sizes based on the given evaluation criteria. The model is better at lowering the RMSE, MAE, AIC, and BIC and higher R^2.

The RMSE values of the Freundlich adsorption equation for various aggregate sizes varied from 6.01 to 7.12, 2.58 to 3.88, 2.80 to 3.09, and 3.49 to 4.83 for the forest orchard, rainfed agriculture, and irrigated agriculture, respectively. The corresponding values for the Langmuir adsorption equation were 17.41–19.92, 11.38–13.42, and 9.27–9.79, and 11.33–19.29 for forest, orchard, rainfed agriculture, and irrigated agriculture, respectively. The MAE values of the Freundlich model for various aggregate sizes varied from 5.04 to 6.18, 2.11 to 3.68, 2.22 to 2.62, and 1.97 to 4.01 for the forest, orchard, rainfed agriculture, and irrigated agriculture, respectively. The corresponding values for the Langmuir adsorption equation varied from 15.34 to 16.92, 10.32 to 11.58, 8.09 to 8.57, and 9.94 to 15.7 for the forest orchard, rainfed agriculture, and irrigated agriculture, respectively (Table 3).

4 | DISCUSSION

4.1 | Physico-chemical properties

The soil texture among the different land uses varied from coarse to fine in the order of forest > orchard > rainfed agriculture > irrigated agriculture, which was in agreement with Najar et al. (2009). Forests have low levels of clay and high levels of sand due to less soil development casued by higher altitudes with steep slopes and low infiltration, more erosion, low temperatures and vice versa in irrigated agriculture with high levels of clay and low levels of sand (Abad et al., 2014; Arun Kumar et al., 2002; Bhuyan et al., 2013; Kiflu & Beyene 2013; Mahapatra et al., 2000; Maqbool et al., 2017). The mean weight diameter of different land uses follows a decreasing trend of forest > orchard > irrigated agriculture > rainfed agriculture. Soil organic carbon led to various stabilities and distributions of soil aggregates under different land-use types. Less disturbance in forest soils and higher soil organic carbon led to the highest mean weight diameter in the forest land use (Abiven et al., 2009; Alagöz & Yilmaz, 2009; Zhao et al., 2017). The soil reaction across different land uses was moderately acidic to neutral, and the pH varied from 6.3 to 6.8 under different land uses. Removal

TABLE 3 Evaluation of different adsorption isotherms

		Langmuir					Freundlich				
Land use	Aggregate size	R^2	RMSE	MAE	AIC	BIC	R^2	RMSE	MAE	AIC	BIC
Forest	>2 mm	0.7976	17.41	15.34	57.31	56.68	0.9994	6.01	5.04	44.56	43.93
	2–1 mm	0.7974	17.87	15.79	57.62	57.00	0.9994	6.40	5.47	45.31	44.69
	1–0.5 mm	0.7972	18.49	16.37	58.03	57.41	0.9993	6.96	6.03	46.31	45.69
	0.5–0.1 mm	0.7971	19.92	16.92	58.42	57.80	0.9990	7.12	6.18	46.59	45.96
Orchard	>2 mm	0.8741	12.93	11.32	53.74	53.12	0.9997	3.71	3.37	38.77	38.14
	2–1 mm	0.7988	13.17	11.58	53.96	53.34	0.9997	3.79	3.51	39.01	38.39
	1–0.5 mm	0.7987	13.42	11.81	54.19	53.56	0.9997	3.88	3.68	39.29	38.67
	0.5–0.1 mm	0.7994	11.38	10.32	52.21	51.58	0.9998	2.58	2.11	34.42	33.80
Unirrigated agriculture	>2 mm	0.7993	9.27	8.09	49.75	49.13	0.9998	2.80	2.22	35.42	34.79
	2–1 mm	0.7993	9.49	8.32	50.03	49.40	0.9998	2.91	2.41	35.85	35.22
	1–0.5 mm	0.8857	9.63	8.45	50.21	49.59	0.9998	2.99	2.53	36.18	35.55
	0.5–0.1 mm	0.7992	9.79	8.57	50.41	49.78	0.9998	3.09	2.62	36.57	35.95
Irrigated agriculture	>2 mm	0.7992	11.33	9.94	52.16	51.53	0.9997	3.49	2.70	38.05	37.43
	2–1 mm	0.8694	12.62	10.87	53.45	52.82	0.9994	4.65	3.73	41.48	40.86
	1–0.5 mm	0.7929	19.29	15.74	86.17	85.55	0.9998	2.59	1.97	34.46	33.84
	0.5–0.1 mm	0.7984	13.28	11.58	54.06	53.44	0.9995	4.83	4.01	41.94	41.32

Abbreviations: AIC, Akaike information criteria, BIC, Bayesian information criteria; MAE, mean absolute error; RMSE, relative mean square error.

of bases by tree biomass, acidic nature of litter after its decomposition, leaching of salts from upper layers led to low pH, as in the case of forest and irrigated agriculture, and buildup of calcium carbonate and salts in the case of rainfed agriculture due to less leaching (Bhuyan et al., 2013; Kiflu & Beyene, 2013; Kirmani, 2004; Maqbool et al., 2017; Regmi & Zoebisch, 2004; Singh et al., 2012). At higher pleaks, higher biomass production and lower decomposition, low levels of organic matter, and complete removal by crops has been reported as compared to irrigated agriculture, similarly lower biomass due to less vegetation led to lower pH in forest soils has been reported as compared to irrigated agricultural soils (Duguma et al., 2010; Maqbool et al., 2017; Najar et al., 2009; Nisar & Lone, 2013; Regmi & Zoebisch, 2004; Selassie & Ayanna, 2013; Yimer et al., 2007).

4.2 | Phosphorus adsorption under different land uses

The higher specific surface area of smaller aggregates than larger aggregates led to increased adsorbed phosphorus (P) at any level of added P among all land uses. With the increase in the concentration of added P, fewer sites will be available for further adsorption of P regardless of the size of aggregates, which leads to a decreased percent P adsorbed of added P with an increase in the level of P addition. A greater surface area available, as manifested by a higher MWD in forest land use, led to more significant adsorption in forest soils. In addition, the other soil parameters, in particular, the higher organic carbon content in forest land use, contributed to higher adsorption than other land uses. The combination of organic matter and possible stabilization by free sesquioxides, which are sites for P adsorption, is attributed to organic matter improving P adsorption. Phosphorus adsorption decreases at higher pH in comparison with other land uses; it was found to be lower in the forest. In P adsorption, soil organic matter is reported to play a dual role, unwanted due to adsorbent sites being blocked and positive for anionic nature because sites attract positive ions such as Ca, Fe, and Al inducing P adsorption. The highest amount of P adsorbed was found in the smallest aggregate size, that is, 0.5–0.1 mm, and lowest in the aggregate size of >2 mm regardless of the land use, which may be attributed to the lesser buffering capacity of larger aggregates (Bera et al., 2006; Bhattacharyya et al., 2015; Boparai & Sharma, 2006; Fink et al., 2016; Jalali & Jalali, 2016; Pal & Mondal, 2009; Rashmi et al., 2017; Roy & Pal, 2018; Saha et al., 1999; Yadav et al., 2017; H. T. Zhang et al., 2008).

4.3 | Adsorption parameters of various aggregate sizes under four land uses

The higher specific surface area in smaller aggregates led to a higher bonding energy (*b*) or the affinity of the aggregates for phosphate. Among the four land uses, the higher organic matter content and MWD led to higher bonding energy in forest soils. The buffering capacity is higher in smaller than larger aggregates. As the solution concentration of P was in reverse linked to buffering, poorly aggregated (smaller size) soils would have a lower solution concentration of P at a given level of P available for use in plants but would retain P for more extended periods since smaller aggregates have a higher specific surface area. In addition, the differences in other soil properties can also be related, particularly to the organic carbon content. Light textured soils are typically less buffered than heavy textured soils.

On the other hand, forest and agriculture irrigated soils performed differently. Clay content is considered the major soil property that determines phosphorus adsorption. However, in soils with the same amount of clay, buffering capacity may vary as the soil organic matter varies, leading to higher buffering capacity in forest soils than in others. Due to the higher organic carbon in forest land, the Freundlich constant K' (absorbability measure) was highest relative to other land uses. As a surface property, the bonding energy changes with changes in the surface area but declines exponentially with increasing saturation of phosphate on exchange sites. The other Freundlich constant, n (a measure of bonding energy), was found to be highest in forest land use (Bowman & Olsen, 1985; Moughli et al., 1993; Pal & Mondal, 2009; Roy & Pal, 2018; Six et al., 2000).

4.4 | Evaluation of adsorption isotherms

Among the two adsorption isotherms, the Freundlich adsorption equation was fitted better in all aggregate sizes irrespective of land use. A comparison of both models was performed based on model evaluation criteria, viz. R^2, RMSE, MAE, AIC, and BIC (Table 1). The applied Freundlich model best fits all the land uses in all aggregate sizes based on the given evaluation criteria. Lower RMSE, MAE, AIC, and BIC and higher R^2 better fit the model. The R^2 values of the Freundlich adsorption equation for various aggregate sizes of all land uses are higher than those of the Langmuir model. Moreover, the RMSE, MAE, AIC, and BIC values of the Freundlich model are lower than those of the Langmuir model (Ahmad & Idris, 2014; Kinniburgh, 1986; Pal, 2011; Pham, 2019; Roy & Pal, 2018; Shirvani et al., 2005).

5 | CONCLUSION

The results of this study contribute to determining the phosphorus (P) adsorption characteristics of various land uses and the performance of various models to predict the adsorption processes of soils with different physical and chemical properties, in particular MWD. Land use had a pronounced effect on the adsorption characteristics of phosphorus. Variations in different parameters of phosphorus adsorption were attributed to differences in physico-chemical properties reflected by differences in soil properties and organic carbon content in the different land uses. For all land uses, the Freundlich model was more accurate at fitting the data than Langmuir alone. This model can be used to study adsorption properties and reaction processes in any experimental procedure. It is preferable to use the Freundlich phosphorus adsorption isotherm, which correlates the soil solution phosphorus concentration to the amount of P adsorbed in the soil, to predict the phosphorus fertilizer requirement of a particular soil. Unless specifically standardized, soil tests only provide information about the plant-available phosphorus and therefore do not approximate how much P fertilizer is needed.

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DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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