AN EVALUATION OF PHOSPHOROUS ADSORPTION CAPACITY AS INFLUENCED BY NUTRIENT MANAGEMENT PRACTICES IN A VERTISOL OF CHHATTISGARH

M. Sc. (Ag.) Thesis

by

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by

SANDIP KUMAR MOHANTY

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CERTIFICATE - I

This is to certify that the thesis entitled **"An evaluation of phosphorous adsorption capacity as influenced by nutrient management practices in a *Vertisol* of Chhattisgarh"** submitted in partial fulfillment of the requirement for the degree of **Master of Science in Agriculture** of the Indira Gandhi Krishi Vishwavidyalaya, Raipur, (C.G.) is a record of the bonafide research work carried out by **Sandip Kumar Mohanty** under my guidance and supervision. The subject of the thesis has been approved by the Student's Advisory Committee and the Director of Instructions.

No part of the thesis has been submitted for any other degree or diploma or has been published/published part has been fully acknowledged. All the assistance and help received during the course of the investigations have been duly acknowledged by him.

Chairman

Date: 31|10|2020

THESIS APPROVED BY THE STUDENT'S ADVISORY COMMITTEE

Chairman (Shri Vinay Bachkaiya) ____________________

Member (Dr. Alok Tiwari) ____________________

Member (Dr. Nitish Tiwari) ____________________

Member (Dr. R.R Saxena) ____________________

CERTIFICATE- II

This is to certify that the thesis entitled **"An evaluation of phosphorous adsorption capacity as influenced by nutrient management practices in a *Vertisol* of Chhattisgarh"** submitted by **Sandip Kumar Mohanty** to the Indira Gandhi Krishi Vishwavidyalaya, Raipur, in partial fulfillment of the requirements for the degree of Master of Science in Agriculture in the **Department of Soil Science and Agricultural Chemistry** has been approved by the external evaluator and Student's Advisory Committee after oral examination, **under the chairmanship of Head of the Department.**

Major Advisor

Signature of Head of the Department

(Name.....Koshlendra Tedia.....**)**

Date: 18-11-2020

Faculty Dean ____________________

Approved/ Not approved

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Departmental help. I would like to express my sincere gratitude to Dr. M. Pandey (Librarian, Nehru Library, Raipur) for giving me kind help during my present study. I wish to express my thanks to Mr. Vishnu, Mr.Ramesh, Mr. Parmanand, Mr. Tarun, Mr.Bhushan, Miss Sunitha, Mr. Deva and all other staff members working in Soil Testing Laboratory in the Department of Soil Sciences and Agricultural Chemistry for their great help during the entire research work.

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LIST OF SYMBOLS AND ABBREVIATIONS

ABBREVIATIONS	DESCRIPTIONS
%	Per cent
@	At the rate of
cm	Centimeter
°C	Degree Celsius
et al	Et all (and other)
Fig	Figure
Ha	Hectare
i.e.,	id est (that is)
G	Gram
Kg	Kilogram
kg/ha	Kilogram per hectare
M	Meter
mg/kg	Milligram per kilogram
min.	Minimum
max.	Maximum
No.	Number
µg	Microgram
Ppm	Part per million
mg	Mililigram
EC	Electrical conductivity

THESIS ABSTRACT

a) Title of the Thesis	:	An evaluation of phosphorous adsorption capacity as influenced by nutrient management practices in a *Vertisol* of Chhattisgarh
b) Full Name of the Student	:	Sandip Kumar Mohanty
c) Major Subject	:	Soil Science and Agricultural Chemistry
d) Name and Address of the Major Advisor	:	Shri Vinay Bachkaiya Scientist, Department of Soil Science and Agricultural Chemistry, College of Agriculture, IGKV, Raipur (C.G.)
e) Degree to be awarded	:	M.Sc. (Ag.) Soil Science and Agricultural Chemistry

Signature of the Student

Signature of the Major Advisor

Date: 31|10|2020.

Signature of the Head of the Department

ABSTRACT

The field experiment entitled "An evaluation of phosphorous adsorption capacity as influenced by nutrient management practices in a *Vertisol* of Chhattisgarh" was conducted at Research cum Instructional farm, Indira Gandhi Krishi Vishwavidhyalaya, Raipur (C.G.) during *kharif* - 2019 in Randomized Block Design with ten treatments and four replications with rice variety "IGKV-R1" used as test crop. The treatment consists of different level of nutrient management practices i.e T_1 (Control), T_2 (50% NPK), T_3 (100% NPK), T_4 (150% NPK), T_5 (100% NPK + Zn), T_6 (100% NP), T_7 (100% N), T_8 (100% NPK + FYM), T_9 (50% NPK + BGA) and T_{10} (50% NPK + GM) were applied. In *Vertisol* of Chhattisgarh, phosphorus adsorption behaviour influenced by various nutrient management practices were studied by applying Langmuir and Freundlich adsorption equations to the data of P adsorption. Solid phase P adsorption was closely correlated with its concentrations in the solution phase. Among the treatments, control recorded the highest P adsorption followed by 100% N due to long year stress at a given equilibrium P concentration implying that P ions are most tightly held in the soil. For both Langmuir and Freundlich Adsorption Isotherms, the similar and high R^2 values were observed, suggesting that the P adsorption data verified to both isotherms indicating their goodness of fit. The P adsorption maxima ‘b’ was the maximum for control and 100% N whereas the minimum was recorded in 100% NPK along with FYM. In the same order, the Langmuir 'K' value showed a growing trend showing a high affinity for P in control followed by 100% N, which had resulted in higher value of ‘b’. The value ‘n’ that give the degree of linearity were maximum in 100% NPK with FYM and minimum in control, however, the value of ‘k’ represented a decreasing trend in same sequence. The value of buffering capacity obtained for all the treatment receiving different fertilization and with increased P fertilization, the values declined significantly and minimum was observed in the soil getting the additional input of farmyard manure.

शोध सारांश

a) शोध शीर्षक : छत्तीसगढ़ के वर्टिसोल में पोषक तत्व प्रबंधन कर स्फुर अवशोषण क्षमता का मूल्यांकन करना
b) विद्यार्थी का पूरा नाम : संदीप कुमार मोहंती
c) प्रमुख विषय : मृदा विज्ञान और कृषि रसायन शास्त्र
d)प्रमुख सलाहकार का नाम और पता: श्री विनय बचकैया वैज्ञानिक, मृदा विज्ञान और कृषि रसायन शास्त्र विभाग,कृषि महाविद्यालय, इ.गां.कृ.वि.वि. रायपुर (छ.ग.)
e) सम्मानित किये जाने वाली उपाधि : एम.एस.सी.(कृषि) मृदा विज्ञान और कृषि रसायन शास्त्र

प्रमुख सलाहकार के हस्ताक्षर

विद्यार्थी के हस्ताक्षर

दिनांक 31/10/2020.

विभागाध्यक्ष के हस्ताक्षर

सारांश

प्रक्षेत्र प्रयोग शीर्षक “छत्तीसगढ़ के वर्टिसोल में पोषक तत्व प्रबंधन कर स्फुर अवशोषण क्षमता का मूल्यांकन करना " को अनुसंधान सह अनुदेशात्मक प्रक्षेत्र, इंदिरा गांधी कृषि विश्वविद्यालय रायपुर (छ.ग.) में खरिफ 2019 के दौरान यादृच्छिक खंड रचना में दस उपचार और चार प्रतिकृति में धान की IGKV R1 किस्म पर आयोजित किया गया। दस अलग अलग उपचार में विभिन्न स्तर के पोषक तत्व जैसे T_1 (नियंत्रण), T_2 (50 प्रतिशत NPK), T_3 (100 प्रतिशत NPK), T_4 (150 प्रतिशत NPK), T_5 (100 प्रतिशत NPK+Zn), T_6 (100 प्रतिशत NP), T_7 (100 प्रतिशत N), T_8 (100 प्रतिशत NPK+FYM), T_9(50 प्रतिशत NPK+BGA), T_{10} (50 प्रतिशत NPK+GM) दिया गया । छ. ग. के वर्टिसोल में स्फुर अवशोषण की क्षमता विभिन्न प्रकार के पोषक तत्व प्रबंधन से प्रभावित होती है जिसे लांगमुईर एवं फ्रेंडलीच अवशोषण समीकरण के द्वारा मूल्यांकन किया गया । स्फुर अवशोषण का ठोस अवस्था से अत्यधिक सम्बंधित होता है ! स्फुर अत्यधिक रूप से नियंत्रित एवं 100 प्रतिशत N से जुड़ा होता है । लांगमुईर एवं फुन्डलीच अवशोषण आइसोथेरम दोनों के लिए R^2 के समान और उच्च मूल्यों ने संकेत दिया कि P अवशोषण डेटा दोनों को इज़ोटर्मस में फिट होने का संकेत दिया

गया है जो उनके फिट होने के संकेत देता है। लांगमुईर एवं फुन्डलीच अवशोषण आइसोथेरम में एक सामान एवं अत्यधिक R^2 यह दर्शाता है की स्फुर अवशोषण अत्यधिक नियंत्रित एवं 100 प्रतिशत N एवं न्यूनतम 100 प्रतिशत NPK के साथ FYM में होता है लैंगमुइर 'K' के ने उसी क्रम में एक बढ़ती प्रवृत्ति दिखाई, जिसमें उपचार प्राप्त करने की उच्च लगाव और स्फुर के लिए 100 प्रतिशत N का संकेत मिलता है, जिसके परिणामस्वरूप 'b' अधिक था। ‘n’ जो कि रैखिकता की डिग्री देते हैं, FYM के साथ-साथ 100% NPK में अधिकतम थे और नियंत्रण में न्यूनतम थे, जबकि ‘k' के मूल्य में समान क्रम में घटती हुई प्रवृत्ति दिखाई दी। विभिन्न उपचार और खाद प्राप्त करने वाले सभी उपचारों के लिए प्राप्त बफ़रिंग क्षमता का मूल्य यह दर्शाता है ।

CHAPTER –I

INTRODUCTION

Next to nitrogen, P is the second most essential nutrient element for plant. Phosphorous is very important nutrient for vigorous growth and development of reproductive part (fruits, seeds etc.) (Havlin *et al*., 2012) and also for the better root growth of the plant. Phosphorus has oxidation states ranging from (-3) to (+5). However, common oxidation states are 3 and 5 of which +5 valences is more important than other for most of the reactions in soils as well as in P fertilizer production (Tiwari, 2012).

Plant roots take up P from soil mostly as the primary orthophosphate ($H_2PO_4^-$) but it is taken up also in the form of secondary orthophosphate ions bysome plants. With the increase in soil pH, the amount of secondary orthophosphate form of P increases (Tiwari, 2012).

For enhancing crop maturity, particularly in grain crops, P is essential. P also reduces the time required for grain ripening. Adequate P is associated with increased straw strength in cereals and increased N_2-fixation capacity of legumes. P enhances disease resistant power of plants and improves quality of certain fruit, forage, vegetable and grain crops (Havlin *et al.*, 2012).

Due to the high soil matrix reactivity of phosphorus, its management is somewhat uncommon and distinct from other nutrients. In fact, the issue is not P reserves in the soil, but its occurrence in forms that are inaccessible for plant. The intensive cultivation of high yielding varieties with P application to each crop and poor recovery of applied phosphorus (8% to 33%) by the first crop had resulted in significant build-up of phosphorus in soil (Brar *et al.*, 2004). Rest of the added P is in the soil as less soluble products of phosphorus (Dhillon and Dev, 1988 and Murthy *et al.,* 2002). Therefore, the chemistry of P in fertilized soil was practically the chemistry of solubility and interaction of meta stable phosphorus compounds with other components and plant components. (Mukherjee *et al.*,1979).

Different type of secondary Ca-phosphate is found in neutral to alkaline soil pH. On the surface of soil particles adsorption of P occurs. It also sorbed to positive edges of Kaolinite clay and in acid soils to Al and Fe oxides and hydroxides, such as gibbsite, haematite, goetite, ferrihydrate. The phosphorus sorbed on the surface of oxides and hydroxides of Al and Fe can be physically encapsulated or occluded by the minerals at which it is sorbed and therefore rendered much available to the plants (Smeck,1985).

During one season, the soil solution needs to be replenished with P several times. This is gained by the dynamic relationship between labile P and solution P. The process of “chemisorption” is two dimensional surface process of adsorption of P to the surface of the soil component. Sorption may also involve some precipitation processes where a new solid phase is formed under high P concentration or longer periods of time (Vander Zee and Van Riemsdijk, 1988). In calcareous soils, small amounts of phosphate can be sorbed by replacement of CO_3^{2-} on the $CaCO_3$ surface. At low P concentration, surface adsorption is more dominants. However, at high P concentration, Ca-P minerals precipitate on the CaCO3 surface. Adsorption of solution P in calcareous soils may also be possible by other minerals, mostly $Al(OH)_3$ and $Fe(OH)_3$ (Havlin *et al.*, 2012).

P adsorption capacity is governed by some soil properties such as soil texture (Leclerc, *et al.*, 2001), organic matter (Daly *et al.*, 2001), oxides of iron and aluminium (Toor *et al.*, 1997), soil pH (Barrow, 1984) and $CaCO_3$ content (Bertrand, 2003). Even in calcareous soils, hydrous oxides are important for adsorption of P (Holford, 1974). Organic acids including oxalate, malate and citrate are exuded by plant roots and they have positive effect on enhancing P desorption (Jones, 1998, Ryan *et al.*, 2001).

Phosphate sorption is a complex reaction between the soil and P source and involves both adsorption and precipitation reactions, the former found to be dominant over a short period at low P concentration in soil solution (Rajan and Watkinson, 1976; Mehdi and Taylor, 1958) and precipitation at higher concentration for longer period (Lin *et at.,* 1983). At first, reaction between phosphate and soils is rapid and then becomes slower and continues for long time without achieving any true equilibrium (Rajan and Fox, 1972; Barrow, 1983 b). Adsorbed and precipitated phosphate functions as a reservoir for solution P regeneration, the concentration of which affects the diffusion of phosphate to the root of the plant and the absorption of phosphate by the plant. (Barrow, 1979; Tomar and Pundir ,1997; Tomar and Biswas, 1998).

The P adsorption by soils is important because adsorbed Phosphate equilibrates with soil solution P which, in turn, is immediate source of P for plants. Phosphate adsorption isotherm integrates P intensity ability and quantity parameters of soils and these factors play key role in controlling P flux to the roots of growing plants (Doddamani and Seshagiri Rao, 1989 and Milap Chand *et al.* 1995). A number of adsorption isotherms have been used for describing the sorption of phosphate in soil and calculating their intensity and capacity factors using Langmuir, Freundlich, BET and Tcmkin equations.

Phosphorus adsorption phenomenon is one of the widely studied subjects on Indian soils. Vertisols originated from different parent materials differ in their properties, which in turn influence significantly phosphorus adsorption and desorption that are the key processes that govern its availability in Vertisols (Shailja & Sahrawat, 1990). However phosphorus adsorption studies on Vertisols are meagre. Long-term experiments play a significant role in understanding the complex interactions between inputs added, plant, soil, climate management and their effect on sustainable crop production. These experiments can be seen as an important tool for providing information on the effect of application of the continuous fertilizers involving various combinations of nutrients on soil fertility and crop productivity. Management of phosphate fertilizers is an important aspect for balancing the concentration of biologically available soil P at a level adequate for plant growth

(Afsar *et al.,* 2012). Soil has the capacity to adsorb phosphorous in selective amount with a great possibility to drain excess P into surface or ground water when a critical P sorption saturation level is fulfilled (Paulter, 2000). Hence, it is very crucial to predict the partitioning of applied P fertilizer between soil solid and soil solution. In view of the environmental aspect, sorption-desorption of P also takes a greater role in P management (Afsar *et al.,* 2012).

In view of the above facts the present experiment entitled, **"An evaluation of phosphorous adsorption capacity as influenced by nutrient management practices in a *Vertisol* of Chhattisgarh"** will be carried out with the following objectives:

1. To evaluate the effect of nutrient management on P adsorption indices in a Vertisol.
2. To evaluate suitability of adsorption equations for assessing the P sorption behaviour in a Vertisol.

CHAPTER-II
REVIEW OF LITERATURE

This literature pertinent to the present investigation entitled **"An evaluation of phosphorous adsorption capacity as influenced by nutrient management practices in a *Vertisol* of Chhattisgarh"** have been reviewed in this chapter under the following heads:

2.1 To evaluate the effect of nutrient management on P adsorption indices in a Vertisol.

2.2 To evaluate suitability of adsorption equations for assessing the P sorption behaviour in a Vertisol.

2.1 To evaluate the effect of nutrient management on P adsorption indices in a Vertisol.

In some cases, the adsorption process, which refers to the surface accumulation of P on soil components, may be preceded by the penetration into the adsorbent body of the adsorbed P by diffusion, leading to further adsorption of the adsorbed species. The general term "sorption" is often used to denote the simultaneous occurrence of any of these processes.

In acid soils, adsorption is usually attributed to iron (Fe) and aluminium (Al) hydrous oxide and (1: 1) layer lattice clays, particularly in low-pH tropical soils. Ryden and Pratt (1980) have documented the possibility of precipitation in these soils as natural aluminium and iron phosphates (such as Variscite and Strengite). In neutral and alkaline soils, the stable minerals that control P concentration are the different forms of calcium phosphates, after a long period of contact; it declines to as low as 1 to 2 mg of P kg^{-1} soil (Al-khateeb *et al.*, 1986). The slow formation of Ca-P compounds (Barrow, 1987) can better describe this behavior.

Various employees used phosphate sorption isotherms such as Langmuir, Freundlich, Brunauer-Emmett-Teller (BET) and Temkin equations to predict soil requirements for P fertilizer. The main objectives of presenting adsorption curves were (i) to identify the soil constitutes involved in adsorption (Loganathan *et al.,* 1987), (ii) to predict the amount of fertilizer requirements of soils to meet the demand for plant uptake in order to get optimum yield (Fox and Kamprath 1970, Fox 1974, Fox and Kang 1978, Greenland and Datta 1985, Kalages *et al.,* 1988 and Chaudhary *et al.,* 1997) and (iii) to study the mechanism of adsorption (Barrow 1984 and Barrow 1987b).

In acidic soils, P sorbed at low energy was at least two times greater than the high energy surface, according to Patiram *et al.* (1990) and he found that the adsorption maxima at high energy level, bonding energy, P buffering ability and sorbed P which was strongly and positively correlated to organic carbon and amorphous and crystalline forms of iron and aluminium. Forms of aluminium have been reported to contribute more to P adsorption than forms of iron.

Sharma *et al.* (1995) observed the effect of continuous cropping and fertilization on adsorption and desorption of soil phosphorus and they concluded that Phosphate adsorption has increased in all soils with rising levels of added P. In the plots receiving P, the degree of P adsorption was relatively lower. Data on phosphorus adsorption was found to follow the both isotherms of Langmuir and Freundlich best. Phosphorus adsorption data was found to fit best both to Langmuir and Freundlich isotherms. In six differentially fertilized plots, soil P adsorption maxima obtained from Langmuir isotherm ranged from 123 to 498 mg g^{-1} soil. The bonding energy values obtained from Langmuir isotherm plot were the lowest in control and $N_{120}P_OK_O$ treatments whereas these values tended to increase with P addition.

The effect of the long-term use of fertilizer, manure and lime on phosphate adsorption parameters in Alfisol acid was investigated by Prasad and Mathur (1997). They concluded that the rate and degree of adsorption of P in soils receiving NPK plus lime or Farm Yard Manure was significantly lower.

In unfertilized plots, the adsorption maxima(b) was highest and lowest in NPK plus FYM plots, followed by NPK plus lime. Bahl *et al.* (1998) observed that the impact of green manuring and cropping on P sorption in Punjab and Himachal Pradesh soils and stated that with P application and green manuring, the amount and rate of P adsorption decreased while increased by cropping and they also reported that with phosphorus application and green manuring, adsorption maxima decreased.

Bahl *et al.* (1998) studied phosphorus sorption as influenced by green manuring and cropping with twenty surface (0-0.15 m) non-calcareous, calcareous and acid surface (0 - 0.15 m) soils of Punjab and Himachal Pradesh. The data were fitted to Freundlich as well as the Langmuir adsorption isotherms. The extent and rate of P adsorption declined with P application and green manuring while it increased by cropping. Phosphorus application and green manuring also resulted in decrease in adsorption maxima in all the category of soils, the decrease being higher (20.7%) in calcareous soils.

Kumar and Singh (1998) concluded that, with the increase in the initial level of P in the solution, the amount of P sorbed by the soils has shown a steady increase. A reverse trend was followed by the proportion of added P and sorbed, steadily decreasing from the lowest to the highest level. The effect of P sorbed by soil was quite evident.

In relation to fertilizer P and manure applied in soybean-wheat rotation, Reddy *et al*. (1999) studied phosphate sorption behaviour of a typical Haplustert. In the control plot soil, the degree of P sorption was comparatively greater and gradually decreased with increasing P fertilizer rates in both manured and unmanured plots. For all samples, the P sorption data was found to best fit the classical Langmuir isotherm equation. For control plot soil, the values of P sorption maxima (b), bonding energy constant (K); maximum phosphate buffering capacity (MPBC) and standard P requirement (SPR) were highest and decreased as P fertilizations rates increased. But, a reverse pattern was followed by the P supply parameter (SP). In manured plots, the effects of fertilizer P rates on sorption parameters were more pronounced than in un- manured ones.

Patil *et al.* (2000) carried out adsorption studies on Vertisols and Inceptisols and reported that these soils differed in their adsorption properties. The P ions were more tightly held by Vertisol. The adsorption capacity and binding energies appeared to decrease with increase in the soil extractable P in both soils.

While evaluating the impact of long-term differential fertilizations on phosphate adsorption, Josan (2000) found that P sorption in control soil was relatively higher and decreased gradually as fertilizer P application rates increased. Sharma *et al.* (1995) also documented a similar effect of continuous cropping and fertilizations on soil adsorption behaviour after 11 years of long- term experimentation. The pattern of P availability in various soils was studied by Toor *et al.* (1997) by fitting adsorption data to various adsorption equations. In all the soils under analysis, Freundlich equation was stated to describe P adsorption better than the Langmuir equation. However, Vig and Dev (1975) found that Langmuir's isotherm was best suited to the P adsorption data. Upadhyay *et al.* (1993) reported similar findings while researching P adsorption in some essential North-West Himalayan soils.

Vig *et al.* (2000) recorded that P sorption was increased by the addition of calcium carbonate, the impact being greater in coarse textured soils than in fine textured soils. However, the application of organic manures was found to decrease P sorption with greater reduction being observed in case of organic residues having higher P content.

Singh *et al.* (2006) studied the long-term usage of fertilizers and FYM and their effect on P adsorption and desorption behaviour in soils. They found that in soil receiving 100 per cent NPK plus FYM, P adsorption was much lower compared to treatments where only inorganic fertilizers were used. Similarly, in soil receiving 100 % NPK plus FYM treatment, desorption was higher compared to biogas slurry, raising overall soil P status to a higher level compared to FYM.

Chen *et al.* (2001) studied the effect of applied compost on the inorganic P sorption potential of highly acidic soil (clay loam, pH 4.5), slightly acidic (clay loam, pH 6.2) and slightly alkaline soil (clay, pH 7.4). Two of the compost used was prepared from swine manure or cattle manure, while the third was made of straw. The findings showed that the inorganic P sorption capacity and P sorption percentage were improved by three types of compost.

Mohammadi *et al.* (2009) examined the influence of cumulative and residual effects of organic fertilizer effect on Olsen-P and P sorption index. They reported that long-term application of P-containing fertilizers, in particular organic fertilizers, generally increases the level of water soluble and available P in the soil and at the same time, can lead to soil accumulation of P.

The effects of sources and the amount of phosphorus on sorption kinetics were examined by Brauer *et al.* (2007). They found that when P was added as fertilizer instead of turkey litter, phosphorus bonding capacity decreased to a greater extent.

The effect of the incorporation of crop residues and organic manure on phosphate bioavailability was examined by Singh *et al.* (2006) and they found that crop residue incorporation increased P adsorption maxima as well as resistance to soil release of P. They also reported that with the incorporation of crop residues, both P desorption and P sorption in soil decreased.

Singh *et al.* (2007b) studied the impact on phosphorus sorption due to P source in soil that varying in organic matter content and they analysed that with increasing organic carbon content in soils, Langmuir adsorption maxima values decreased, regardless of soil and P source, and the Freundlich isotherm also showed a more or less similar pattern.

The effects of organic materials on soil chemical characteristics were evaluated by Opala (2011) and concluded that FYM, when applied in combination with triple superphosphate (TSP) lowered the P adsorption capacity of the soil as compared to control. Regarding the application of green manure residues in two weathered soils, Pypers *et al*. (2005) examined changes in P availability and they concluded that the increased in P availability following residues amendment depends on residues characteristics which decrease P adsorption strength in soils.

Singh (2000) interpreted the desorption behaviour of P in neutral to alkaline soils in term of Dm (desorption maxima) and Kd (a constant related to P mobility). Dm values were found to exhibit a decline with increasing clay content and organic carbon while Kdvalues showed an increase. These results were exactly opposite to those observed in case of adsorption. However, among different P carriers, Dm values showed similar trend as adsorption maxima (DAP> SSP> ANP> NP). While Kdvalues followed similar trend as bonding energy (DAL> SSP> ANP> NP). Singh *et al* (2006) shows that during the past 32 years the quantity of P desorbed was far less in unfertilized soil and the soil receiving only 50% NPK. The soil that adsorbed a high proportion of applied P during the adsorption reaction tended to release a lower proportion during the desorption reaction and vice versa.

Phosphorus adsorption desorption models provide vital data for better understanding of P dynamics in the soil in long-term fertilizer experiments. Singh *et al*. (2006) conducted a study to understand the effects of long-term use of fertilizer and farmyard manure on the action of adsorption- desorption and bioavailability of phosphorus in soils, the adsorption maxima and the degree of P adsorption calculated from the isotherm equation in unfertilized soil at its maximum and P adsorption decreased with increased P applications. The incorporation of farmyard manure decreased P adsorption even more than a super-optimal application of P fertilizers. The experiment indicated beneficial effects of an annual incorporation of farmyard manure with optimal P levels, and P bioavailability in these soils was found to be even higher than the soil P application. The P sorption maxima and buffering capacity of the soil are the major parameters in governing P availability in the soil.

Pal *et al.* (2009) conducted a study to determine P sorption in 35 years long-term experiment on maize-wheat sequence at PAU Research farm, Ludhiana. They reported the extent of P adsorption was comparatively lower in plots receiving higher amounts of P. Phosphorus adsorption data was found to fit best to Langmuir (R^2- 0.94) and Freundlich isotherms (R^2- 0.92) for soil samples. Soil P adsorption maxima obtained from Langmuir isotherm ranged between 196 and 313μg g^{-1} soil. The bonding energy values obtained from Langmuir isotherm plot were the lowest in control and $N_{200}P_0K_0$ treatments whereas these values tended to increase with P addition. Freundlich constants 'a' and' 'n' (extent and rate of adsorption) calculated from the regression lines also showed similar trends. The plot of desorbed P/adsorbed P was linearly correlated for each of the seven soil samples. Computation of desorbable P capacity (or desorption maxima, Dm) and desorption rate constant (Kd) from this relationship indicated higher Dm values in soil samples collected from control ($N_0P_0K_0$) and alone N fertilized ($N_{100}P_0K_0$ and $N_{200}P_0K_0$) plots were compared to plots treated with P fertilizers. The Kd values were higher in P fertilized plots than control ($N_0P_0K_0$) and $N_{200}P_0K_0$ treated plots .

An experiment was performed by Dhillon *et al.* (2006) to illustrate the adsorption-desorption behaviour of phosphate (P) in soils. After three decades of long-term fertilization, Phosphate adsorption increased with increasing levels of added P while percentage P adsorbed decreased gradually. In unfertilized soil, the adsorption maxima and the degree of P adsorption were at its maximum and P adsorption decreased with increased P applications. The incorporation of farmyard manure with optimal P levels decreased P adsorption even more than a super-optimal application of P fertilizers. With increased P application and with the addition of farmyard manure, bonding energy and Freundlich constant "a" and "n" also decreased.

2.2 To evaluate suitability of adsorption equations for assessing the P sorption behaviour in a Vertisol.

Stumm (1992) explained adsorption as the accumulation of matter at the solid water interface. A major implication of this process is an alteration in the distribution of molecules between the solid and solution, consequently affecting their transport. Adsorption can also alter particulate the electrostatic properties of particles and affect flocculation and adhesion. Lastly, adsorption can influence the reactivity of surfaces, altering rates of precipitation, dissolution and subsequent ion retention. Surface precipitation and polymerization are not considered as forms of adsorption, but collectively the three processes are referred to as ‘sorption’ (Sparks, 1995; Stumm, 1992).

Adsorption mechanisms are mainly separated by inner-sphere complications, outer sphere complications and retention in the diffuse swarm. Inner-sphere complexes are a result of a chemical reaction which are highly specific and quite strong. For formation of outer sphere complexes electrostatic attraction is the main cause and retention in the diffuse swarm. The outer- sphere complexes result from localized charge imbalances and are not specific (Sparks, 1995).

Anions are commonly found to be sorbed to oxide and silicate minerals within soil sand in some cases are also bounded to organic matter, with iron or aluminium which typically act as a bridging ions. On ionizable functional groups on mineral surfaces, Chemisorption of anions is found. In the ligand exchange process, the anion displaces H_2O or OH^- during the adsorption phenomena. The water (H_2O) is a more mobile ligand than OH^-, sorption is more favoured at lower pH soil. Ligand exchange have four key characteristics namely, the release of hydroxyls, high specificity toward binding sites, apparent hysteresis, and more negative surface charge after adsorption (McBride, 1994).The mechanism by which o-phosphate is adsorbed in non-calcareous, non-allophonic mineral soils with hydroxyl groups is by the process of ligand exchange phenomena (Parfitt, 1978; Mott, 1981;White, 1981).

Many equations, e.g., Langmuir, modified Freundlich, Gunary, Tempkin and mechanistic models have been used to illustrate P adsorption in most of the work establishing the phosphate adsorption relationships (Huang, 1998).

2.2.1 Langmuir isotherm model:

Langmuir adsorption isotherm, originally developed to describe gas– solid-phase adsorption onto activated carbon, has traditionally been used to quantify and contrast the performance of different bio-sorbents (Langmuir, 1916). In its formulation, this empirical model assumes monolayer adsorption (the adsorbed layer is one molecule in thickness), with adsorption can only occur at a finite (fixed) number of definite localized sites, that are identical and equivalent, with no lateral interaction and steric hindrance between the adsorbed molecules, even on adjacent sites (Vijayaraghavan *et al.*, 2006). In its derivation, Langmuir isotherm refers to homogeneous adsorption, which each molecule possess constant enthalpies and sorption activation energy (all sites possess equal affinity for the adsorbate) with no transmigration of the adsorbate in the plane of the surface. (Kundu and Gupta, 2006).

This equation was initially derived for the adsorption of gases by solids based on three assumptions.

- A constant energy of adsorption that is independent of the extent of surface coverage (i.e., a homogenous surface)
- Adsorption on specific sites, with no interaction between adsorbed molecules
- Maximum adsorption equal to a complete monomolecular layer on all reactive adsorbent surfaces.

Mathematical` expression of Langmuir adsorption isotherm is can be represented by

$$\mathbf{Ce/x/m = 1/kb + Ce/b}$$

Where;

x/m = Amount of P adsorbed per gram of soil (μg/g) Ce = Equilibrium P concentration (μg P mL−1)

b = Langmuir adsorption maximum (μg/g) which is reciprocal of the slope (1/b) of the regression line

k = Langmuir bonding energy constant obtained by dividing the slope (1/b) by the intercept (1/kb)

An advantage of using Langmuir equation is that it defines a limit to adsorption on a given array of sites. Therefore, this equation has been used by several investigators to estimate the adsorption capacity of soils as well as adsorption behaviour (Thompson *et al*. 1960; Das *et al*. 1983; Vig and Dev, 1984; Krishna Kumari *et al*. 1985).

Vig and Dev (1984) using Langmuir equation observed that acid soils adsorbed more P as compared to alkaline soils. Krishna Kumari *et al*. (1985) used this equation to study the nature and extent of P adsorption in black, red and lateritic soils and found that black soils adsorbed greater amount of P than red and lateritic. Singh and Singhpuri (1986) also found that Langmuir equation could be fitted to adsorption data of P in some soils of Bihar. Ram *et al*. (1987) using this equation found that Entisols exhibited large values for P adsorption, adsorption maxima and bonding energy indices than Alfisols. Chutia *et al*. (1988) also found it suitable for describing P adsorption in a calcareous soil of Bihar. Kundu *et al*. (1988) used Langmuir equation and observed that black soils registered highest P adsorption maxima followed by laterite and alluvialsoils.

Langmuir in many studies gave a curved than a linear isotherm for a wide range of solution P concentration. Similar results had also been reported by various workers (Syers *et al*. 1973); Ryden and Syers (1975 a, b). Mehadi and Taylor (1998).Tekchand and Tomar (1998). Each isotherms however, showed a linear relationship at lower concentration.

2.2.2 Freundlich adsorption isotherm:

This empirical model can be applied to multilayer adsorption, with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface (Gast and Adamson, 1997). The slope ranges between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becomes more heterogeneous as its value gets closer to zero. Whereas, a value below unity implies a mechanism of chemisorptions process where 1/n above one is an indication of cooperative adsorption (Haghseresht and Lu, 1998). At present, Freundlich isotherm is currently widely applied in heterogeneous systems, particularly in organic compounds or highly interactive species on activated carbon and molecular sieves.

The Freundlich equation can be represented as

$$\mathbf{x/m = K \times Ce1/n}$$

The linear form of the equation is

$$\mathbf{Log\ x/m = log\ k + 1/n\ log\ Ce}$$

Where;

x/m = The amount of phosphorus adsorbed per unit mass of adsorbent. Ce = The equilibrium solution in the solution (µg P/mL)

The frequent good fit of adsorption data to this equation is undoubtedly uninfluenced by the insensitivity of log-log plots and by their greater flexibility afforded curve fitting by the two empirical constants (K and n) in the Freundlich equation. This flexibility does not guarantee accuracy, however, if the data are extrapolated beyond the experimental range. The Freundlich equation has the further limitation that it does not predict a maximum adsorption capacity. Despite its shortcomings, the Freundlich equation is a common adsorption equation employed for adsorption studies. Both of these equations have been used extensively in soil research to study the P adsorption behaviour.

Singh and Tomar (1996) and Tomar and Gautam (1998) proposed that constant 'K' could be interpreted as a hypothetical index of adsorbate adsorbed from a unit concentration solution and thus taken to provide a measure of the relative capacity of different soils for phosphate sorption. Constant 'n' reflects the affinity of adsorbate to adsorbent in such a way that greater affinity reduces the value of 'n'. Definitely, with increasing equilibrium concentration of adsorbate, affinity decreases exponentially in solution phase and fractional surface coverage.

Different researchers have shown that the Freundlich isotherm actually explains P sorption on a solid surface that is energetically heterogeneous, i.e. with fractional surface coverage, the energy of contact between the sites and adsorbate differs. Therefore, the Freundlich equation offers a clearer understanding of phosphate sorption in soils at a wide range of P concentrations in equilibrium solution than the Langmuir equation (Gunary, 1970; Tomar and Gautam, 1996; Gautam and Tomar, 1997; Murthy *et al*.1996; Tomar and Gautam,1998).

Toor *et al.* (1997) inserted P adsorption data into adsorption equations of Langmuir, Freundlich and Tempkin. They noticed that the Freundlich equation better described the action of P adsorption than the Langmuir equation, as demonstrated by higher values of the coefficient of correlation (ranging from 0.934 to 0.998). As the equilibrium P concentration increased, the adsorbed P increased. P desorption was for less compare to the P adsorption. Higher P adsorption was found in the soils having higher clay content, $CaCO_3$ or extractable iron and aluminium exhibited but low P desorption indicating lower P concentration in soil solution for plant use at a point of time.

Saha *et al.* (1999) examined phosphate sorption and desorption at 35 and 45 ° C by eight acidic surface soils with contrasting properties. Phosphate sorption data were satisfactorily described by the Freundlich and Langmuir adsorption isotherms. A positive correlation between the standard sorption parameter and soil properties such as organic carbon content, Fe and Al extractable oxalate, reactive Al and surface area was observed.

P adsorption data were fitted to different adsorption equations in the studies conducted by Toor *et al*. (1997) who found that Freundlich equation explained P adsorption behaviour better than the Langmuir equation as evidenced by higher correlation coefficient values.

Davis (1935) and Kurtz *et al.* (1946) have documented the relationship between the amount of phosphate adsorbed by soils and the concentration of equilibrium phosphate that complying with the isotherm of Freundlich and Langmuir adsorption. The benefit of these techniques is that sorption curves estimate the 'P' requirement without calibrated field rate-yield trails and that curves are on adequate basis for P-requirement across a diversity of soils and environment. It was demonstrated by Subramanian (1965) that adsorption of ‘P’ by some Indian soils and clays can be defined by Langmuir’s equation. Similar result for the adsorption of P on some soils had also been reported by various workers (Bahl and Sinha, 1971; Kumar and Singh, 1998; Palliyal and Verma, 2002). On the other hand, Bahl *et al*. (1986) found that the Langmuir equation could not describe P adsorption in all soils studied, whereas, Freundlich described P adsorption in all soils. They suggested that in soils having high adsorption maxima adsorption may be better explained by Freundlich equation. They also found that the adsorption capacity was higher in soils with higher clay content. Yadav (1987) compared Freundlich, Langmuir and Tempkin equations. He also found Freundlich as suitable and observed that calcareous soils adsorbed maximum P followed by blacksoils.

A number of adsorption studies (Syers *et al*. 1973; Holford *et al*. 1974; Holford and Mattingly, 1975; Rajan and Perrott, 1975; Holford, 1982; Das *et al*. 1983; Vig and Dev, 1984; Yadav, 1987) have resulted indata suggesting the possibility of multiple-site adsorption. On the basis of these, several different arrays of sites are postulated, each of which fulfils the requirements of the Langmuir equation. In such cases the P adsorption capacity is greatly underestimated by the simple Langmuir equation and the two surface equations gives meaningful estimate of adsorption capacity (Holford *et al*.1974).

The data reported by Syers *et al.* (1973) suggested two sets of sites each with its own binding strength and adsorption maximum i.e., two mechanisms of adsorption on similar sites. The adsorption curve, therefore, has been resolved, by dividing it, into two straight-line components. Such form of Langmuir equation can be used to describe adsorption in soils whose total adsorption appears to be the sum of both a high energy and a low energy component. Such a distribution of adsorption energies is reasonably well established for soil P (Holford and Mattingly, 1975; Olsen and Khasawneh, 1980). To fit the adsorption data more closely to the Langmuir equation even three-site models have been involved (Ryden *et al.* 1977).

Many workers have used this form of Langmuir equation. Krishna Kumari *et al.* (1985) found that in case of lateritic soils the isotherm exhibited two distinct linear segments. They found that the bonding energy constant value was much higher in the lower region of the isotherm than in the upper one. Conversely, the adsorption maxima values were greater in upper region than in the lower. An evaluation of P adsorption indices was undertaken in 23 Inceptisols samples collected from different altitude of North and east Sikkim by Patiram *et al.* (1990). Out of 23 soil samples 19 gave two linear components of P adsorption (b1 and b11) and P sorbed at low energy surface (b11) was at least two times greater than the high energy surface (b1). Ram *et al.* (1987) also observed similar adsorption behavior of P in Alfisols and Entisols of Meghalaya.

CHAPTER-III
MATERIALS AND METHODS

This chapter deals with the description of materials used and techniques adopted during the course of investigation.

A laboratory study was undertaken to investigate the phosphorous adsorption capacity as influenced by nutrient management practices in a *Vertisol* of Chhattisgarh.

3.1 Experiment site

The study was conducted on *Vertisol* of Long Term Fertilizer Experiment (LTFE), research farm of Indira Gandhi Krishi Vishwavidyalaya, Raipur, Chhattisgarh.

3.2 Geographical situation

Raipur is situated between 22^{o} 33’ N to 21^{o} 14’ N latitude and 82^{o} 6’ E to 81^{o} 38’ E Longitude with the altitude of 293m above Mean Sea Level.

3.3 Climate and weather conditions

The climate in the Raipur region is sub-humid, temperatures remain moderate throughout the year, except from March to June. It receives an about 1200 – 1300 mm (51”) of rain, mostly in the monsoon season from late June to early October.

3.4 Soil characteristics

The soil of the experimental field was Vertisol, which was Fine Montmorillonite, Hyperthermic, Chromustert, also locally called as *Kanhar* and identified as Arang II series. It is usually dark brown to black in colour, with heavy clayey and neutral to slightly alkaline in reaction due to presence of lime concentrations. The initial characteristics of the soil were analyzed as per the methods mentioned below and some important physico-chemical properties of the soil are given in Table 3.1.

Table 3.1: Important initial physico-chemical properties of the soil under study

S.No.	Properties	Value
1.	Mechanicalcompositions	
	Sand(%)	20
	Silt(%)	34
	Clay(%)	46
2.	Texture	Clayey
3.	Hydraulic conductivity(mmhr^{-1})	4.8
4.	Bulk density(Mgm^{-3})	1.37
5.	Soilclassification	Fine Montmorillonitc, hyperthermic,Chromustert
6.	pH-(1:2.5)	7.5
7.	EC -(dSm^{-1})	0.23
8.	Available Nitrogen(kgha^{-1})	236
9.	Available Phosphorus(kgha^{-1})	16
10.	Available Potassium (kgha^{-1})	474
11.	Total phosphorous(kgha^{-1})	4025.98
12.	Organic Carbon(%)	0.60

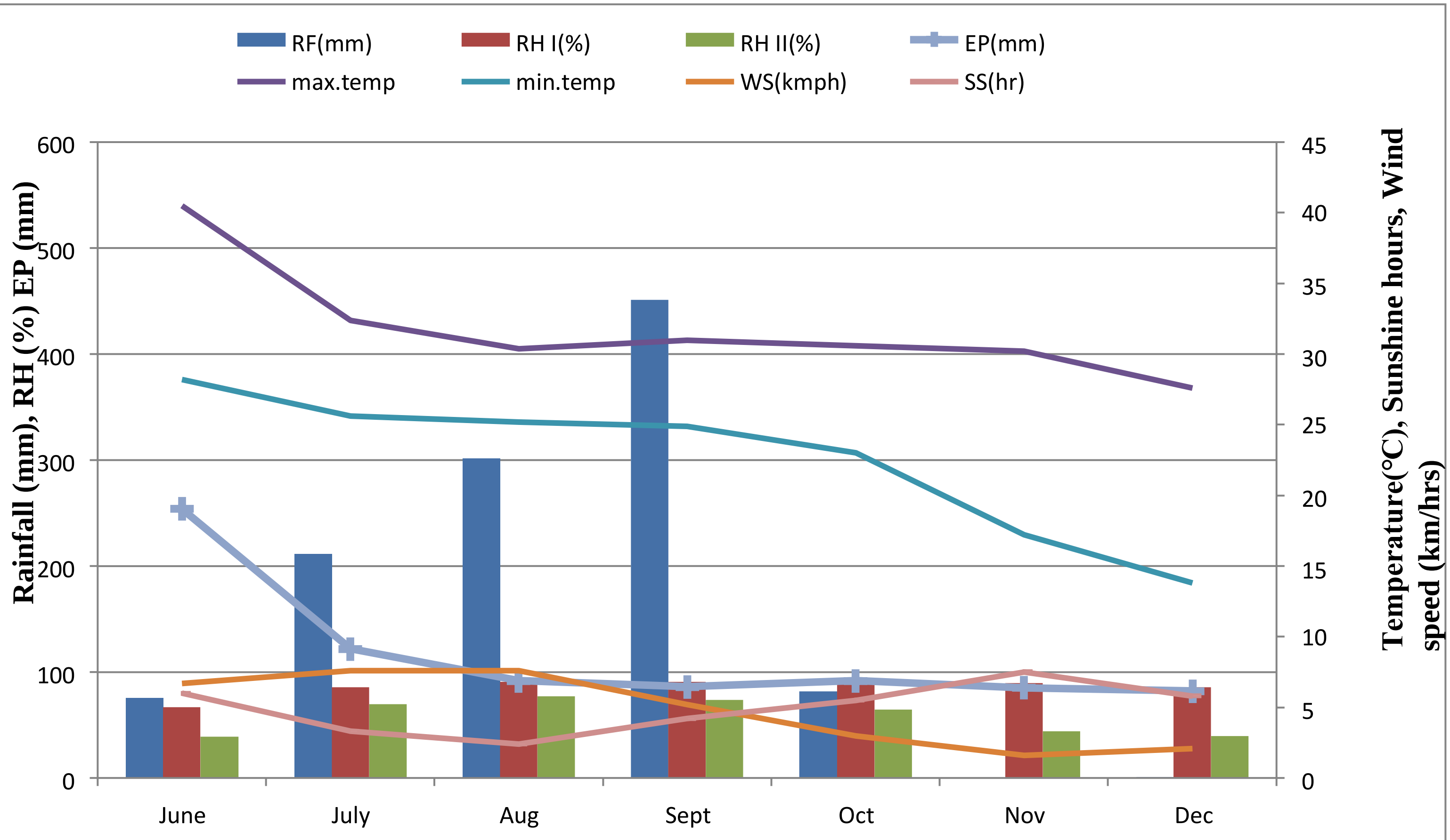


Fig. 3.1 Monthly meteorological data prevailing during crop growth period, *Kharif* (2019)

3.5 Experimental details and layout

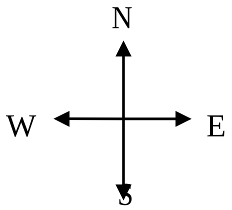
Location	:Long Term Fertilizer Experiment (LTFE), Research Farm, I.G.K.V,Raipur.
Season	:*Kharif*-2019
Crop	: Rice (IGKVR-1)
Plotsize	: 20m x10m
Spacing	: Row x Plant (20cm x 10cm)
Treatments	: 10
Replication	: 04
Design	: Randomized Block Design (RBD)

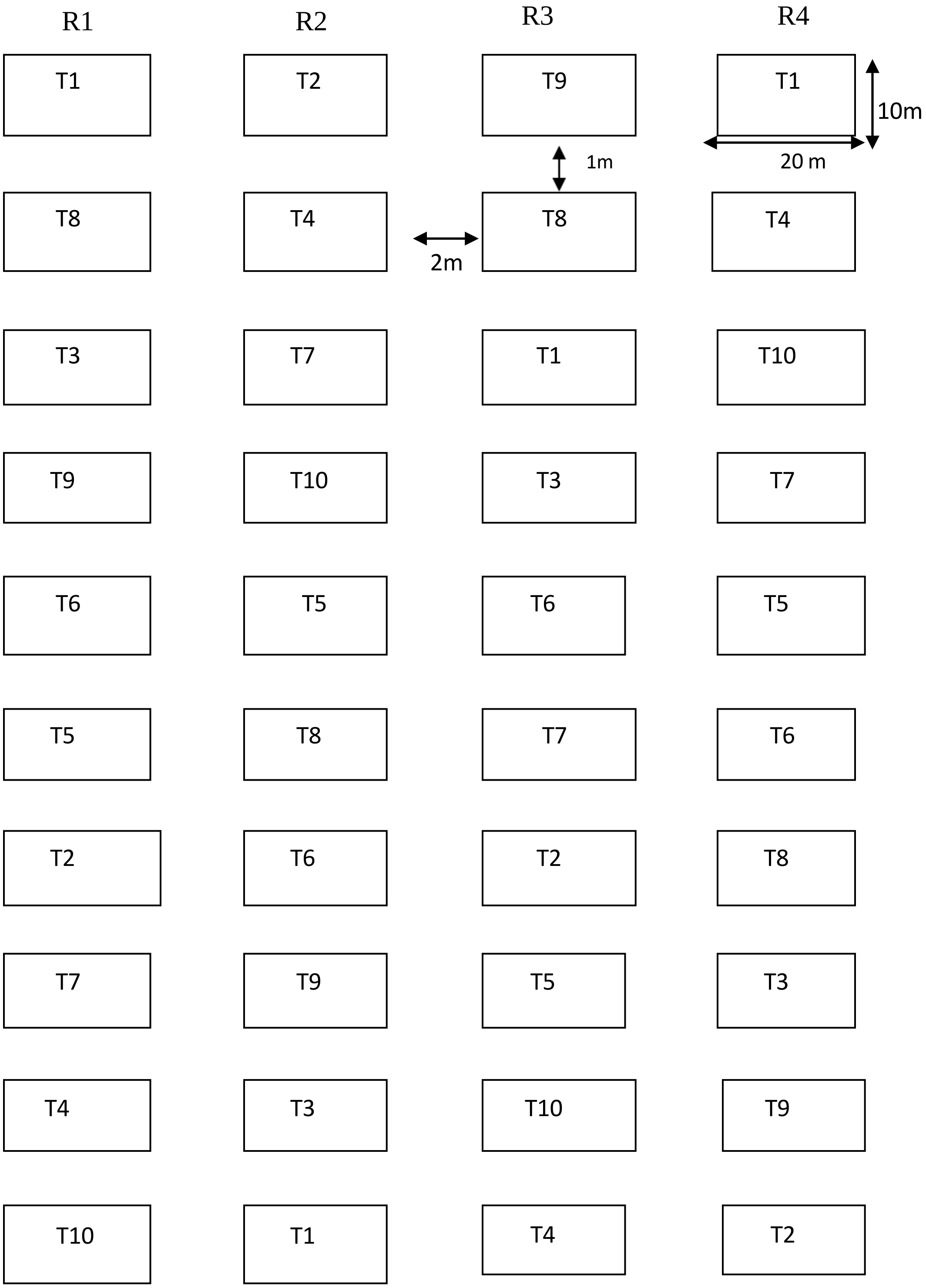
Table 3.2: Treatment details

Treatment no.	Treatment name
T_1	Control
T_2	50% $N:P_2O_5:K_2O$ (60:30:20) kg ha^{-1}
T_3	100% $N:P_2O_5$: K_2O (120:60:40) kg ha^{-1}
T_4	150% $N:P_2O_5$: K_2O (180:90:60) kg ha^{-1}
T_5	100% $N:P_2O_5$: K_2O + Zn @ 10 kg/ha (through $ZnSO_4$) kg ha^{-1}
T_6	100% $N:P_2O_5$ (120:60:0) kg ha^{-1}
T_7	100% N (120:0:0) kg ha^{-1}
T_8	100% $N:P_2O_5$: K_2O + FYM @ 5 t/ha
T_9	50% $N:P_2O_5$: K_2O + BGA @ 10kg/ha
T_{10}	50% $N:P_2O_5$: K_2O + Green Manure

N, P and K nutrients were applied through Urea, Single Super Phosphate and Muriate of Potash, respectively. One third of Urea and recommended dose of P and K were applied at the time of transplanting. Remaining equal two splits (1/3rd of Urea) of nitrogen were given at tillering and panicle initiation stage of rice.

Layout plan of experimental field:





R1	R2	R3	R4
T1	T2	T9	T1
T8	T4	T8	T4
T3	T7	T1	T10
T9	T10	T3	T7
T6	T5	T6	T5
T5	T8	T7	T6
T2	T6	T2	T8
T7	T9	T5	T3
T4	T3	T10	T9
T10	T1	T4	T2

3.6 Soil analysis

3.6.1 pH

Soil pH was determined in 2.5:1 water-soil suspension after stirring for 30 minutes, by glass electrode pH meter as suggested by Piper (1967).

3.6.2 Electrical conductivity(EC)

The soil sample used for pH determination was allowed to settle down for 4 hours then conductivity of supernatant liquid was determined by Solu-bridge as described by Black (1965).

3.6.3 Organic carbon(OC)

Organic carbon was determined by Walkley and Black rapid titration method (1934).

3.6.4 Available Nitrogen

To estimate the available nitrogen, alkaline potassium permanganate method was adopted as described by Subbiah and Asija (1956) and expressed in kg ha^{-1}.

3.6.5 Available phosphorus

Available phosphorus was estimated from the soil with 0.5M $NaHCO_3$. Measurement of the quantitative determination of phosphorus in soil given by Olsen *et al*. (1954) and expressed in kg ha^{-1}.

3.6.6 Available potassium

Available potassium is determined by extracting soil with neutral normal ammonium acetate solution. The estimation of potassium is carried out by Flame photometer as described by Hanway and Heidel (1952).

3.6.7 Total Phosphorus

Total Phosphorus was determined by using $HClO_4$ – 60% solution as suggested by Olsen and Sommers ,1982.

3.6.8 Phosphorus Adsorption Study

Data for plotting P adsorption isotherms were obtained by equilibrating 5 g soil in triplicate for 24 hours at 25° C in 50 ml of 0.01 M $CaCl_2$ solution containing varying amounts of P (0, 30, 60,90, 120, 150, 180, 210, 240, 270 and 300 ppm) as KH_2PO_4.

Equilibration was carried out in 50 ml centrifuge tubes by shaking for 24 hours. After shaking, the samples were centrifuged at 2500 rpm for 10 minutes and then the concentration of P in the clear solution was determined by ascorbic acid method using Double Beam Spectrophotometer. The P which disappeared from the solution was considered to be adsorbed and was calculated as:

Amount of P adsorbed in µg g^{-1} (x/m) = Initial conc. of the equilibrium solution – final concentration of the equilibrium solution in ppm (C).

3.6.9 Preparation of P Adsorption Isotherms

Two adsorption equations were fitted to the adsorption data obtained at different concentrations of added P as per the procedure of Fox and Kamprath, (1970).

3.7 Statistical analysis

The different graphs were plotted using Microsoft Excel and the numerical values of slopes and intercept for both the isotherms and slope for buffering capacity were worked out. Correlation and Regression analysis were performed using the Data analysis tool of OPSTAT (Sheoran *et al.*,1998).

CHAPTER-IV
RESULTS AND DISCUSSION

The field experiment was conducted during *kharif* 2019 on instructional cum research farm of Indira Gandhi Krishi Vishwavidyalaya, Raipur, Chhattisgarh, entitled **“An evaluation of phosphorous adsorption capacity as influenced by nutrient management practices in a *Vertisol* of Chhattisgarh”** is with an aim to study the effect of long term continuous nutrient management practices on phosphorous adsorption in *Vertisol*. The result obtained are presented and discussed in this chapter under the following heads.

4.1 Phosphorous adsorption characteristics of soils

The amount of P adsorbed (x/m), amount of P remaining in the equilibrium solution (C) and correlation coefficient, (r) between C and (x/m) as influenced by different nutrient management practices are given in Tables and presented graphically in Figures.

The correlation coefficient `r‘ between C and (x/m) was found to be highly significant (Table 2-4) in *vertisol* having different treatments through fertilization and manuring indicating that P adsorption at the solid phase was strongly related to its concentrations in the solution phase. The adsorption of P was low at lower equilibrium P concentration and increased with an increase in equilibrium P concentration as also reported by Toor *et al.* (1997).

The soils having divergent fertilization showed widely different behaviour as is evident from the shape of the C- (x/m) curve which indicates that treatment which has received 100%N and control plot adsorbed maximum P and the treatment which received optimum dose of NPK along with FYM and 150% NPK adsorbed minimum at a given equilibrium P concentration while other treatment having different doses of fertilization and manuring remained intermediate. The soil under long term fertilization practices differed widely with respect to P adsorption behaviour.

Following an application of graded levels of P (30-300 μg P g^{-1}soil), the amount of P adsorbed (expressed as micrograms P per gram soil) varied between 28.1 and 252 (control), 27.6 and 229.7 (50% NPK), 26.9 and 216.9 (100% NPK), 27.6 and190.7 (150%NPK), 26.8 and 218.3 (100% NPK + Zn), 26.6 and 206.7 (100% NP), 28.2 and 249.7(100%N), 26.2 and 178.8 (100% NPK + FYM), 27.3 and 226.9 (50% NPK + BGA), 27.7 and 228.0 (50% NPK + GM) (Table-4.1). The amount of P adsorbed increased with an increase in the amount of P added, irrespective of the fertilization history of the soil and similarly, the concentration of equilibrium solution P continued to increase with increasing amounts of P applied to each soil. However, with the increasing rate of added P, the percentage of adsorbed P decreased over time. The decrease was expected, while the addition of fertilizer P subsequently reduces the electrical potential of the reacting surfaces and making them less attractive to more P. For example, in the control soil, when 30 μg P g^{-1} was added, P adsorption was 28.1 μg P g^{-1}, showing a percentage adsorption of 93.6 % and an equilibrium P concentration of 1.9 μg ml^{-1}. However, when 300 μg P g^{-1} was added the corresponding values were 252.1 μg P g^{-1}, 84 and 47.9 μg P ml^{-1}, respectively. Similarly, for T_8 soil, the percentage of P adsorbed decreased from 87 to59%.

The results showed that the amount of P adsorbed in the control plot (T_1) was relatively higher than the other treatments of the long-term fertilizer experiment (fig). Because of the 20 year continuous stress on the soil P reserves to fulfill the crop requirements, higher adsorption of P in the control plot soil can be ascribed to more exchange sites. The data shown in fig reveal that soil which received 100% N adsorbed more P than other treatments except control. Thus an increase in the rates of long term P fertilization caused a considerable reduction in P adsorption. The results are in conformity with those of Singh *et al.* (2005) who reported phosphate adsorption increased while percentage P adsorbed decreased gradually with increasing levels of added P and the extent of P adsorption was at its maximum in unfertilized soil and P adsorption decreased with increased P applications during 32 years maize-wheat-cowpea (fodder) crop rotation sequence. Similarly, Sharma *et al* (1995) also reported reduced P adsorption with continuous application of P during 11 cycles of maize-wheat crop rotation sequence.

It is interesting to note that the P adsorption was much lower in the soil receiving 100% NPK along with FYM than other treatments with varying fertilization. In fact P adsorption in soil receiving is even less than that observed in the soil receiving 150% NPK. The results clearly indicate that FYM application had played key role in keeping the applied P in a more available form and consequently, in decreasing P adsorption. Similar results were reported by Grinsted *et al.*1982 who attributed this behaviour of soil could be due to organic acid anions released during the decomposition of FYM accumulate in rhizosphere and compete with orthophosphates for adsorption sites. Singh *et al.* (2005) has also shown that FYM application depresses the precipitation of applied P as meta stable compounds of P, resulting in increased soil solution P concentration and decreased P adsorption.

Table 4.1: Phosphorous adsorption characteristics of different soils (T_1, T_2, T_3, T_4, T_5)

Initial conc.(ppm)	**T_1(Control)**		**T_2(50% NPK)**		**T_3(100% NPK)**		**T_4(150% NPK)**		**T_5(100% NPK+Zn)**	
	C	**x/m**	**C**	**x/m**	**C**	**x/m**	**C**	**x/m**	**C**	**x/m**
30	1.9	28.1	2.4	27.6	3.1	26.9	2.4	27.6	3.2	26.8
60	4.2	55.8	5.8	54.2	5.4	54.6	8.4	51.6	5.9	54.1
90	6.4	83.6	8.5	81.5	9.1	80.9	13.8	76.2	9.3	80.7
120	7.6	112.4	11.5	108.5	14.6	105.4	26.1	93.9	14.7	105.3
150	11.5	138.5	20.4	129.6	27.2	122.8	34.2	115.8	26.3	123.7
180	17.2	162.8	25.3	154.7	31.2	148.8	47.3	132.7	33.0	147.0
210	24.8	185.2	34.3	175.7	45.9	164.1	58.8	151.2	46.5	163.5
240	37.0	203.0	47.4	192.6	58.5	181.5	76.9	163.1	58.6	181.4
270	36.8	233.2	55.8	214.2	76.7	193.3	88.8	181.2	76.7	193.3
300	47.9	252.1	70.3	229.7	83.1	216.9	109.3	190.7	81.7	218.3
	r =0.95**		r=0.95**		r=0.95**		r=0.97**		r=0.95**	

C=P remaining in solution(μgml^{-1}) x/m= P adsorbed (μg g^{-1}) of soil

'r' is the correlation coefficient between P adsorbed (x/m) and equilibrium P concentration (C)

Table 4.2: Phosphorous adsorption characteristics of different soils (T_6, T_7, T_8, T_9, T_{10})

Initial conc.(ppm)	**T_6(100% NP)**		**T_7(100% N)**		**T_8(100% NPK+FYM)**		**T_9(50% NPK+BGA)**		**T_{10}(50% NPK+GM)**	
	C	**x/m**	**C**	**x/m**	**C**	**x/m**	**C**	**x/m**	**C**	**x/m**
30	3.4	26.6	1.8	28.2	3.8	26.2	2.7	27.3	2.3	27.7
60	5.3	54.7	4.7	55.3	11.1	48.9	5.8	54.2	5.0	55.0
90	7.3	82.7	6.8	83.2	22.1	67.9	8.9	81.1	8.4	81.6
120	15.1	104.9	7.8	112.2	34.2	85.8	11.3	108.7	13.9	106.1
150	25.3	124.7	14.4	135.6	46.7	103.3	20.0	130.0	21.1	128.9
180	31.5	148.5	19.6	160.4	66.0	114.0	26.0	154.0	26.5	153.5
210	45.1	164.9	27.8	182.2	78.0	132.0	35.1	174.9	35.1	174.9
240	58.4	181.6	38.7	201.3	103.5	136.5	47.8	192.2	49.1	190.9
270	75.7	194.3	38.1	231.9	116.5	153.5	57.8	212.2	60.0	210.0
300	93.3	206.7	50.3	249.7	115.6	184.4	73.1	226.9	72.0	228.0
	r=0.93**		**r=0.96****		**r=0.97****		**r=0.94****		**r=0.95****	

C=P remaining insolution(μgml^{-1})   x/m= P adsorbed(μg g^{-1}) ofsoil

'r' is the correlation coefficient between P adsorbed(x/m) and equilibrium P concentration (C)

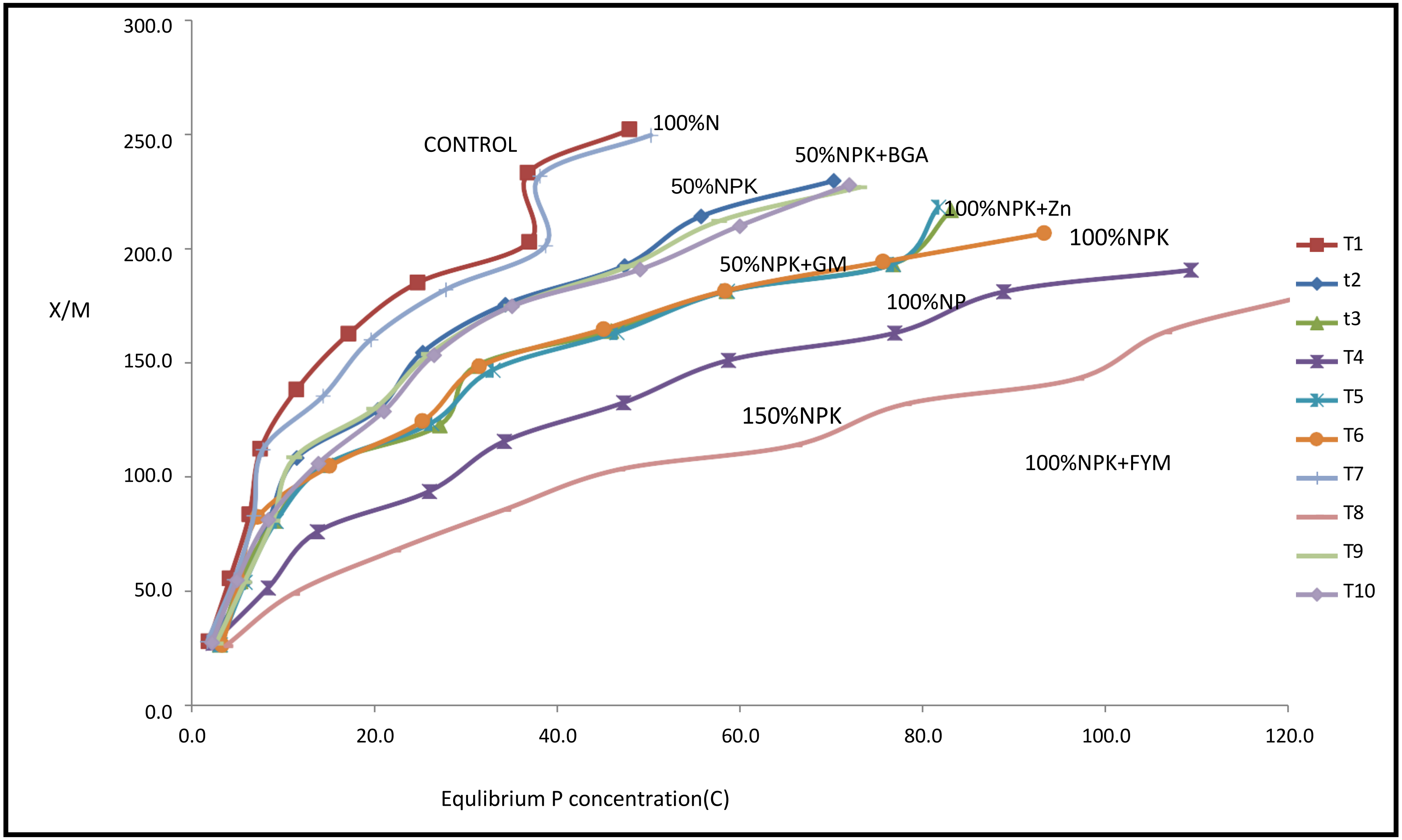


Fig.4.1 Phosphate adsorption isotherms of soils of the long-term fertilizer experiment

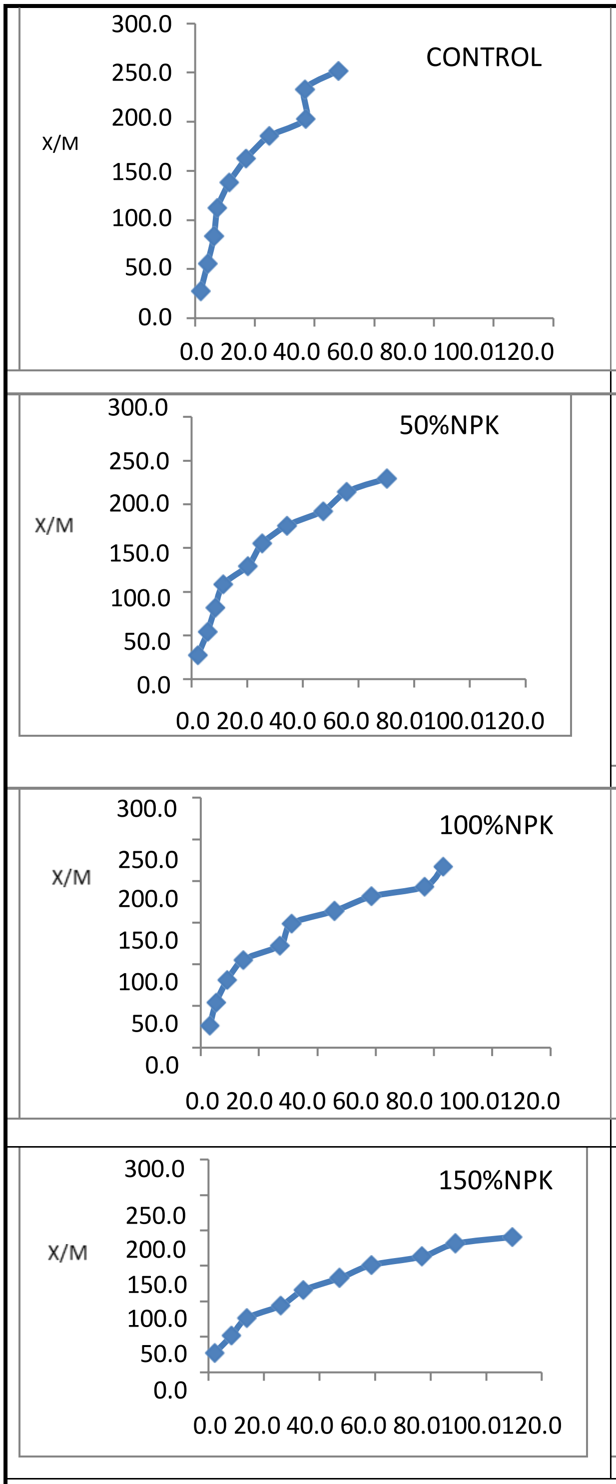
4.2 Phosphate adsorption isotherms and adsorption parameters

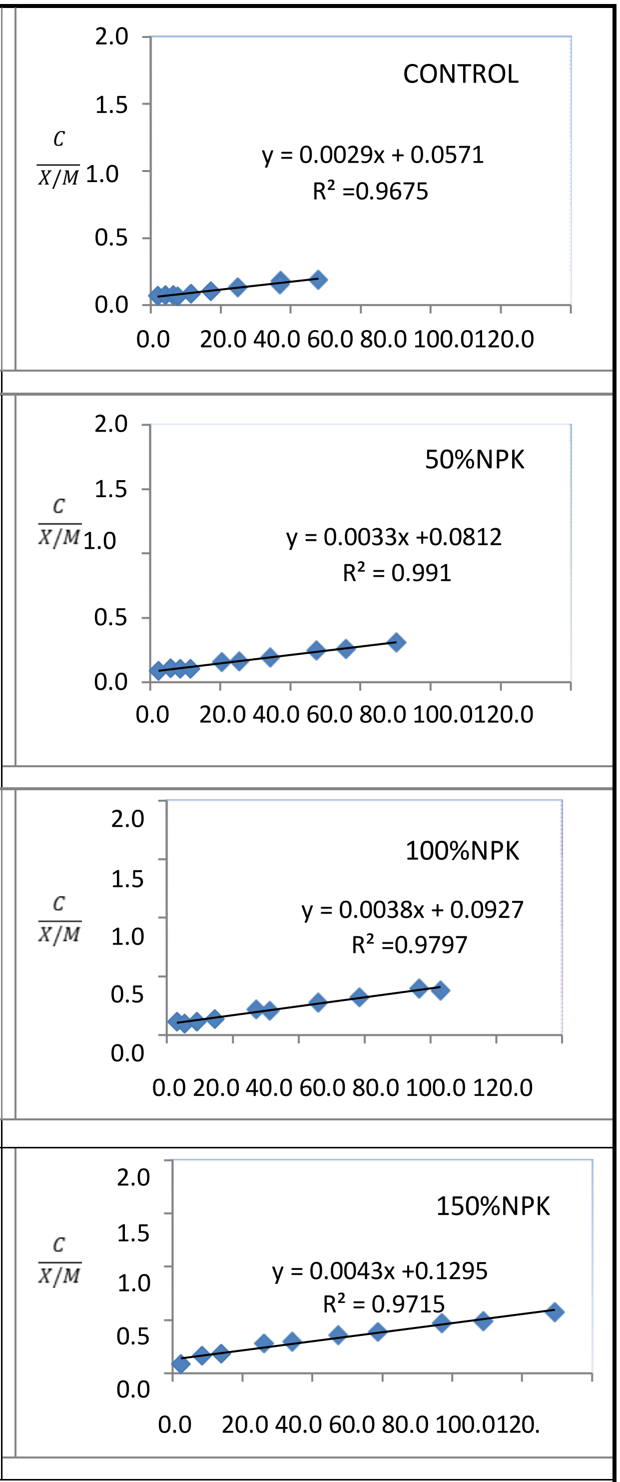
4.2.1 Langmuir adsorption.

The adsorption data obtained were fitted to Langmuir and Freundlich equations and adsorption isotherms were plotted for both the equations. The adsorption parameters pertaining to these equations were computed from these isotherms.

The Langmuir adsorption isotherm along with the adsorption equation and value of $R^2$is presented in fig. The highly significant value of R^2 indicated that data fitted well to Langmuir equation for all the treatments of varying fertilization under experiment which corroborated with the earlier findings of Bhattacharyya *et al,* (2015). The isotherms are linear even at the highest amount of added P in this soil. This perhaps indicates that in these soils, the P adsorption sites are still open.

The adsorption maxima ‘b’ and binding energy ‘k’ were calculated from the slope and intercept of the Langmuir equation, both of which are presented in table. The values of the adsorption maxima, which are measures of the P adsorption capacities of soil, were highest under the control treatment (344.8μg P g^{-1}) and decreased with the increasing levels of P applied, and were lowest under 100% NPK along with FYM treatment (222.2 μg P g^{-1}). Bonding energy which is a measure of resistance to P release in soils, varied from 0.021 to 0.05 mL μg^{-1} (table).The results showed that the addition of FYM resulted in decrease the values of both adsorption maxima and bonding energy, implying a beneficial effect on P availability in the soil. The finding also show that as the fertilizer rate increased from 50% NPK to 150% NPK, the values of both adsorption maxima and bonding energy were substantially reduced, these findings corroborate those of reported by Sharma et al.(1995). Reddy *et al*. (1999) also found that continuous use of NPK fertilizers and FYM led to marked decrease in the P adsorption maxima and bonding energy constant. The bonding energy constant and adsorption maxima were directly proportional to each other but were inversely related to the supply of P.

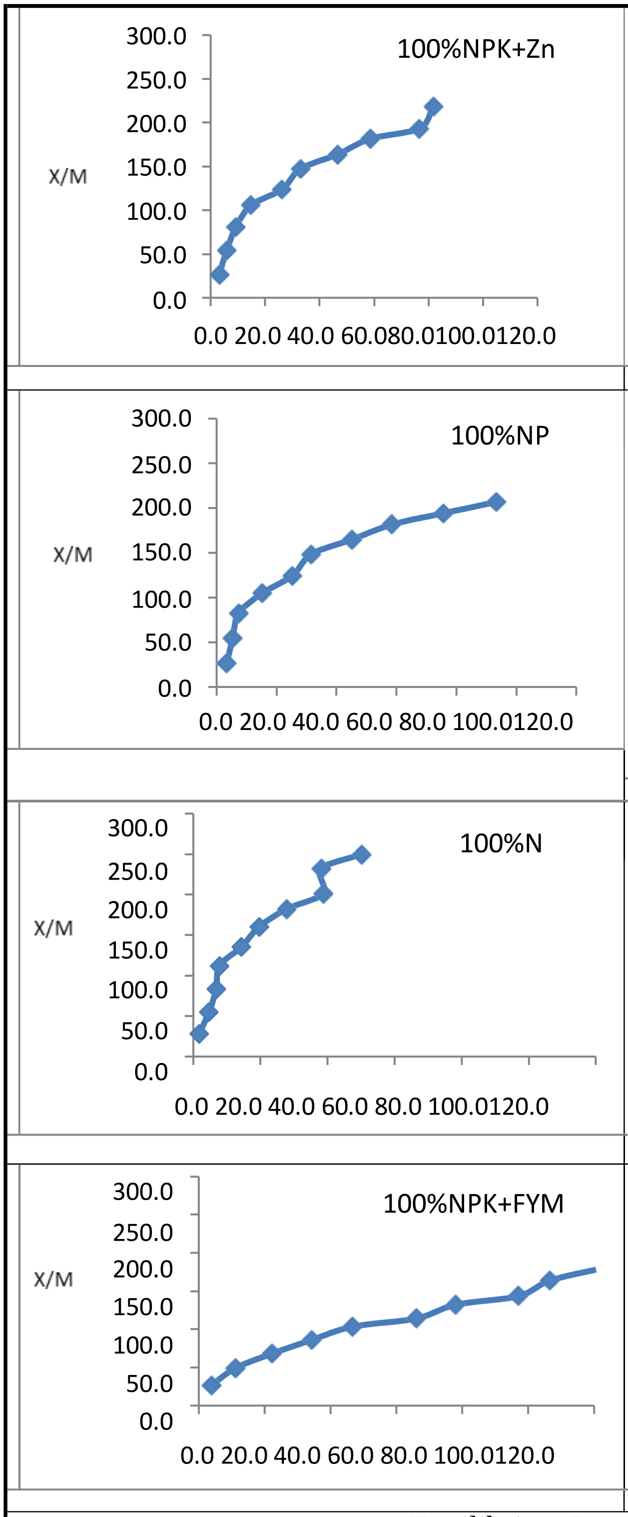


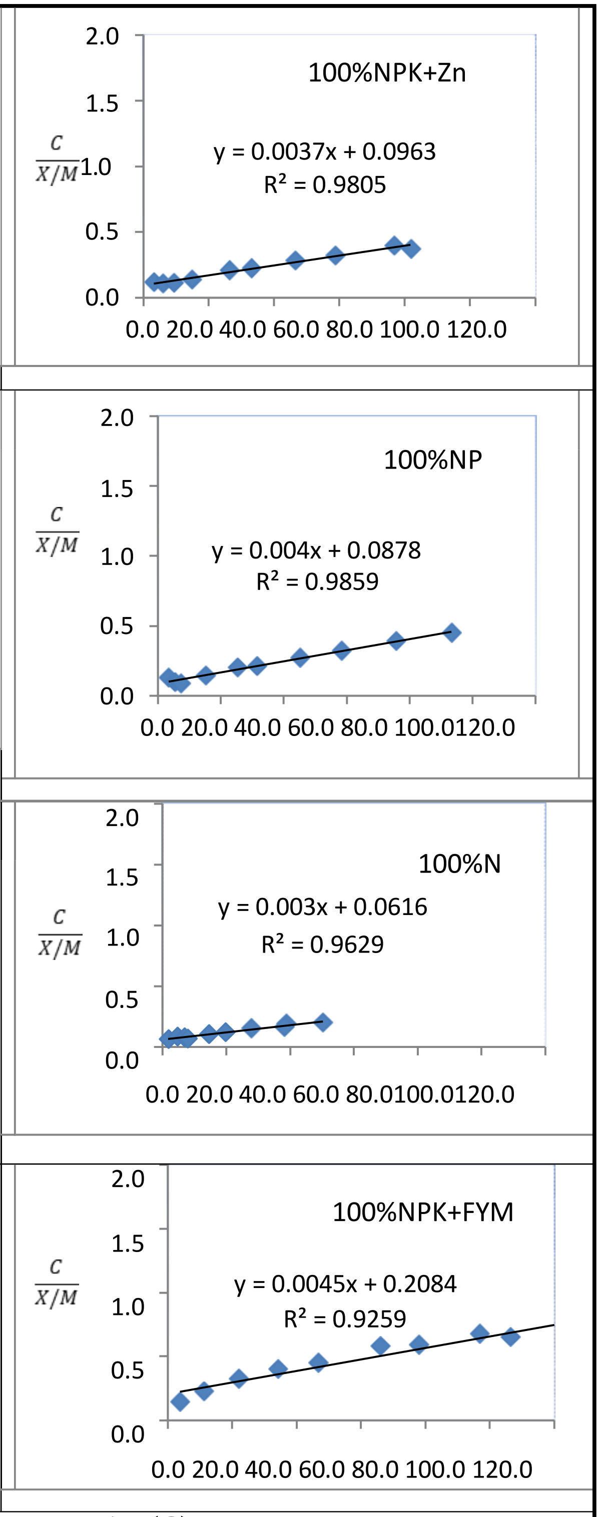


Equilibrium P concentration(C)

Fig.4.2a: P adsorption in T_1,T_2,T_3,T_4

Fig.4.2b: Langmuir isotherm in T_1,T_2,T_3,T_4

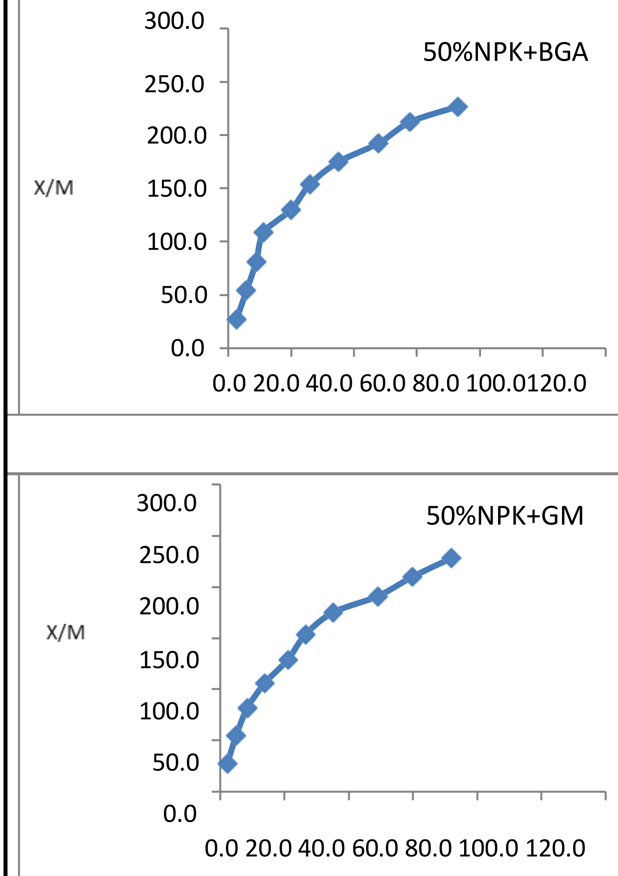


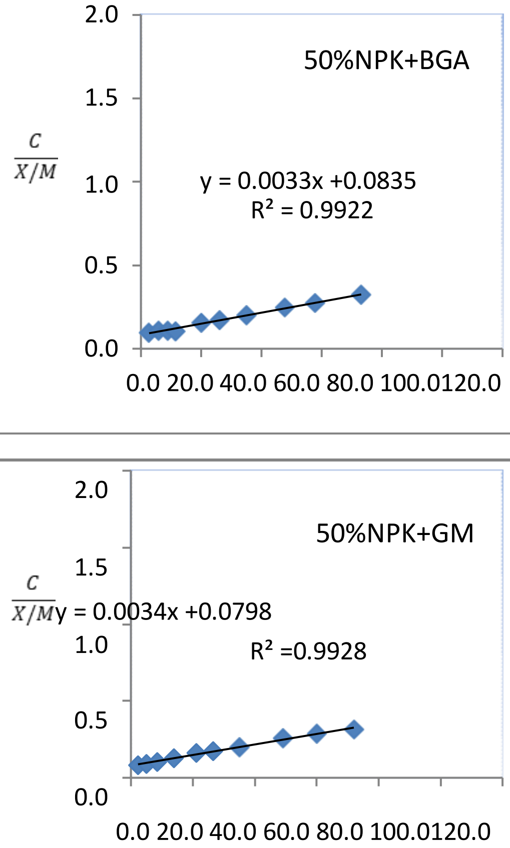


Equilibrium P concentration(C)

Fig. 4.3a: P adsorption in T_5,T_6,T_7,T_8

Fig.4.3b: Langmuir isotherm in T_5,T_6,T_7,T_8





Equilibrium P concentration(C)

Fig.4.4a: : P adsorption in T_9, T_{10}

Fig.4.4b: Langmuir isotherm in T_9, T_{10}

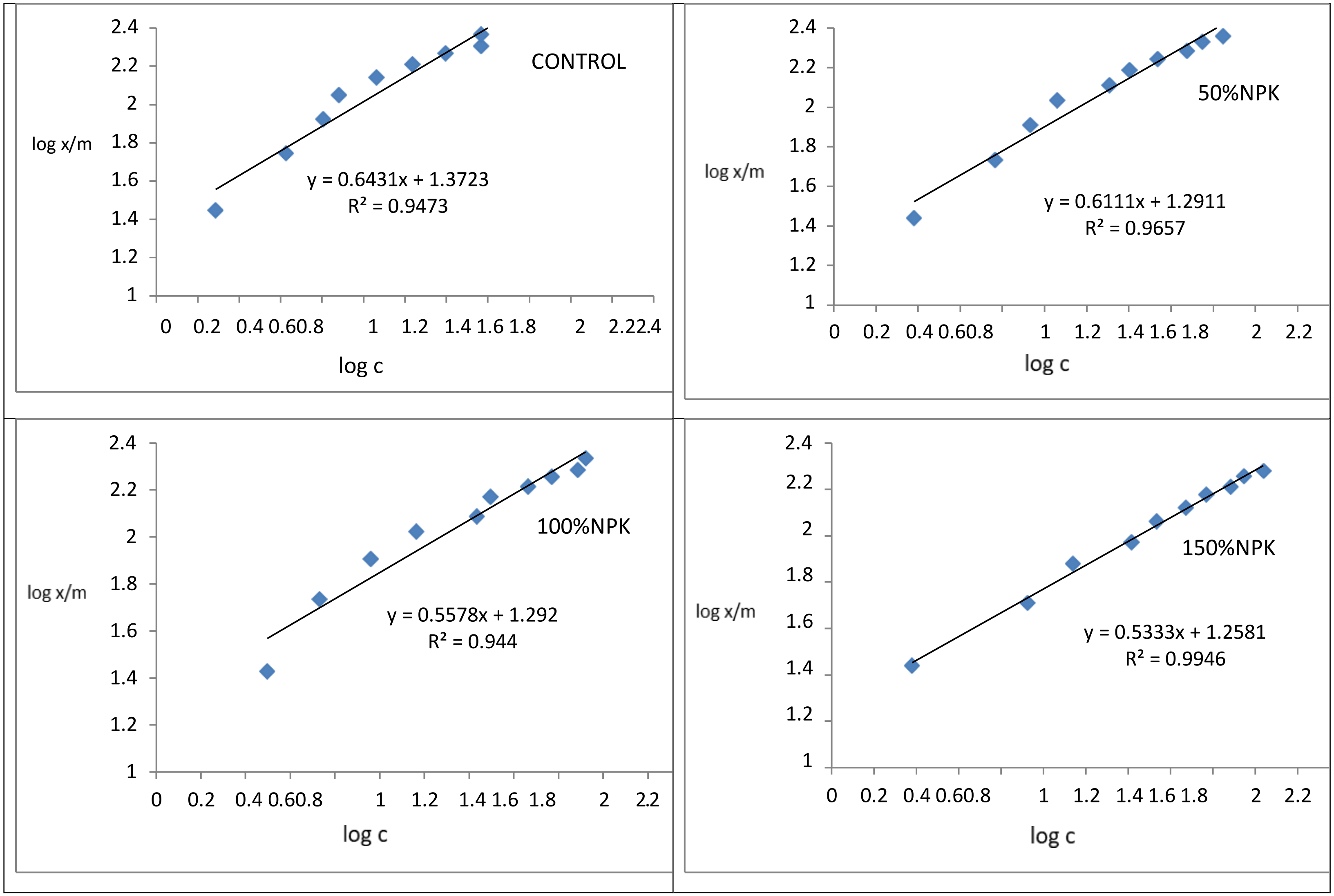


Fig.4.5: Freundlich isotherms of T_1, T_2, T_3, T_4

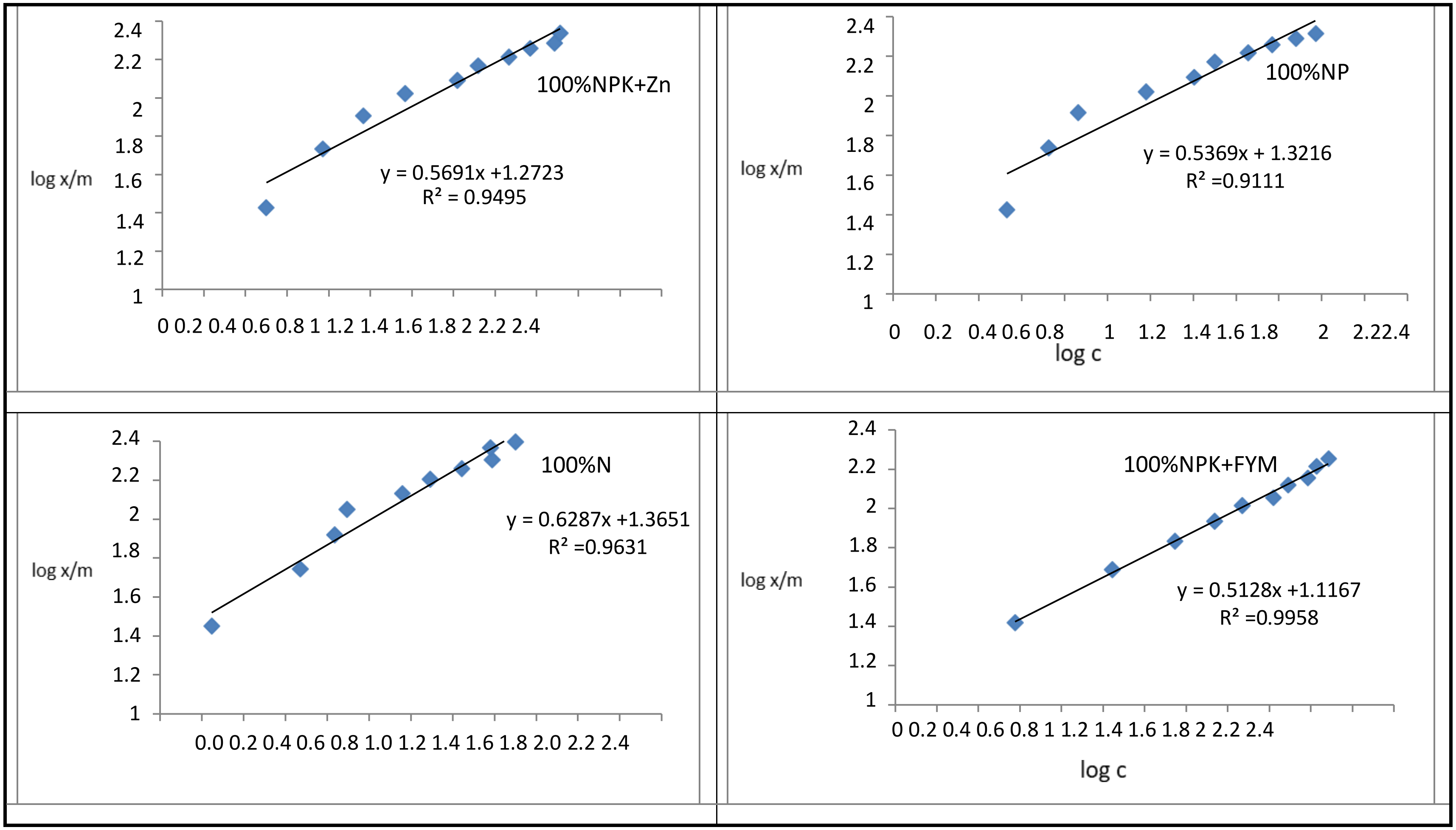


Fig.4.6: Freundlich isotherms of T_5, T_6, T_7, T_8

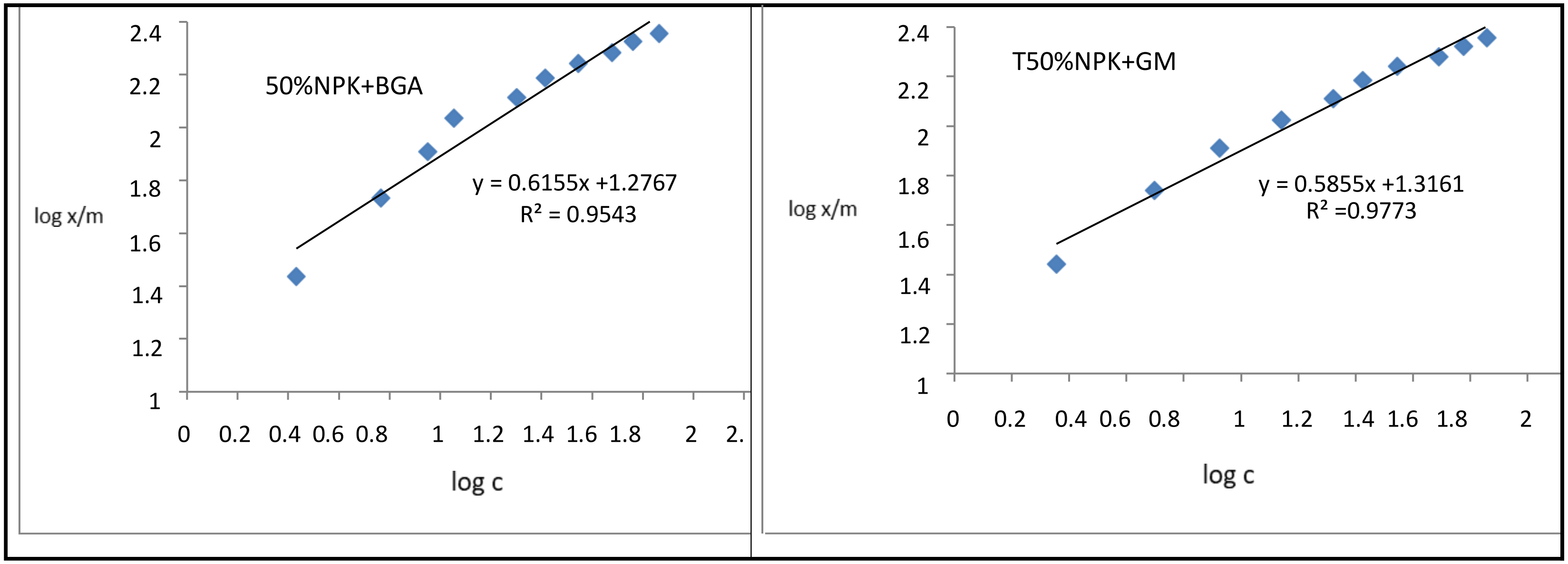


Fig.4.7: Freundlich isotherms of T_9, T_{10}

Table 4.3 Langmuir equation and adsorption parameters for P

Soil	Intercept(1/Kb)	Slope(1/b)	Adsorption Parameter	
			b (adsorption max)	k(bonding energy)
T_1(Control)`	0.0571	0.0029	344.8276	0.0508
T_2(50%NPK)	0.0812	0.0033	303.0303	0.0406
T_3(100%NPK)	0.0927	0.0038	263.1579	0.0410
T_4(150%NPK)	0.1295	0.0043	232.5581	0.0332
T_5(100%NPK+Zn)	0.0963	0.0037	270.2703	0.0384
T_6(100%NP)	0.0878	0.004	250.0000	0.0456
T_7(100%N)	0.0616	0.003	333.3333	0.0487
T_8(100%NPK+FYM)	0.2084	0.0045	222.2222	0.0216
T_9(50%NPK+BGA)	0.0835	0.0033	303.0303	0.0395
T_{10}(50%NPK+GM)	0.0798	0.0034	294.1176	0.0426

Table 4.4 Freundlich equation and adsorption parameters for P

Soil	Intercept (Log k)	Slope (1/n)	- Adsorption Parameter	
			n	K
T_1(Control)`	1.3723	0.6431	1.5550	23.5668
T_2(50%NPK)	1.2911	0.6111	1.6364	19.5479
T_3(100%NPK)	1.292	0.5578	1.7928	19.5884
T_4(150%NPK)	1.2581	0.5333	1.8751	18.1176
T_5(100%NPK+Zn)	1.2723	0.5691	1.7572	18.7197
T_6(100%NP)	1.3216	0.5369	1.8625	20.9701
T_7(100%N)	1.3651	0.6287	1.5906	23.1793
T_8(100%NPK+FYM)	1.1167	0.5128	1.9501	13.0828
T_9(50%NPK+BGA)	1.2767	0.6155	1.6247	18.9104
T_{10}(50%NPK+GM)	1.3161	0.5855	1.7079	20.7062

4.2.2 Freundlich adsorption

The Freundlich adsorption isotherm along with the equation and value of R^2 are presented in fig. The highly significant value of R^2 obtained for Freundlich equation indicated that the data fitted well to Freundlich equation for the soil under continuous long term fertilization. The Freundlich constants ‘k’ and ‘n’ were calculated from the slope and intercept respectively and both are presented in table. These constants also showed a wide variability for the soils under long term fertilization (table). The constant ‘k’ ranged from 23.56 to 13.08 µg g^{-1}soil, which is a measure of the amount of P adsorption at the unit equilibrium concentration. The k value in the control was greater, and as the rate of added fertilizer increased, it decreased. The higher 'k' values in the control soil suggest that native soil P has been depleted. In order to satisfy crop P requirements, continuous cropping without any P addition resulted in a higher demand for the native soil P, thus increasing the value of 'k', these findings is in conformity of Sharma *et al.*(1995).

Similarly, the ‘n’ values that give the degree of linearity between solution equilibrium concentration and adsorption were at a maximum in the 100% NPK along with FYM and at a minimum in control these findings corroborate those of Bhattacharya *et al.* (2015).

4.3 Buffering capacity

The P Buffering capacity was computed from the slope of the graph plotted between (x/m) and equilibrium P concentration for the soil under different fertilization and manuring. The graph depicting the straight line equation is presented in figure. Buffering capacity is the replenishment factor and is an index which demonstrates the ability of a soil system, when its concentration has been diminished, to replenish the concentration of any given ion in the soil solution. The value of buffering capacity obtained for all the treatment receiving different fertilization and manuring showed that it was highest for the control (T1) plot followed by 100%N (T7) and the values decreased sharply with increased P fertilization and minimum in soil receivingthe additional input of farmyard manure as also reported Singh *et al*. (2005), who showed that the soils with high adsorptive capacities of P also had a higher phosphorous buffering ability. These soils, therefore, would maintain a low supply of P for a longer duration relative to poorly buffered soils which would supply more P but for a shorter period. Thus, we assume that a soil's high buffer potential would result in greater adsorption of the phosphate ion into the solid phase with very little of it in the soil solution for plant root exploitation; thus, the phosphate ion would have low mobility. Conversely, a low buffered soil means that there would be more of the in the soil solution and there would be high mobility. Holford and Mattingly (1976) found buffering capacity to be inversely related to the ease with which solid-phase labile phosphate will move into the solution phase. In this sense therefore, buffer capacity may be taken as an expression of the immobility of labile phosphate.

Table .4.5 Buffering capacities of soil under long term fertilization

Soils	**Buffering Capacity(Slope)**
T_1(Control)`	4.4021
T_2(50%NPK)	2.8087
T_3(100%NPK)	2.0149
T_4(150%NPK)	1.4712
T_5(100%NPK+Zn)	2.0525
T_6(100%NP)	1.8051
T_7(100%N)	4.2344
T_8(100%NPK+FYM)	1.1848
T_9(50%NPK+BGA)	2.6625
T_{10}(50%NPK+GM)	2.6662

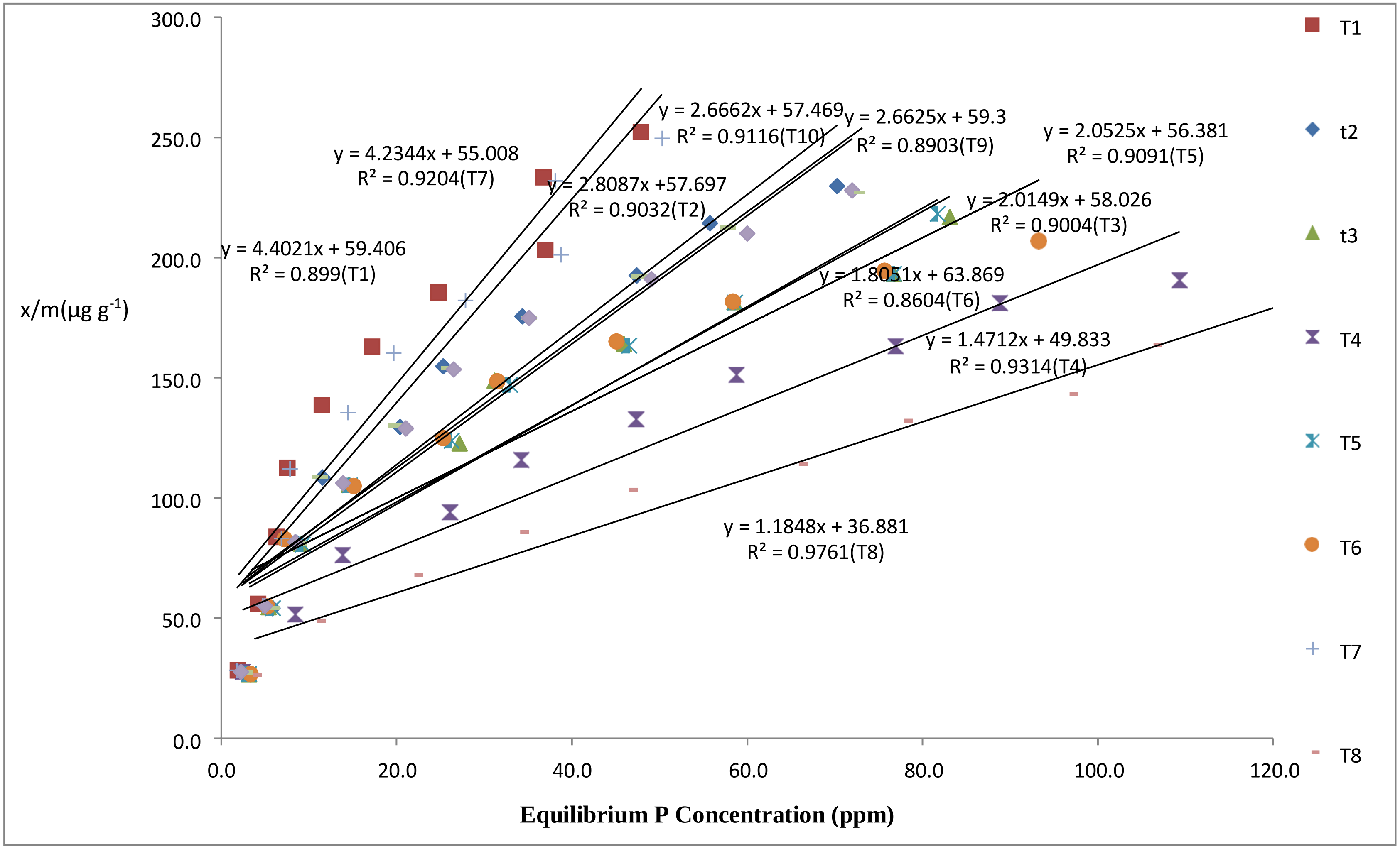


Fig.4.8: Relationship of P adsorption with equilibrium P concentration

CHAPTER-V

SUMMARY, CONCLUSIONS AND SUGGESTION FOR FUTURE RESEARCH WORK

A study was undertaken to investigate the P adsorption behavior as influenced by nutrient management practices in a *Vertisol* of Chhattisgarh. The soil of the experimental field was *Vertisol,* which was fine Montmorillonitic, hyperthermic, chromustert, also called locally as *kanhar*. It is usually dark brown toblack in colour, heavy clayey and neutral to slightly alkaline in reaction due to presence of lime concentrations.

Data for plotting P adsorption isotherms were obtained by equilibrating 5 g soil in triplicate for 24 hours at 25°C in 50 ml of 0.01M $CaCl_2$ solution containing varying amounts of P (0, 30, 60, 90, 120, 150, 180, 210, 240, 270 and 300 ppm) as KH_2PO_4. Equilibrium was carried out in 50 ml centrifuge tubes by shaking for 24 hours. After shaking, the samples were centrifuged at 2500 rpm for 10 minutes and then the concentration of P in the clear solution was determined and the P, which disappeared from the solution, was considered to be adsorbed. The Langmuir and Freundlich adsorption equations were fitted to the adsorption data obtained at different concentrations of added P. The adsorption parameters P adsorption maxima ‘b’ and binding energy coefficient ‘k’ in case of Langmuir isotherm, whereas, the empirical constants ‘n’ and ‘k’ of the Freundlich isotherm were computed for these soils.

The correlation coefficient ‘r’ between the equilibrium P concentration C and amount of P adsorbed (x/m) was found to be highly significant for all the soils indicating that P adsorption at the solid phase was strongly related to its concentration in the solution phase as it was low at lower equilibrium P concentration and increased with increase in equilibrium P concentration. P adsorbed maximum in 100% N and control and minimum in the soil receiving 100% NPK along with FYM and 150% NPK adsorbed minimum at a given equilibrium P concentration while other treatment having different doses of fertilization and manuring remained intermediate.

With an increase in the quantity of P applied, the amount of P adsorbed increased, regardless of the fertilization history of soil. With increasing amounts of P applied to each soil, the equilibrium solution P concentration also continued to increase. However, with the increasing levels of added P, the P adsorbed percentage decreased steadily. The decrease was expected because the addition of P fertilizer subsequently reduces the electric potential of the reacting surfaces and thus, causing them less attractive to more P. The FYM application played a key role in preserving a more available form of the applied P and, subsequently, in minimizing P adsorption. The organic anions released during FYM decomposition accumulate in the rhizosphere and compete for adsorption sites with orthophosphates.

The adsorption data obtained were fitted to Langmuir and Freundlich equations and adsorption isotherms were plotted for both the equations. The adsorption parameters pertaining to these equations were computed from these isotherms. The highly significant value of R^2 indicated that the data fitted well to Langmuir equation for all the soils receiving varying fertilization and manuring under long-term fertilizer experiment. The adsorption maxima ‘b’ was highest for control plot treatment followed by 100% N and lowest for treatment receiving 100% NPK along with FYM. The value of ‘K’ showed an increasing trend in the same order indicating a high affinity of control plot for P, which had resulted in higher value of ‘b’.

The higher value of P adsorption maxima in control and 100% N clearly indicates that these soils would require heavy doses of P for crop production. The variation in bonding energy coefficient ‘K’ showed besides higher amount adsorbed, P is also held with higher tenacity in control. Thus the release of P can be expected to be low in these soils having higher bonding energy coefficient.

The high value of R^2 obtained in the Freundlich isotherm indicated that the data also fitted well to the Freundlich equation. The value ‘n’ that give the degree of linearity were maximum in 100% NPK along with FYM and minimum in control, whereas, the value of ‘k’ showed a decreasing trend in same order. Thus in present investigation, the P adsorption behavior of the soils under study were explained equally well both by Langmuir and Freundlich adsorption isotherm.

The Buffering Capacity was computed by plotting a graph (scatter diagram) by taking x/m (Quantity) on Y-axis and C (Intensity) on X-axis and fitting a straight line equation to the data to obtain the value of slope (BC). The value of buffering capacity obtained for all the treatment receiving different fertilization and manuring showed that it was highest for the control followed by 100% N and the values decreased sharply with increased P fertilization and minimum were found in soil receiving the additional farmyard manure input.

Conclusions

- The effect of nutrient management on P adsorption indicates that the adsorption of P were higher in control followed by 100% N due to more exchange sites because of 20 years continuous stress on soil P reserves for meeting crop requirements and gradually decreases with inclusion of P fertilization, lowest in 100% NPK+FYM and 150%NPK.
- For both Langmuir and Freundlich Adsorption Isotherms, the similar and large R^2 values suggested that the P adsorption data conformed to both isotherms indicating their goodness of fit.

Suggestions for future work

1. P desorption characteristics of the soils should also be studied to predict the availability of P in the soil more accurately.
2. For effective P management its adsorption and desorption studies should be carried out under diverse agro-ecosystem with different cropping system and soil type.

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APPENDICES

APPENDIX-A: Weekly Meteorological Data during the crop growth period (2019)

Met. weeks	Max temperature (°C)	Min temperature (°C)	Rainfall (mm)	Relative humidity -I (%)	Relative humidity -II (%)	Wind speed (kmph)	Evaporation (mm)	Sunshine (hr)
30	27.2	24.4	2.4	91	78	12.6	1.2	0
31	29.8	25.11	26.51	89.85	83.28	9.94	3.21	2.48
32	30.94	25.75	1.57	88.85	73.28	7.47	3.24	4.28
33	31.71	25.02	8.4	92	73.85	4.88	3.1	2.88
34	30.57	24.98	8.42	92.42	76	5.1	2.54	1.08
35	30.5	25.05	33.94	94	84.14	5.14	1.97	1.24
36	29.9	24.92	1.91	91.28	75.85	8.17	2.72	3
37	32.85	25.47	0.34	88.85	66.71	3.8	3.95	6.98
38	30.61	24.64	18.2	91.14	72.85	3.94	2.94	4.84
39	31.64286	24.15714	7.5	90.14286	65.85714	4.271429	3.4	6.685714
40	31.45	23.67	0.171	91.28	64.28	2.5	3.414	5.55
41	28.3	22.3	3.94	91.85	69.85	3.77	1.94	2.72
42	31.12	22.64	0	92.57	53.57	1.45	2.81	6.42
43	30.94	19.76	0	91.4	47.2	1.14	2.82	6.84

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