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PHOSPHORUS BIOGEOCHEMISTRY OF AGROECOSYSTEMS

Yukti Verma[1] and Indra Bahadur[2]

Department of Soil Science and Agricultural Chemistry, Banaras Hindu University, Varanasi-221005, E-mail: ibm07025@gmail.com, Corresponding Author: Indra Bahadur

Abstract *Phosphorus (P) has been considered as the ultimate limiting soil nutrient in terrestrial ecosystems. Its biogeochemical cycle is complex due to no source in atmosphere and low availability in soil where it commonly becomes immobilized for short as well as long durations in a wide range of inorganic and organic. Both geochemical and biological processes regulate the availability of P in soils. At the global scale and over the long term, geochemical processes link the movement and distribution of P between two large pools - terrestrial soils and ocean sediments. In the short-term, biological processes influence P distribution because most of the plant-available P is derived from soil organic matter. Long term paddy cultivation may be a soil degrading pathway as the loss of soil materials (e.g., $CaCO_3$) by physical and chemical processes damage the P holding capacity. Intercropping can lead to changes in microbial biomass C:P stoichiometry and points to the need to better account for the soil microbial activity as an integral part of P storage and cycling in the rhizosphere.The community of actinobacteria and AMF (Arbuscular Mycorrhizal Fungi) is associated with the underlying P fertility gradient and is important in the biogeochemical cycling of soil P.*

Keywords: *Phosphorus, Biogeochemistry, Agroecosystem, VAM, Eutrafication.*

Introduction: Phosphorus (P) is an essential nutrient for all life forms that often limits plant productivity. Unlike nitrogen (N), which is supplied by N fixers or directly from the atmosphere in fixed form, the primary source of P for terrestrial ecosystems is rock weathering. Therefore P has been considered the ultimate limiting soil nutrient in terrestrial ecosystems [1]. Its biogeochemical cycle is complex due to no source in atmosphere and low availability in soil where it commonly becomes immobilized for short as well as long durations in a wide range of inorganic and organic compounds [2,3]. Phosphorus occurs in soil as inorganic and organic P compounds. Its oxidation state varies from -3 to +5. Phosphorous in sediments is present as carbonate flour apatite form and is sequestered more by calcium than iron and aluminium oxides. In future the potential of combining novel techniques (NMR, µ -XRF, µ -XANES) at the micro and nano scale is to be explored and collaboration with other streams is required to assess P biogeochemistry of agro-ecosystems.

Biogeochemistry of P: The P cycle is the biogeochemical cycle that describes the transformation and translocation of P in soil, water, and living and dead organic material. P additions to soil occur due to additions of inorganic and organic (manure) fertilizer and the degradation and decomposition of organic (plant and animal) material. Export of P from soil occurs mainly through plant uptake. P may also be exported from soil via surface runoff and erosion or subsurface loss through leaching. Sorption and desorption reactions of P occurs on the surfaces and edges of hydrous oxides, clay minerals, and carbonates. Precipitation and dissolution reactions greatly influence the availability of P in the soil. Precipitation and dissolution are very slow processes. Dissolution and precipitation of P can also occur due to changes in redox potential caused by seasonal or periodic water logging and draining soil. The microbial cycling of P from inorganic soluble forms to insoluble organic forms is known as immobilization. The reverse is known as mineralization. Mineralization of P is catalyzed by the phosphatase enzyme.

Why Biogeochemistry of P is Important?

1. P is an essential component of adenosine triphosphate (ATP) which transports chemical energy within cells for metabolism (i.e. uptake and transport of nutrients); deoxyribonucleic acid (DNA) which is a nucleic acid that contains the genetic instructions used in the development and functioning of all known living organisms; and ribonucleic acid (RNA) which is important for protein synthesis in plants and animals.
2. P is also a building block of certain parts of the human and animal body, such as the bones and teeth.

Factors Affecting Biogeochemistry of P: Factors which affect biogeochemistry of P are: precipitation, rock phosphorous content, vegetation, soil microbial activity, organic matter content in soil, soil pH, mineral phosphorous fertilization and disturbance to atmosphere and soil. These factors by their active or passive effect control P biogeochemistry.

Processes in Biogeochemistry of P

1. **Geochemical Processes:** The geochemical processes involved in P biogeochemistry are adsorption, desorption, precipitation and dissolution.
2. **Biological Processes:** The biological processes involved in P biogeochemistry are mineralization and immobilization.
3. **Physical Processes:** The physical processes involved in P biogeochemistry are leaching and runoff.

Both geochemical and biological processes regulate the availability of P in soils. At the global scale and over the long term, geochemical processes link the movement and distribution of P between two large pools - terrestrial soils and ocean sediments. In the short-term, biological processes influence P distribution because most of the plant-available P is derived from soil organic matter [4].

Hedley Sequential Extraction Procedure for Soil P: In spite of the importance of phosphorus (P) as a limiting nutrient in terrestrial ecosystems, our understanding of terrestrial P dynamics and our ability to model P cycling are hampered by the lack of consistent measurements of soil P. The Hedley fractionation method provides a comprehensive assessment of soil P and has been widely used in recent decades. Hedley sequential fractionation method which first removes labile inorganic P (Pi) and organic P (Po) and then the more stable Pi and Po using sequentially stronger extracting agents (first anion exchange resin, followed by 0.5 *M* $NaHCO_3$, 0.1*M* NaOH and 1*M* HCl), has gained considerable attention as a useful tool to examine different forms of soil P and provides a comprehensive assessment of available P in soils. A conceptual model is given (Fig. 1) to understand its different components and their transformations in soil.

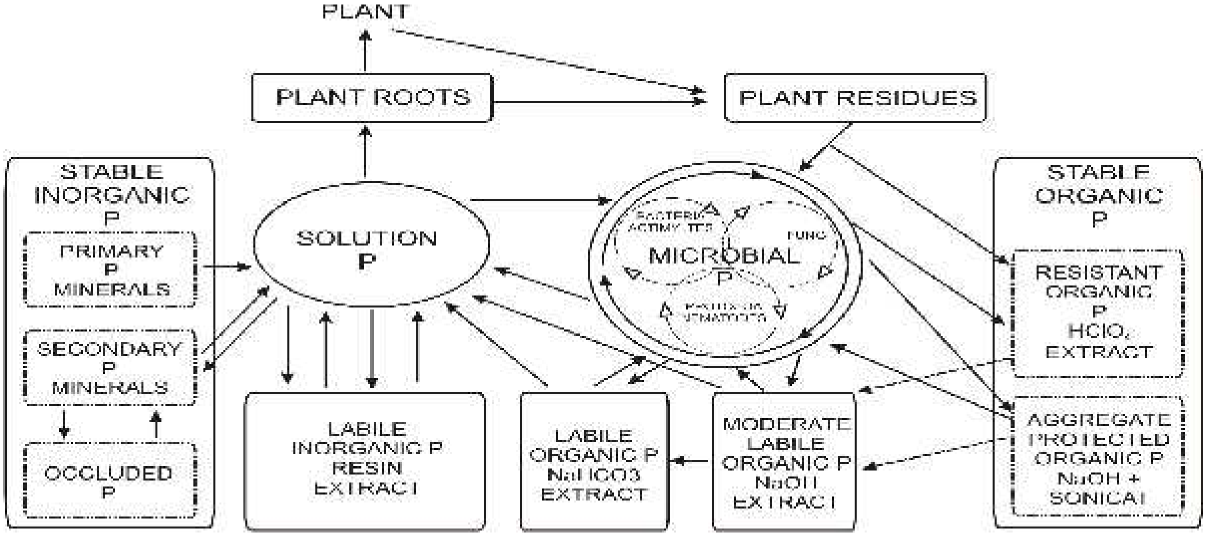

Fig.1. Conceptual model of P transformations with its measurable components in soils

P Availability as a Function of pH: Phosphorus reactions in soil are pH dependent. In acid soils, soluble phosphorus in the soil solution reacts with Fe and Al to form low solubility Fe and Al phosphates. In calcareous soils, soluble phosphorus in the soil solution reacts with Ca to form low solubility Ca phosphates.

Phosphorus Biogeochemistry in Agroecosystems

Transformation of P as a Function of Pedogenesis: Investigated the relationship between distribution of different P forms and stage of soil development by surveying the peer-reviewed literature that cited the Hedley fractionation method [5,6]. In this study, Hedley P fractions were grouped into five soil P fractions (Table 1) based on previous studies [4]. Furthermore, labile P in soil is defined as the sum of resin Pi, bicarbonate Pi and bicarbonate Po.

Table 1: Terminology of P forms used in this study and their correspondence to the defined P fractions using Hedley method.

This study	Hedley method
Labile Pi	Resin Pi, Bicarbonate Pi
Secondary mineral Pi	Hydroxide Pi, Sonic Pi
Primary mineral P	Apatite P
Occluded P	Residue P
Organic P	Bicarbonate Po, Hydroxide Po, Sonic Po
Labile P (Available P)	Resin Pi, Bicarbonate Pi, Bicarbonate Po
Soluble P	Resin Pi
Non- occluded P	Bicarbonate Pi, Sonic Pi, Hydroxide Pi

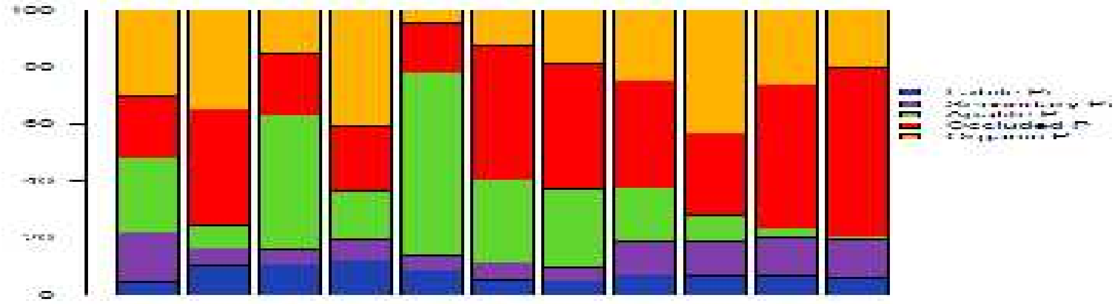

Fig.2. Fractions of different soil P expressed as a percentage of total soil P.

Fractions of different soil P as a percentage of total soil P are shown in fig. 2. Labile Pi, which is considered readily available for plants, constitutes a small fraction of total soil P for all soil orders. Apatite P decreased with soil weathering. However, it makes up 64% of total soil P in Aridsols, the highest among all soil orders. This reflected both the moderate weathering stage of Aridsols due to dry climate condition and the generation of secondary calcium phosphate in Aridsols. In contrast to apatite P, occluded P increases with the weathering stage of soils.

The mean labile P decreased with the weathering stages of the soils. The importance of bicarbonate Po to soil labile P increases as soil development proceeds. Two special soil orders, Andisols and Histosols, have a high percentage of labile P as bicarbonate Po. The high value in Andisols reflects the rapid soil particle formation from easily weathered volcanic ash [7], while the dominance of bicarbonate Po in Histosol labile P is mainly from P in accumulating organic matter.

Application of Hedley Fractionation to Biogeochemical Cycle of Soil P in Natural Ecosystem: Both geochemical and biological processes regulate the availability P in soils. At the global scale and over the long term, geochemical processes link the movement and distribution of P between two large pools terrestrial soils and ocean sediments. In the short-term, biological processes influence P distribution because most of the plant-available P is derived from soil organic matter. The biological portion of the P cycle is controlled primarily by bacterial and fungal decomposition, immobilization, and mineralization, and secondarily via plant uptake. The geochemical portion of the P cycle is controlled initially by soil parent material and subsequently by soil properties resulting from pedogenesis.

Studied long term P evolution during anthropogenically influenced pedogenesis at two contrasting paddy chronosequence developed on calcareous marine sediments at Cixi (coastal plain) and acidic quaternary clays at Jinixian (hilly region) respectively in Beijing, China [8].

The Cixi paddy soils accumulated P_T in surface and subsurface horizons (Ap1 and Ap2) at 50 and 300 yr of cultivation which was due to accumulation of fertilizers, while P_T became depleted in these horizons at 700 and 1000 yr of cultivation due to complete removal of $CaCO_3$ and substantial loss of Fe and clay minerals. Hence long term paddy cultivation is a soil degrading pathway as the loss of soil materials (e.g., $CaCO_3$) by physical and chemical processes damage the P holding capacity In contrast, paddy soils derived from quaternary red clays at Jinxian accumulated P_T throughout the soil profile following 60, 150, and 300 yr of paddy cultivation relative to the uncultivated soil. Hence upland paddy cultivation not only results in surface P enrichment but also causes significant movement of P to lower horizons.

In Cixi chronosequence, occluded P made up the largest proportion of P_T in older soil and in Jinxian chronosequence also it made up the highest proportion at both the horizons (Fig.3).

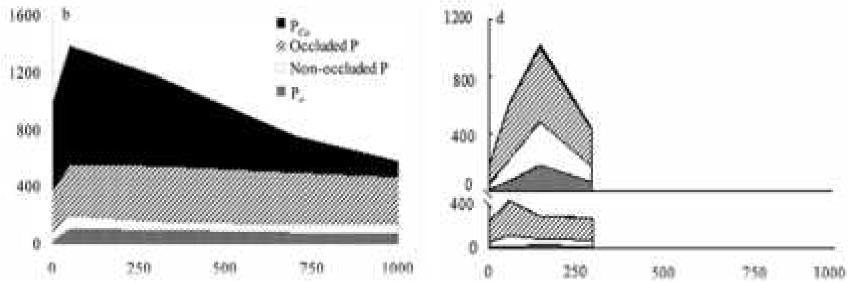

Fig. 3. Changes in soil P fractions during paddy soil development at Cixi within 0–50 (a) and Jinxian (b) within 0–50 (upper panel) and 50–120 cm (lower panel).

P Biogeochemistry in different Cropping Systems: Studied biogeochemical cycling of P in sugarcane agroecosystem to quantify the P distribution during its period of growth near San Felipe, Yaracuy State, Central, Venezuela. The soil was mollisol, Haplaquoll (fine loam) [9].

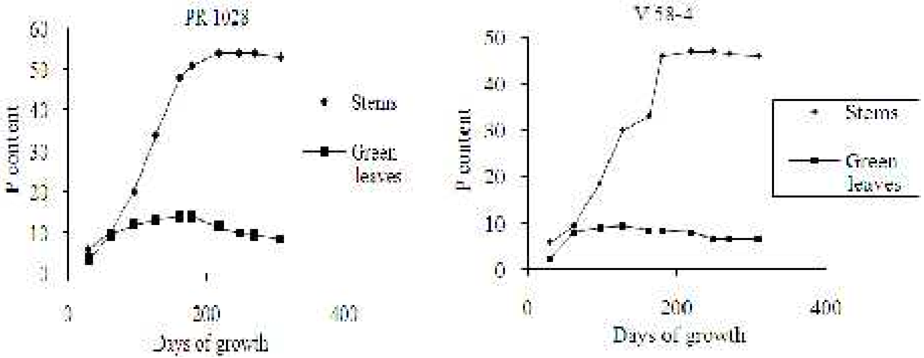

Fig. 4. P contents in leaves and stems (kg ha $^{-1}$)

Fig. 4 shows the accumulation of P in the different plant fractions for the PR 1028 and V 58-4 varieties. The amount of P accumulated in the stems increases speedily and almost linearly during the first 160 days of development. After this interval, it stabilizes and reaches a total accumulation of 57.0 and 48.8 kg ha-1for PR 1028 and V58-4, respectively.

When P annual budget was calculated for the two varieties it was found negative for both of them (Table 2). It was due to high levels of P export via stem.

Table 2. Annual P budget in kg P ha^{-1} for the two sugarcane varieties analyzed

Transferences	PR-1028	V 58-4
Inputs		
Precipitation	14	14
Fertilization	11	11
Irrigation	0	0
Outputs		
Ashes	3	2
Leaching	3	3
Harvesting	42	37
Balance	-23	-17

These losses could be replaced with the application of fertilizers, however no response to fertilization with P have been registered in the zone, a fact that indicates that the internal mineralization of the organic P reserves together with the inputs from ashes and precipitation, as well as the possible dissolution of calcium phosphates, operate efficiently in this mollisols.

Studied increase in microbial biomass and phosphorus availability in the rhizosphere of intercropped cereal and legumes under field conditions at INRA experimental station, France [10]. The soil was sandy clay loam (Calcareous cambisol). MBC increased significantly in the rhizosphere relative to the bulk soil in all three intercropped species and intercropped legumes (chickpea and lentil) showed an even more pronounced increase. MBP increased significantly by up to 4-fold in the rhizosphere relative to bulk soil in intercropped chickpea and durum wheat. Hence we can conclude that in the rhizosphere, microorganisms deriving carbon from rhizo-deposition thus need P to satisfy their growth demand and MBP is another pool of soil P which can act as sink or source of P.

Studied geochemical and biological forms of P under long-term grazing as well as mobility and lability of these nutrient forms in the soil profile (Fig.5) [11]. The experiment was established in 2001 in an Oxisol and consisted of soybean (*Glycine max* L.) rotated to a winter cover crop of black oat (*Avena strigosa* Schreb.) and Italian ryegrass (*Lolium multiflorum* Lam.) under no-tillage in Brazil. The soil was Clayey Oxisol (Rhodic Hapludox). To 20 cm depth, both geochemical and biological moderately labile P forms increased in both systems despite greater P surplus under no-grazing treatment, while soybean yields were similar to the grazed treatment. Long term integrated-no till crop-livestock system enhances P cycling ensuring P surplus, and provides greater economic returns than a no tillage soybean-cover crop system without grazing.

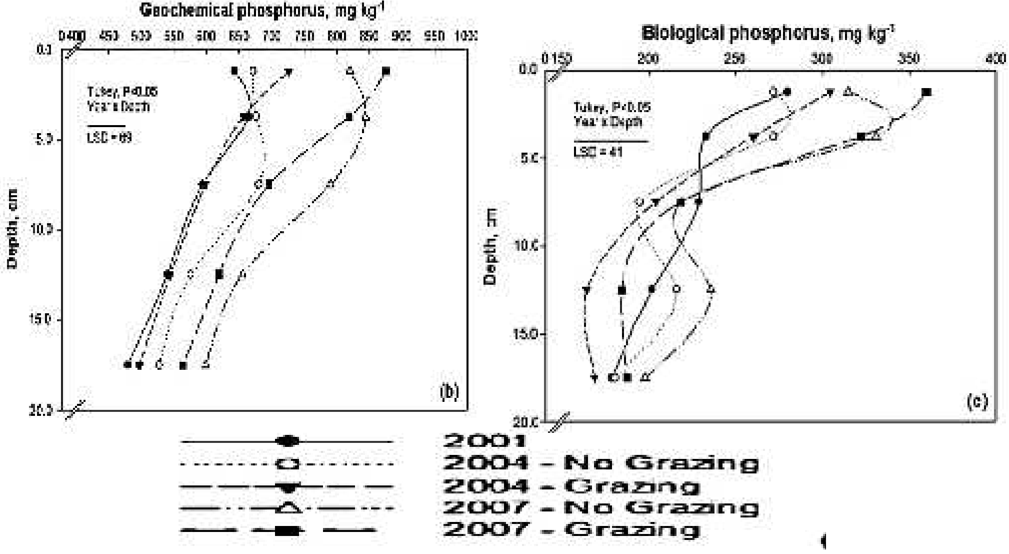

Fig. 5. Geochemical and biological phosphorus concentration under no grazing and grazing in integrated crop–livestock system with time.

P Biogeochemistry in Wetland Soils / Sediments: Studied P biogeochemistry in sediments of high altitude lakes near Kumaun Himalayas, India. Biogenic apatite+calcium carbonate bound fraction (Fig.6) contains most of the phosphorus (>90 %) and shows a decreasing trend up core which may be may be due to presence of calcareous rocks such as limestone, dolomite, and calcareous shales in the catchment area [12]. Exchangeable fraction is the next dominant fraction in Nainital and Bhimtal, followed by organic fraction.

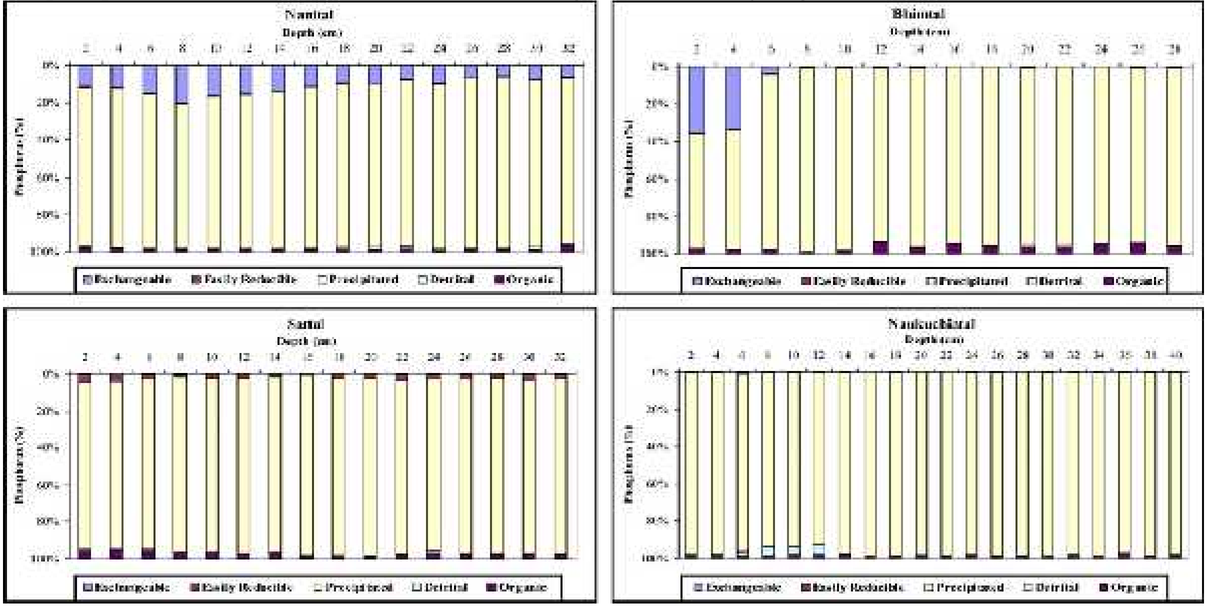

Fig.6. P fractions in sediments at different depths

Fig.7 shows high positive correlation of Ca with P in Nainital, Bhimtal and Naukachiatal lakes whereas Fe has very low positive correlation coefficient. Hence it was concluded that lake sediments are derived from catchment rocks and P in sediments is sequestered more by Ca than Fe and Al oxides, as carbonate flourapatite.

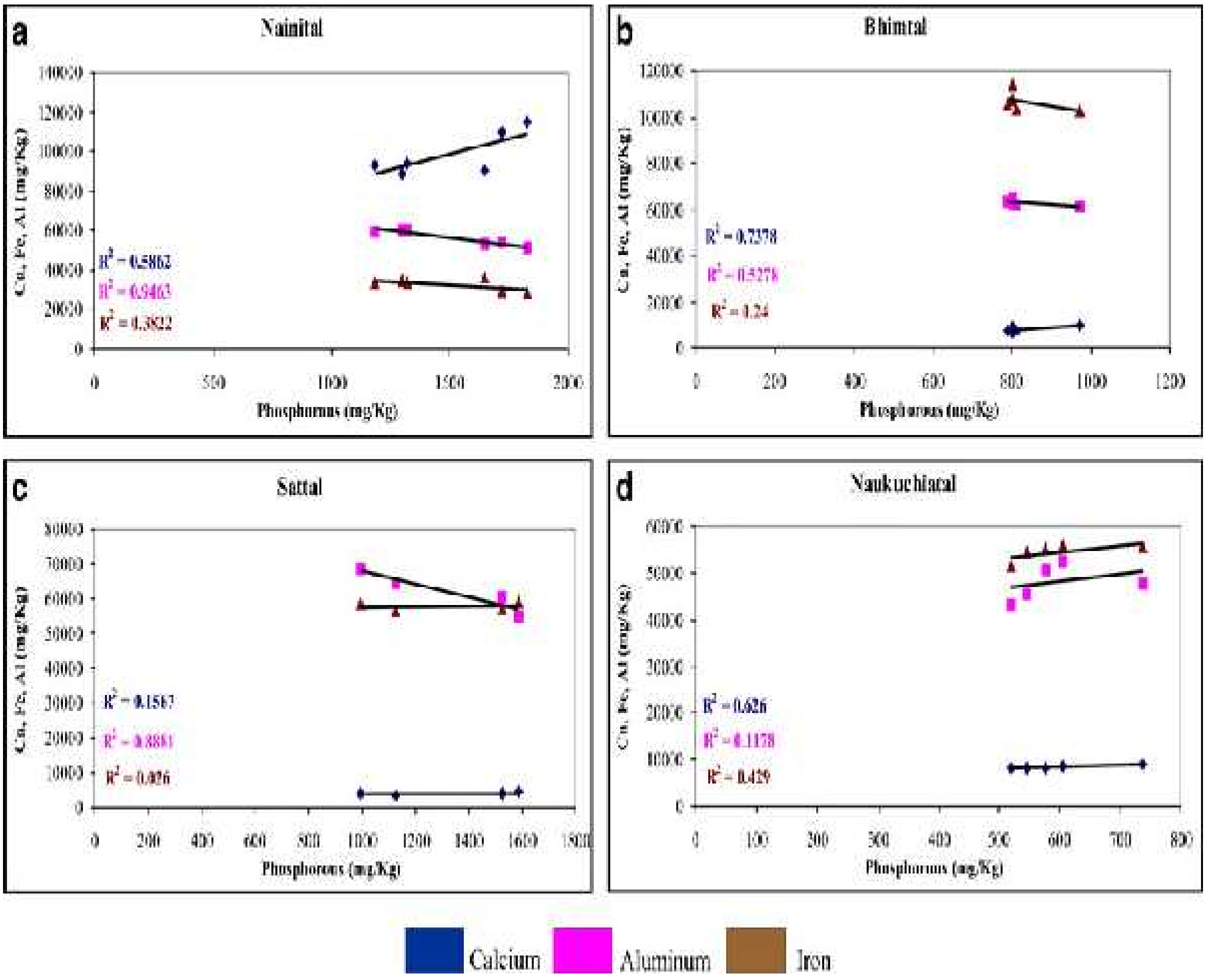

Fig.7. Relationship between P with Ca, Al and Fe in lake sediments

Advanced Techniques to Study Biogeochemistry of P: A combination of solution analysis, micro-x-ray fluorescence (µ-XRF) and micro-x-ray absorption near edge structure (µ-XANES) spectroscopy were used [13] in Australia to investigate the degree to which sorption of fertilizer P is determined by reaction with Al compounds, the extent to which carboxylic acid addition can influence these reactions, and the relative distribution of sorbed P in an acid soil. When no P was added oxalic acid addition significantly increased P as well as Al concentration in solution which was due to oxalic acid mediated dissolution of Al species from soil surface which resulted in exposure of previously occluded P (Table 3).

Table 3. Solution chemistry results

Sample	Solution P (mM)	Solution Al (mg/L)
OP	0.006	7.92
OX	0.011	15.64
HB	0.003	0.68
COU	0.004	1.06
100P	94.46	15.82
OX+P	94.53	24.95
HB+P	94.45	36.69
COU+P	94.67	5.17

According to P L-Xanes spectra, endogenous concentration of P was below the detection limit in case of coumaric and hydroxybenzoic acid whereas a strong P signal was obtained in case of oxalic acid treatment. Hence it was attributed that oxalic acid compete with P for solid phase binding sites.

Studied the influence of fertilizer loaded Nanoclay Superabsorbent Polymer Composite (NCPC) on dynamics of P and uptake by pearl-millet (*Pennisetum glaucum)* in an inceptisol (Fig. 8) [14]. In general, availability of P (Olsen-P and 0.01M $CaCl_2$-P) decreased continuously with progress of sampling periods, irrespective of fertilizer treatments, but the rate of decrease was much higher under CF treated soils than that in NCPC treated soils, especially at initial sampling periods. Hence it was concluded that use of

NCPC as a carries of costly nutrients could be an alternative and effective option to save costly chemical fertilizers.

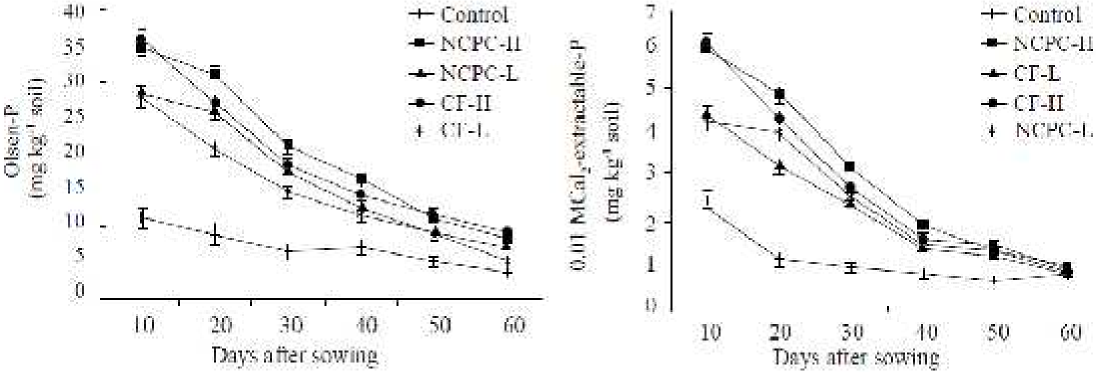

Fig.8. Changes in availability of (a) Olsen-P and (b) 0.01M $CaCl_2$-extractable-P as affected by different fertilizer treatments

Conclusions: Phosphorus cycle in soils occur with both, dynamic biological processes and sluggish pedological processes and evolution of P forms is ultimately toward the P sinks consisting of stable organic P and occluded P. Long term paddy cultivation may be a soil degrading pathway as the loss of soil materials (e.g., $CaCO_3$) by physical and chemical processes damage the P holding capacity. Long term integrated-no till crop-livestock system enhanced P cycling ensuring P surplus, and provided greater economic returns than a no tillage soybean-cover crop system without grazing. The community of actinobacteria and AMF (Arbuscular Mycorrhizal Fungi) was found to be associated with the underlying P fertility gradient and is important in the biogeochemical cycling of soil P.

Path Ahead: To achieve robust P sustainability in agriculture, research should be done on: reducing unintentional P losses, improving P availability, optimizing crop uptake of soil P resource (NCPC) and cycling the P back to the farm. The potential of combining novel techniques at the micro and nano scale (NMR, μ-XRF, μ-XANES,) to assess importance of P biogeochemistry is to be explored.

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