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Phosphorus transformations in mangrove soils under microcosm study

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Abstract

Various phosphorus (P) fractions in the mangrove soils were studied by incubation study (180days) to understand the biogeochemical cycling in the mangrove soils of Eastern coast of India. The soil was analysed using sequential extraction procedure. Total phosphorus were ranged from 18893 mg/kg and 3268 mg/kg and Org-P was the dominant fraction which contributed about 89.2% of total P. Ion bound phosphorus (Fe-P) was the most important fraction among the inorganic P forms may be because of Fe-oxide, sulphate reduction. The study suggested that speciation of phosphorous (P) had good correlation among themselves. In addition, the various P fractions were increased during incubation period and these pools in turn supplement the SP thereby maintaining a high amount of P in the mangrove soil. At surface soils the pH and Eh exhibited stable values during inundation and the Eh dropped significantly from 98 to -215.1 mV, concurrently with pH increase to basic values (6.2-8.1). These results indicate that influence of electro chemical properties on phosphorus geochemistry in mangrove soil. The study concluded that quantifying the relation between P fractions in mangrove soils is required to realize the mangrove ecosystem in connection with human intervention.

Keywords: Mangroves, soil, incubation, phosphorus fractionation, sequential extraction.

Introduction

Mangroves are halophytic plants and trees that grow in the tropical and subtropical region given that a broad range of ecological and economic products and services and are one of the major fecund ecosystems on the earth. About 75% of world's mangroves are distributed in 15 countries, and only 6.9% are protected under the existing protected areas network (IUCN I-IV)[1]. India has a mangrove cover of about 4740 km^2, occupying 0.14% of the land area[2]. Soils of the mangrove systems provide the base matrix to sustain these systems. Mangrove soils are complex systems developing from complex interactions between biotic and abiotic factors[3-5]. They are generally marine alluvium which is rich in organic matter. Top soils of mangroves are porous in nature which facilitate water percolation, whereas sub soils contain a large amount of organic matter[6]. Microbial interaction with the chemical components produces specific conditions in these soils. For example, anaerobic sulphur reducing bacteria (eg. Desulfo vibrio) produces hydrogen sulfide that gives strong odor to mangrove soils[7]. Unlike other terrestrial systems mangrove soils represents submerged conditions, hence have a different system of nutrient transformation. Among the primary nutrients, phosphorus is a vital factor of every living organism for their development and its maintenance. Labile phosphorus is the readily available form to plants and microorganisms and is related to various pH dependent orthophosphate ions. Adequate amount of phosphorus (P) is needed for optimum plant growth and reproduction. When P is limiting, it affects the reduction of leaf expansion, Leaf surface area and number of leaves. It also cause less root mass to reach water and nutrients[8].

P entering a mangrove soil as both organic and inorganic forms. P forms must usually undergo transformations before being bioavailable. Soluble Phosphorus (SP) is considered bioavailable. Both biotic and abiotic process controls the P pool sizes and its transformations within the soils. Bioavailability of limiting nutrients such as P determined the productivity, soil quality and water quality of mangrove systems to some extent[9]. In tropical mangroves, phosphorus fractions vary due to the intermittent flooding of soils with both saline and fresh waters[10]. Biogeochemical changes affect the variability of Total phosphorus (TP) in mangroves. Even Slight alterations results reflect in their concentration[11]. Transformation of P either biotic or abiotic. Chemical speciation of P affect the biogeochemical cycle in the soils. Several authors found that[11-13]. Ion bound phosphorus (Fe-P) fractions are the major fraction generally observed indicating the redox-sensitive mobile fraction in the soils. Organic- bound P (Org-P) was high in Indian mangroves which depend on organic matter load, anthropogenic activity and biogeochemical conditions. Organic carbon had major influence on P fractions and Clay. The entire forms of inorganic P be showed considerably correlated with each other except aluminum bound phosphorus (Al-P) and Occluded Phosphorus[14].

Dissolved reactive phosphorus (DRP), concentrations, plant available P and soil inorganic P fractions were significantly influenced by fertilizing and submerging condition when changes in floodwater and pore water[15]. Labile-P and inorganic P fractions were obtainable for soil microorganisms and to decompose leaf litter and that raise in microbial activity ultimately an increase in the quantity of organic P in forest soil[16].

The extent of pollution from anthropogenic activities, origin of bioavailability phosphorus, burial and digenesis of phosphorus etc can be obtained from the study P dynamics in soils[17-19]. Different fractions of phosphorus and their relationship with each other as well as with different soil properties is useful to understand the capacity of soil to supply phosphorus to plants[14]as well as the transformation of phosphorus with in the soil . Knowledge of phosphorus speciation may help us to recognize the biogeochemical reactions and processes of phosphorus in mangrove systems[20]. The present paper concentrates on the Phosphorus transformations and their relationships in mangrove soil.

Materials and methods

Soil samples were collected from a mangrove area in the Eastern Coast of India (10^{0}54'61.9"N, 76^{0}06'42.5"). *Avicinnia officinalis, Acanthus ilicifolius, Aegiceras corniculatum, Bruguiria cylindrica* and *Rhizophora mucronata* were the six mangrove species observed in the study area. The area has a tropical humid climate with an average rainfall of 2352.6mm and mean annual temperature of 27.1^{0}C. Soil samples were collected up to 30cm depth from different points in the selected mangrove by core method and used for incubation experiments.

Incubation studies: Pots were filled from the core with minimum disturbance and gentle tapping to get field bulk density. Pots were kept in triplicate and distilled water was used to retain submerged conditions. Soil samples were collected from each pot at two weeks interval for 180 days. The collected samples were air dried and sieved through 2mm sieve for further analysis.

Soil analysis: Collected soils were initially characterized for bulk density, texture, pH, cation exchange capacity (CEC), electrical conductivity, redox potential (Eh), organic carbon (OC) and phosphorus (P). Bulk density was estimated by core sampling method[21] and texture by Bouyoucos hydrometer method[22]. The pH and electrical conductivity (EC) were measured in a soil: suspension ratio of 1:2.5 by potentiometery[21]. Walkley and Black method[23] was used for the determination of organic carbon. Total phosphorus was measured by colorimetry after digestion of the soil using spectrophotometer[21]. Ammonium acetate method was used for the CEC determination[24].

Sequential extraction of phosphorus: The sequential extraction of phosphorus was done as per the protocols outlined by Peterson and Corey[25] (Figure-1). The extraction scheme involved addition of 1M NH_4Cl to extract soluble P, 0.5M NH_4F and saturated NaCl to extract aluminium bound phosphorus (Al-P), 0.1M NaOH and saturated NaCl to remove iron bound phosphorus (Fe-P), Sodium citrate-dithionate-bicarbonate to get sesquioxide occluded phosphorus (Occl-P) and 0.25M H_2SO_4 to remove calcium bound phosphorus (Ca-P). Organic bound phosphorus (Org-P) was also determined separately following the procedures outlined by Anderson[26] (Figure-2).

Results and discussion

Initial soil characteristics: The soils were sandy loam in texture with 61.84% sand (Table-1). The soils had a bulk density and organic carbon contents of 0.46 and 1.83%, respectively. Lower bulk density of mangrove soils were related to high organic matter and clay content[27]. This study showed that mangrove soils were acidic and anoxic in nature. According to Boto and Wellington[28] Humic acid, CEC, iron and manganese hydroxide, amount of carbonic acid and carbonates store in soil at certain period had a role in soil acidity of mangrove soils. Waste load like distillery and agriculture waste also leads to lowering the pH[29]. Organic carbon was high (1.83%) in the soils may be due to the accumulation of litter and other plant residues. Considerably high value of CEC (11.87 m.e/100g soil) was found in the study. This behavior was attributed to the occurrence of higher quantity of organic matter in the soil[30]. Nutrients such as Nitrogen (18400mg/kg), Phosphorus (1088mg/kg) and Potassium (3160mg/kg) were high in mangrove soils. Soil physical characteristics may influences the primary nutrients like N, P and K. Eh values showed that the soils were anoxic in nature. It was related to rainfall, seasonal fluctuations and input and output of water[31]. Electrical conductivity of the mangrove soils indicated that they rich in salt content (567.45ds/M) and total phosphorous was1088mg/kg. Electrical conductivity was related to the frequent tidal action and the analogous proportions of the similar ions in the seawater and soil[32].

Variations in pH and Eh during incubation: The pH of the soil different from 6.30 to 8.10 during the 180 days incubation (Figure-3). pH values were found to approach neutrality within 14 weeks of continuous submergence and stabilize at 8.1 by the 24th week. Similar results were reported by various authors[33-35]. The increase in pH of the soil during submergence due to the reduction of Fe (III) to Fe(II)[36]. The decrease in pH soon after inundation is may be due to carbon dioxide produced during respiration of aerobic bacteria[37].

Eh, a measure of the redox potential of the soil was found to vary from an aerated condition (+100mV) during the initial stages to a highly reduced state (-215.1mV) by the end of the incubation time (Figure-4). Similar changes were shown by several authors[34,38-40]. According to Yamane[40] organic matter contents, temperature and duration of submergence were related to the decrease of Eh. The decrease of Eh upon submergence probably due to the release of reducing substances associating oxygen depletion before Mn(IV) and Fe(III) oxide hydrates can mobilize their buffer capacity[39,41]. The pH and Eh were closely related and the hydrogen ion concentration influences the ionization extent that may change the redox potential of the soil[42].

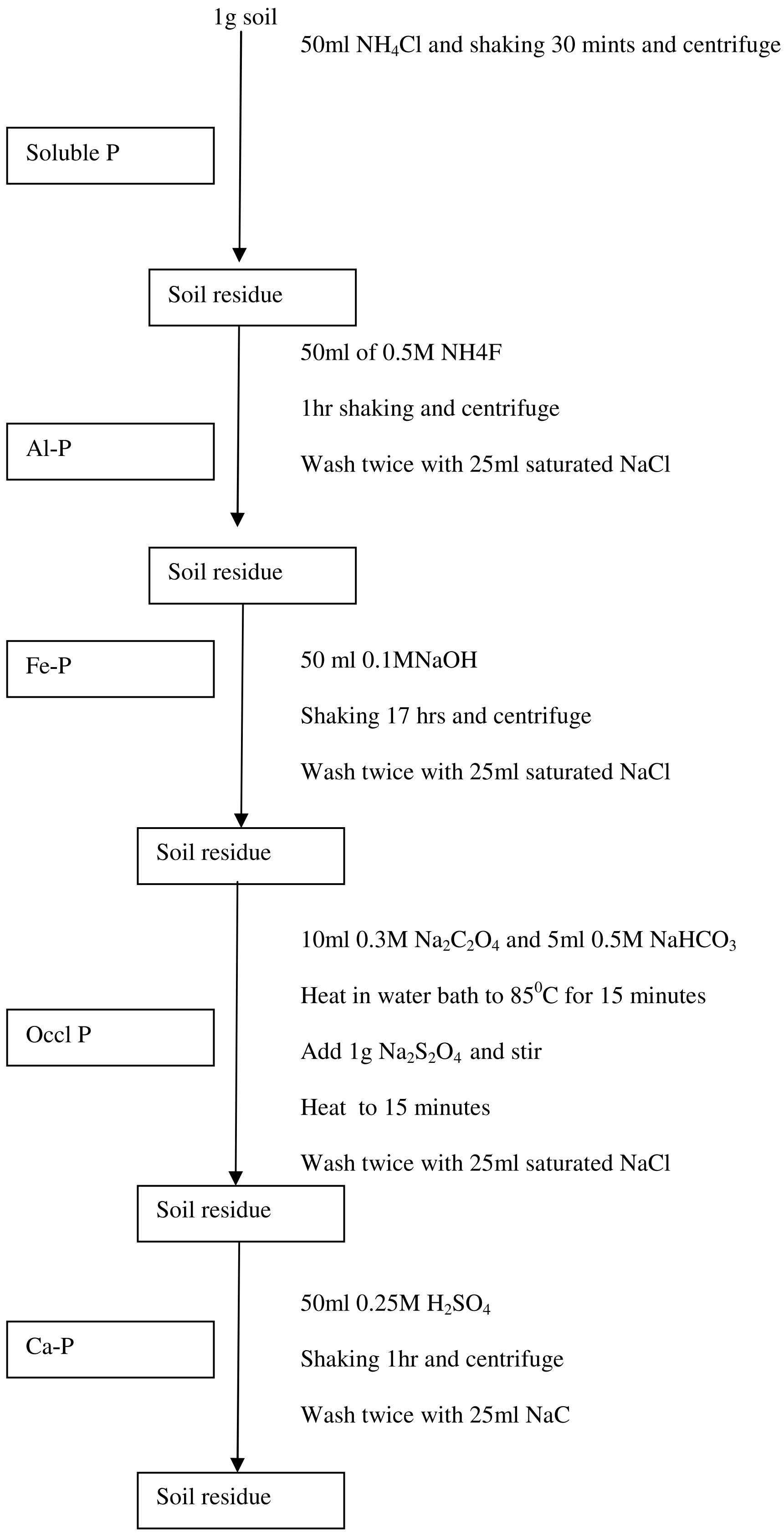
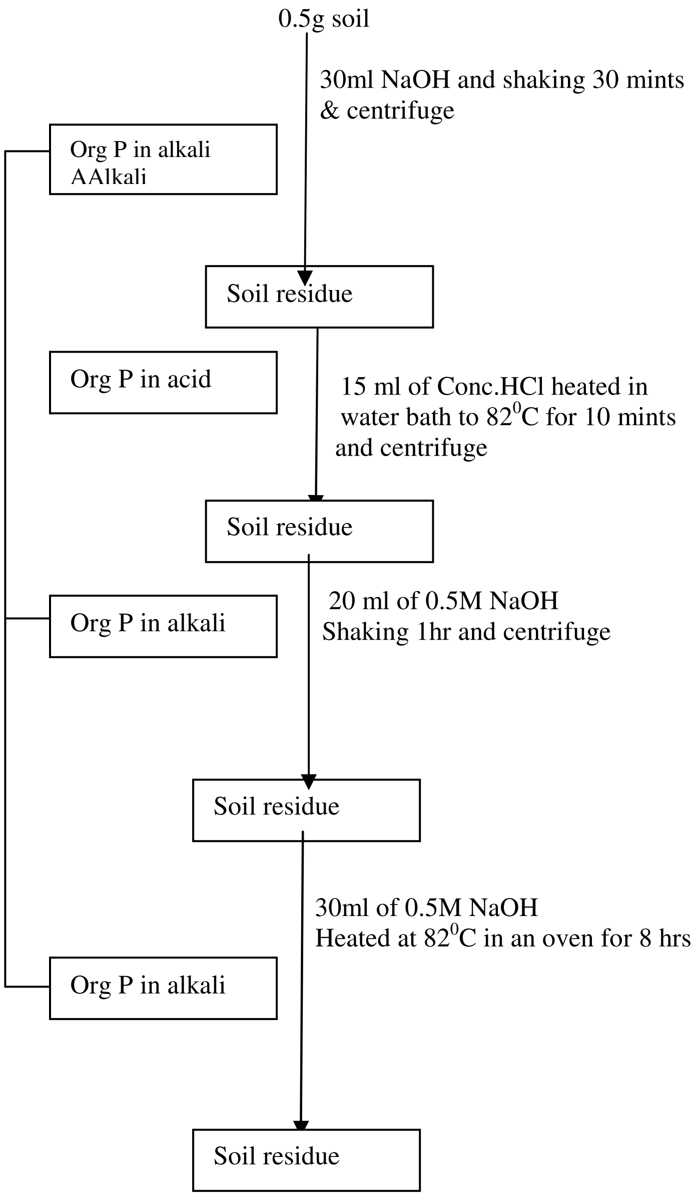


Figure- 1: Schematic diagram of P fractions



Total org P = Org P in Acid + Org P in Alkali

Figure -2: Schematic diagram of Org P fractions

Variation of P–Fractions during incubation period: The P fractions were found in various amounts in the soil during incubation period (Table-2). These differences may be due to the influence on physico chemical properties of the mangrove soils. According to Sharpley[43] the extents of P transformations in mangrove soils are controlled by intermittent aerobic and anaerobic conditions. Soluble P content of the soils increased during incubation period and ranged from 0.567mg/kg to 8.81 mg/kg. They accounted on an average about 0.24% of total P. Soluble P (SP) varied under highly reduced conditions during incubation and strong relationship with Eh (R^2=0.9977) (Figure-10). Under reduced conditions strong sulfide/reactive iron dependency may controlling the solubility of P [39,44-47] SP was significant and positive with all P forms. This finding was agreed with Gleason et al.[47]. The grater the pH of the soil the greater the precipitation of SP in turn maintaining a high amount of P in the solution of soil.

The distribution of Al-P varied from 22.9 to 24.01mg/kg and contributed about 0.81% of total P. Fe-P was found to be most dominant amongst inorganic forms of P. The Fe-P content showed variation in all samples during incubation period and varied between 78.16 and 416.5mg/kg (about 7.89% of total P) and its controlled by sulphate reduction under redox variations[48,49]. According to Jensen *et al.*[50] sulphate respiration may produce sulphide which decrease the Fe –oxides and thus support a discharge of Fe-P. Furthermore Mendoz et al.[51] found that P is trapped as $FePO_4$ due to oxygenated micro environment in flooded salt marshes and mangroves. The fractions of Ca-P (R^2=0.981), Occl-P (R^2=0.733) and Org-P (R^2=0.769) were highly correlated with Fe-P. Devra[52] and Bhavasar et al.[14] were agreed with this result. The Ca-P varied from 13.24–57.01mg/kg and accounted for about 1.13% of total P. This fraction maybe due to the accumulation of calcareous material, such as shells of some molluscs and crustaceans in the soil[20]. According to Goltermann[53] diagenic processes may boost the calcium bound phosphorus. Ca -P was strongly related with pH (R^2=0.9006) with and moderately related with Eh (R^2=0.7721). According to Silva and Sampaio[54] stability of Ca-P was high when soils are acidic in nature. SP displayed that significant and positively correlated with Ca-P (R^2=0.835**). This finding was observed by Lunganmuana et al.[55]. Occl-P ranged from 0.47 to 1.945mg/kg and accounted about 0.04% of total P. It was significant and positively correlated with various P fractions and was controlled by organic carbon. Zhang et al.[56] had reported this finding.

Organic P was the major fraction amongst all forms of P. About 89.2% of total P was held as Org-P content in the mangrove soil and the contents varied from 2417 to 2760mg/kg. They were situated in fulvic acid fractions[14]. Org-P was major fraction among the different P fractions due to their high organic matter content[57]. They were positively correlated with P speciation and it confirmed by Bhavsar et al.[14]. The TP includes the sum of all fractions in the soil. The total content of P higher during incubation period. It proved that mangrove soils perform as Phosphorus sink. They had supported by several authors[58-60].

All these P fractions had good correlation among themselves (Table-3). These results suggested that varous P forms in the mangrove soil simultaneously transform to other forms by means of potentially electro chemical properties and complex microbial biochemical reactions in mangrove soil. Org–P was found not to directly influence SP in these soils, whereas all other fractions had a significant positive relationship with this fraction. Org–P that stores 82% of the total P, was found to have a strong positive relationship with Occl–P (0.599**), Ca–P (0.791**), Fe–P (0.769**) and Al-P (0.729**). These pools in turn supplement the SP thereby maintaining a high P concentration in the soil solution.

Relationship between electrochemical properties and P fractions: Amount of Ca-P and Fe-P increased when soils became alkaline (Figure-5-9). The results showed that strong relationship exists between pH and Ca-P (R^2=0.9006) and Fe-P (R^2=0.9094). These P fractions were found to decline near neutral pH, but got increased when soils became alkaline. A strong relationship was found in SP (R^2=0.997), where as Al- P (R^2=0.5395) and Org P (R^2 =0.4456) and Occl-P (R^2 =0.7904) were found to have relatively weaker relationships with soil pH.

All the phosphorous fractions showed an enhancement in their contents with reduction during incubation period (Figure-10-16). Between Eh 98mV and -215mV the dominant fractions were found to be high. As the Eh drops below-200mV the dominant fractions are SP and Org-P. The effect of Eh on P fractions followed the order SP>Org-P>Ca-P>Fe-Pl>Al-P>Occl P. Strong relationship were found SP (R^2=0.9977) where as moderate relationship were found in Occl P (R^2=0.409). The Ca-P (R^2=0.7721), Al-P (R^2=0.7244) and Fe-P (R^2=0.7305) indicates that moderately strong relationship.

Generally, various P forms were enhanced when soils became alkaline with high reduction during incubation. It is may be due to the consequence of reduction after submergence. The fractions of P had good correlation with pH and Eh (Figure-4-9). These electrochemical properties regulate the entire process of submerged soils. When soil became highly reduced, the concentrations of the P forms were high (Table-3) due to iron content in the submerged soils determines the final fate of soil phosphorus and is largely dependable for the increase of reducing conditions, i.e., ferrous-ferric system significantly influences redox potential differences in soil[61].

Table-1: Initial soil characteristics.

Bulk Density g/cm^3	pH	Eh mV	Electrical Conductivity (EC) (ds/M)	CEC m.e/100 g soil	Organic Carbon (%)	Total Nitrogn (TN) mg/kg	Total Phosphorus (TP) mg/kg	Total Potassium (TK)mg/kg	Texture		
0.462	6.5	-99	567.45	11.87	1.83	18400	1088	3160	Sand%	61.8	Sandy clay loam
									Silt%	8	
									Clay%	30.1	

Table-2: Variation of P-Fractions during incubation period (mg/kg ± SE).

Days submerged	SP	Al-P	Fe-P	Ca-P	Occl - P	Org- P	TP
0	0.567±0.003	22.9 ± 0.20	78.16±0.64	13.24±0.24	0.47±0.02	2417±78.65	2532±141.57
14	0.587±0.19	21.287±1.67	77.35±12.17	14.11±1.52	0.48±2.93	1849.33±121.6	1962.81±44.28
28	0.64±2.2	14.37±0.5	84.68±26.06	14.72± 3.55	0.375±1.85	1774.75±56.31	1889.53±125.7
42	0.617±0.03	14.2±8.4	86.83±12.9	13.44±0.03	0.32±0.07	1647.50±23.08	1762.9±144.9
56	0.436±0.01	15.37± 2.7	87.6±1	19.37±0.23	0.3±48.08	2225.5±158.04	2348.57±146.60
70	0.427±0.28	18.48±0.94	88.34±2.96	19.13±6.23	0.56±1.034	2424.01±161.29	2550.94±128.1
84	0.77±0.006	18.027±2.04	100.43±7.92	19.69±0.24	0.61±0.6	2574.53±194.06	2714.05±62.33
98	0.695±0.003	19.467±0.26	300.90±1.21	38.16±0.21	0.6±0.34	2647.67±106.24	2987.35±158.04
112	0.655±0.03	21.134±0.18	352.67±1.20	40.09±1.52	0.71±1.57	2684.42±156.06	3099.67±993.1
126	1.57±1 .12	22.08±15.88	366.9±10.82	40.12±12.42	0.75±27.4	2692.72 ± 199.8	3124.14±974.8
140	5.65±0.1	22.09±1.02	47.17±0.08	47.17±0.08	0.77±0.46	2694.29 ± 141.5	3145.57±265.10
154	5.54±0.28	22.5±0.31	47.56±2.20	47.56±2.20	0.87±0.46	2706.33±140.08	3193.13±262.5
168	8.57±0.28	23.07± 0.18	53.094±0.14	53.094±0.14	1.747±4.35	2724.11±122.79	3226.931±276.04
180	8.81±0.31	24.01±0.18	57.01±0.21	57.01±0.21	1.945±3.91	2760.60±953.76	3268.27±247.32

Table- 3: Correlation between different phosphorous fractions in the mangrove soils.

Fractions of P	SP	Al -P	Fe- P	Ca - P	Occl - P	Org - P
SP	1					
Al - P	0.620*	1				
Fe - P	0.763**	0.690**	1			
Ca -P	0.835**	0.685**	0.981**	1		
Occl -P	0.904**	0.665**	0.733**	0.816**	1	
Org - P	0.517	0.729**	0.769**	0.791**	0.599*	1

*.Significant at the 0.05 level, **. Significant at the 0.01 level

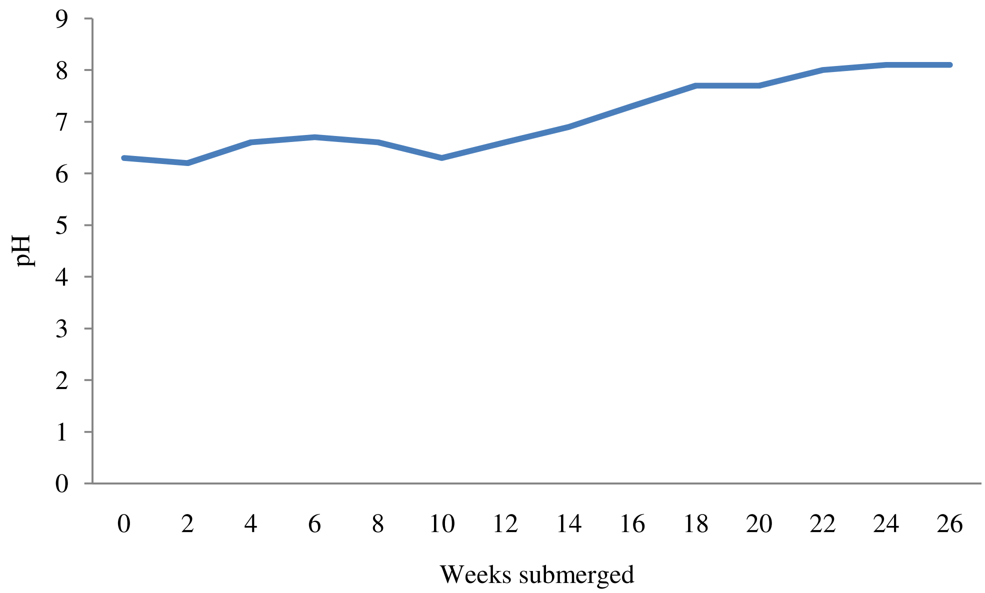


Figure- 3: Variation of pH during incubation period.

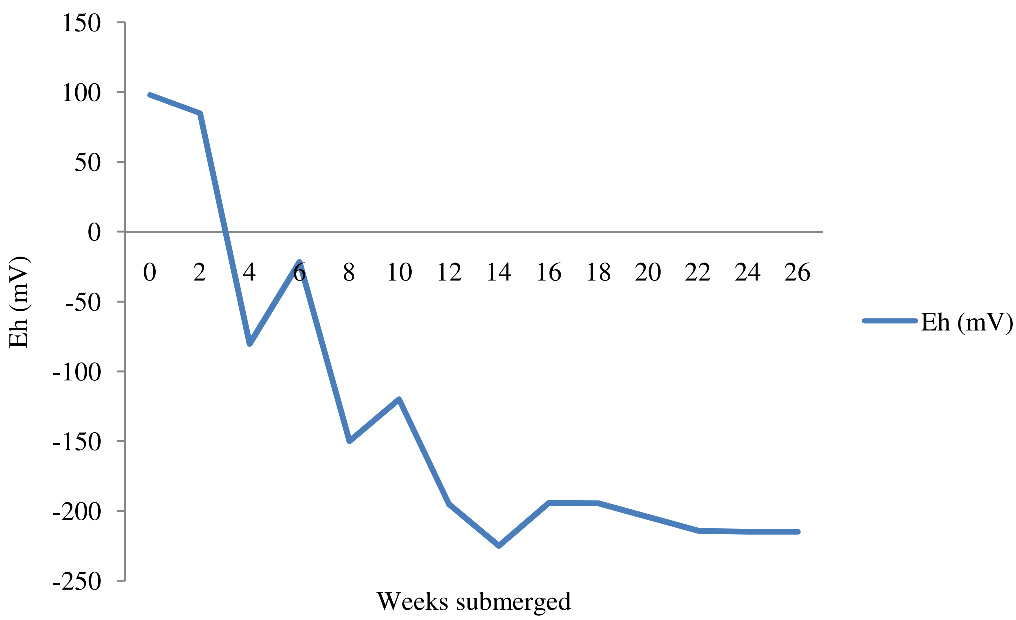


Figure -4: Variation of Eh during incubation period.

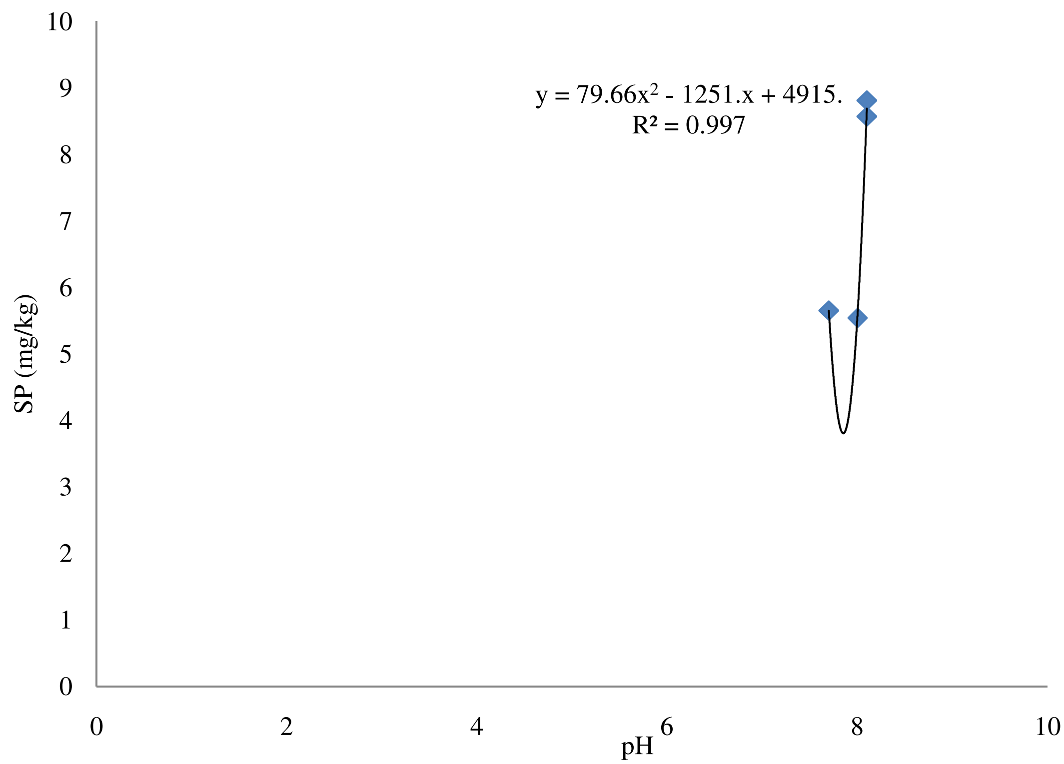


Figure-5: Relationship between pH and SP.

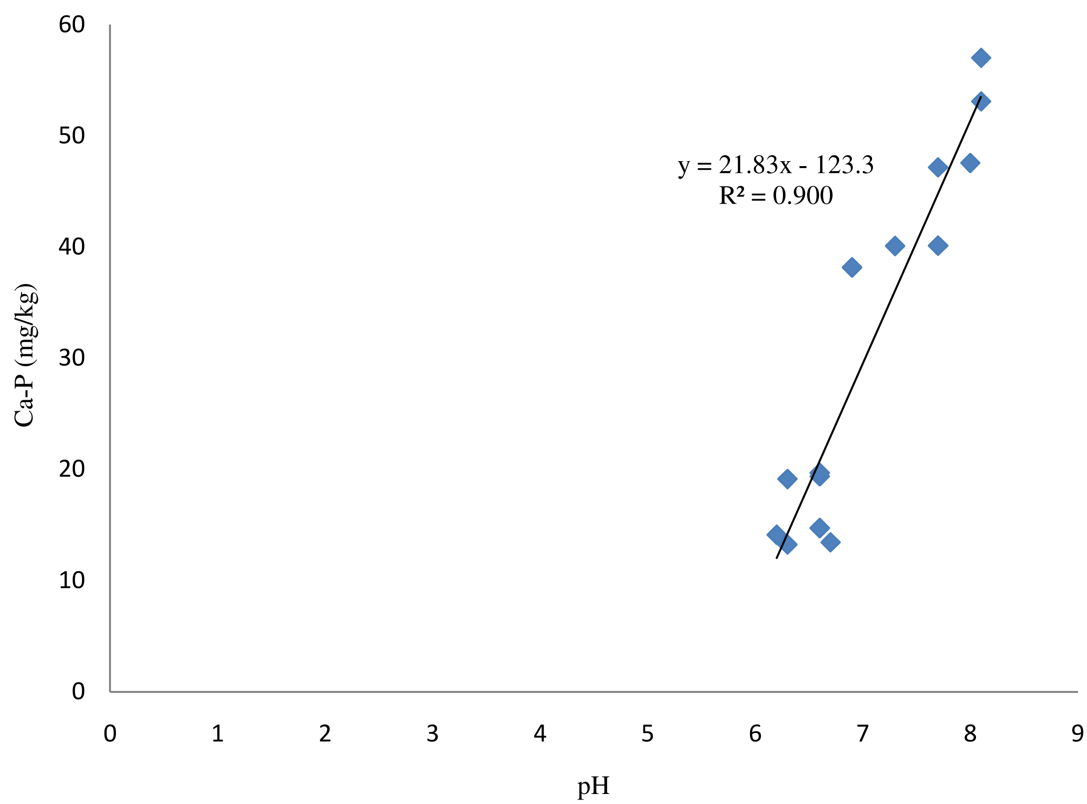


Figure- 6: Relationship between pH and Ca-P.

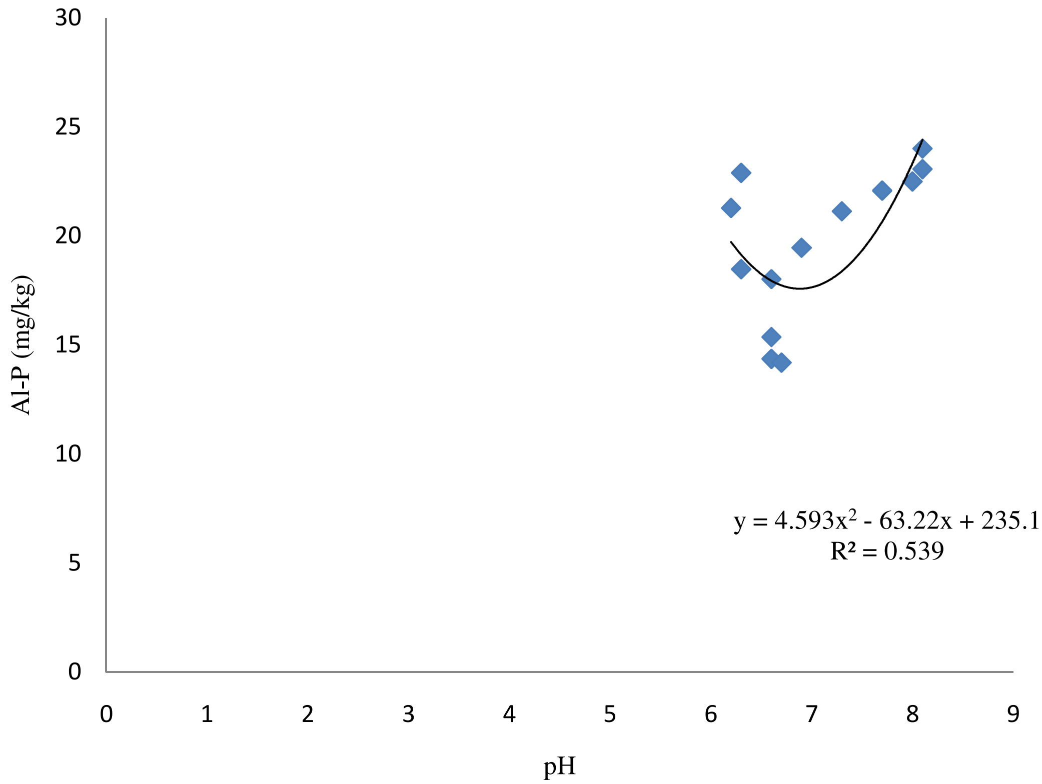


Figure-7: Relationship between pH and Al-P.

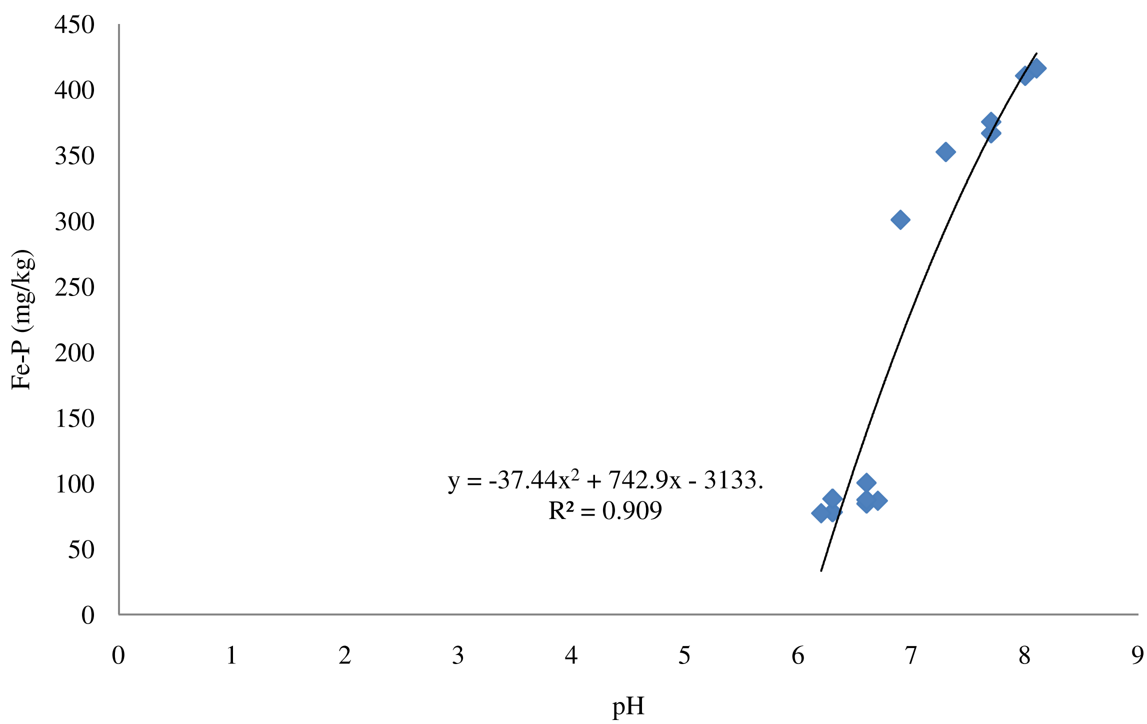


Figure-8: Relationship between pH and Fe-P.

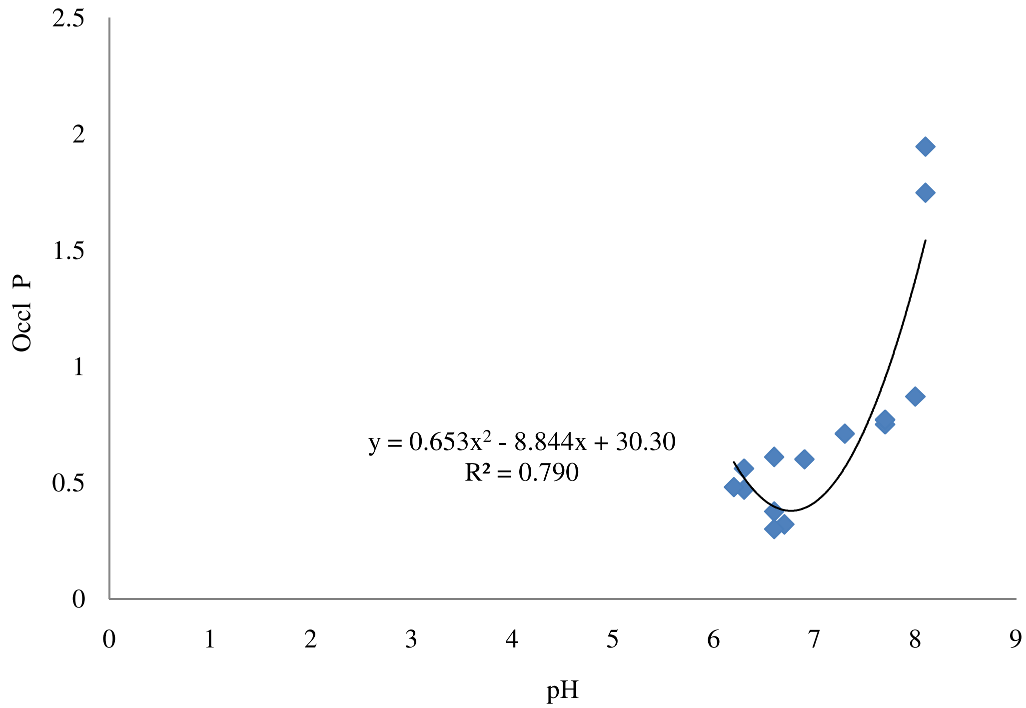


Figure-9: Relationship between pH and Occl P.

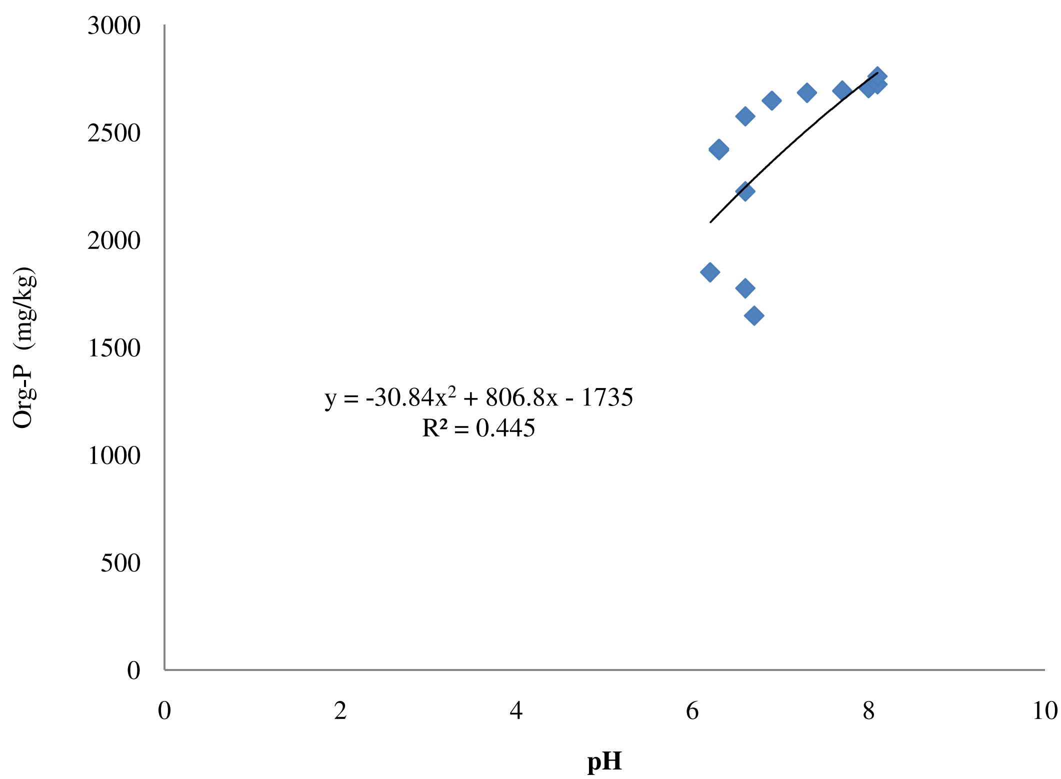


Figure-10: Relationship between pH and Org-P.

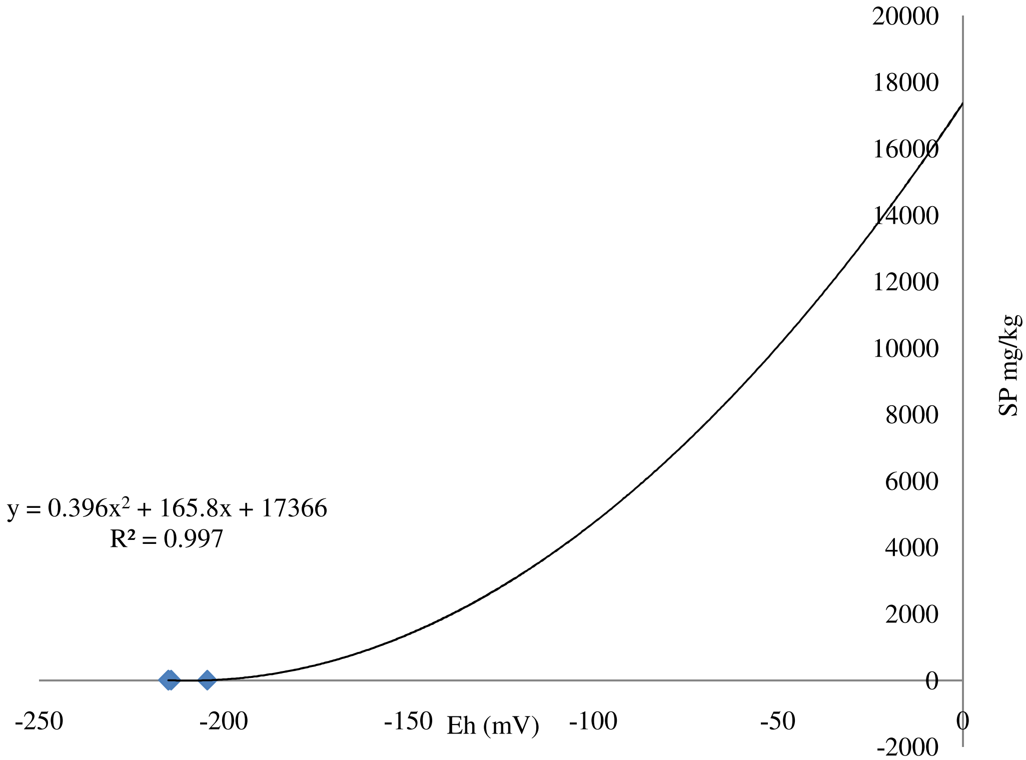


Figure-11: Relationship between Eh and SP.

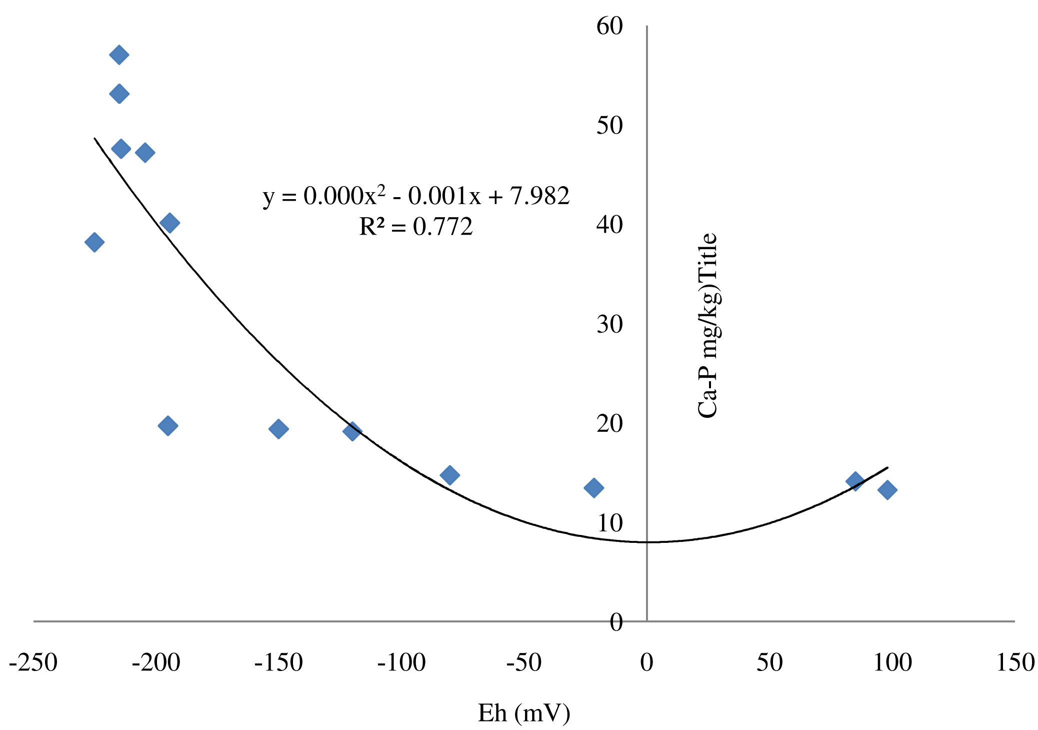


Figure-12: Relationship between Eh and Ca-P.

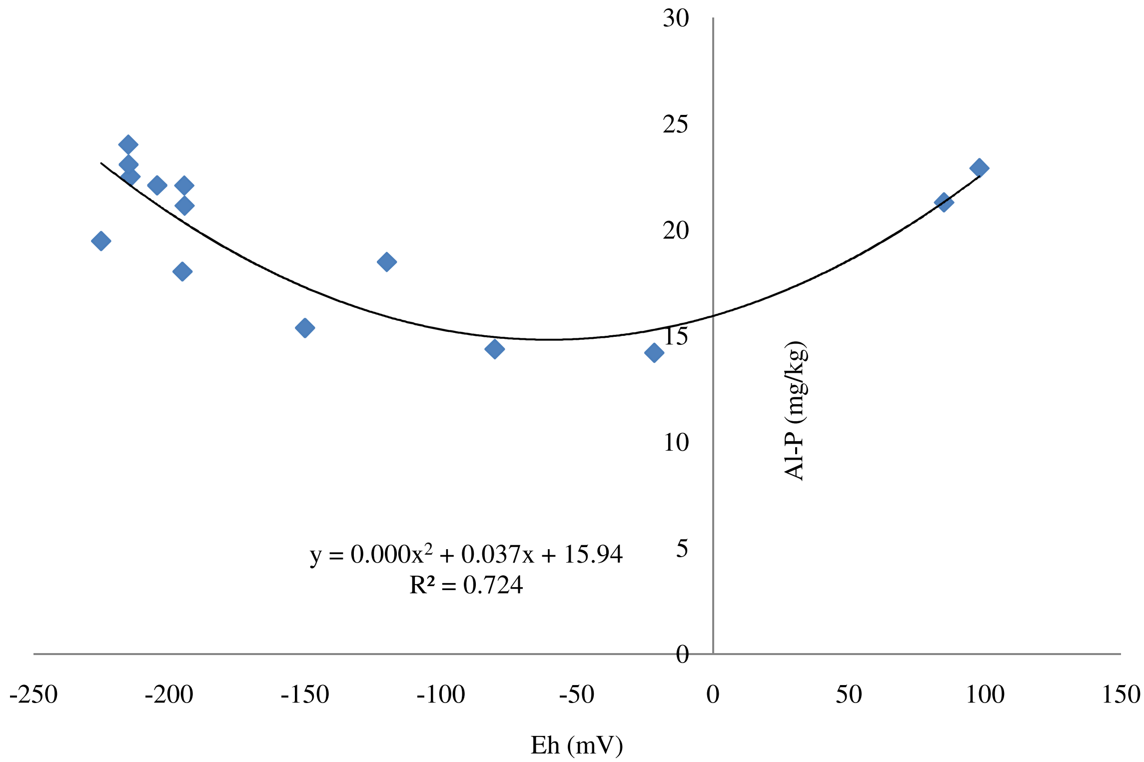


Figure-13: Relationship between Eh and Al-P.

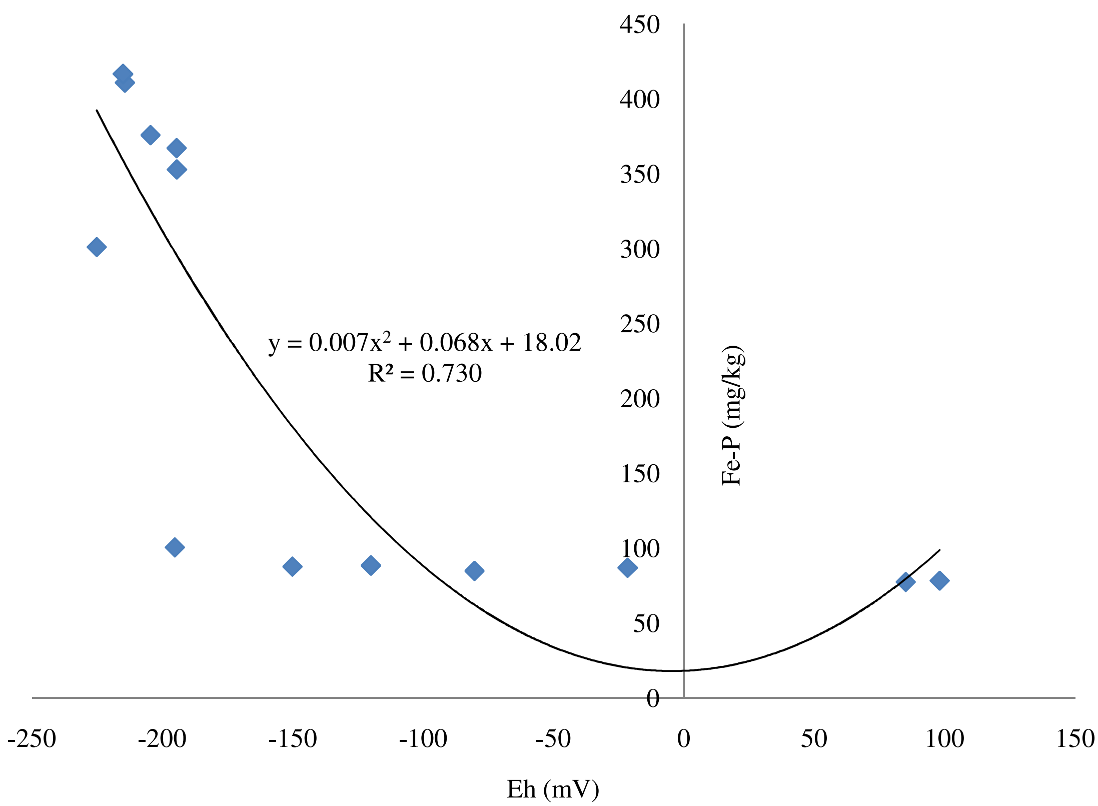


Figure-14: Relationship between Eh and Fe-P.

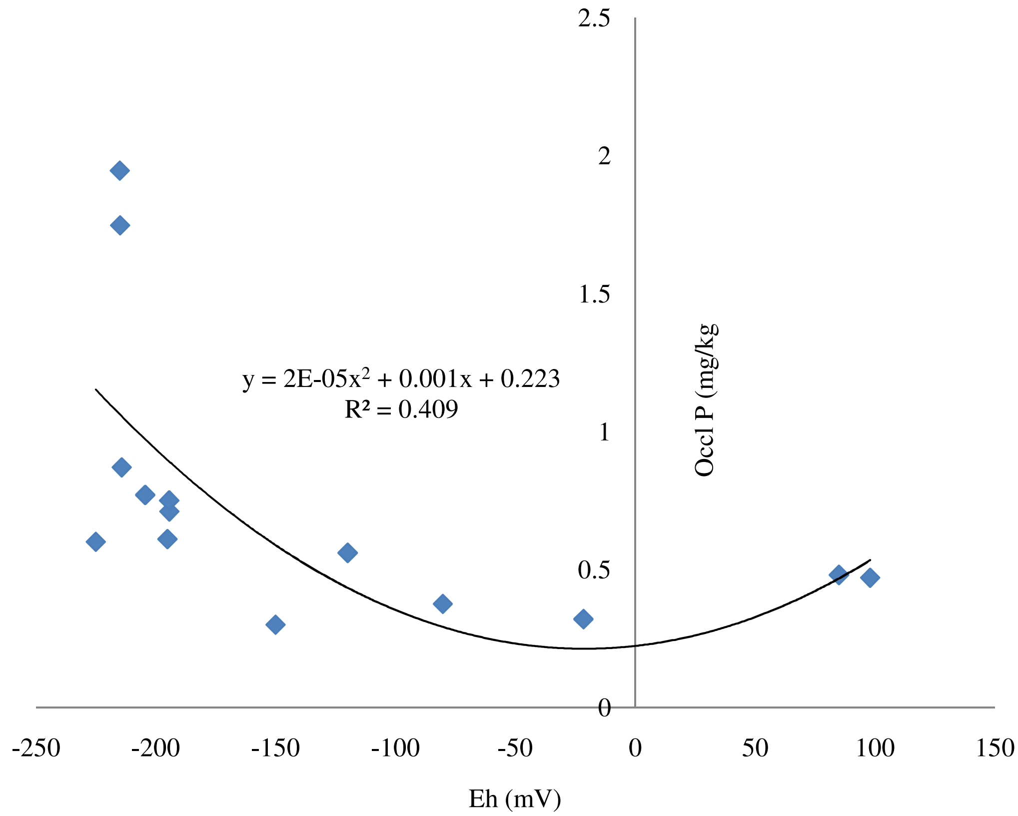


Figure-15: Relationship between Eh and Occl P.

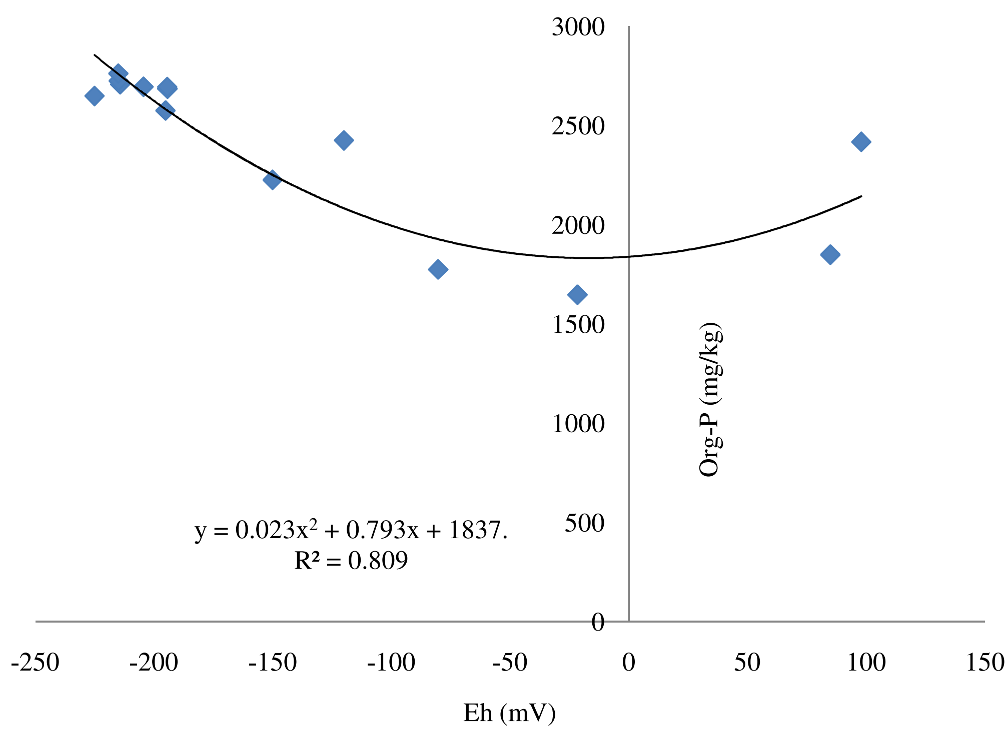


Figure-16: Relationship between Eh and Org-P.

Conclusion

P is a key factor in soil as well as in plant. In this study we described the transformation of P forms during 180 days incubation period. Total content of P ranged between 1889.3 mg/kg -3268mg/kg. Org-P was the dominant fraction due to peak rate of organic matter in the soil. In addition Fe-P was the dominant fraction between the inorganic P forms. It is due to the diminution of Fe- oxides and sulphate reduction. Furthermore, in flooded mangrove soil, P is trapped as $FePO_4$. The study suggests that all P fractions were transformed to other P pools simultaneously by complex microbial biochemical reactions. These pools in turn supplement the SP and sustain a concentration of high P in the solution of soil. Moreover it revealed the unambiguous relationship between physico chemical parameters and changes in P geochemistry in mangrove soils. In conclusion, quantifying the association between various P forms in mangrove soils is needed to realize the mangrove ecosystem in connection with human intervention.

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