



RESEARCH PAPER

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Effects of pH on release of phosphorus from rock phosphate at different temperatures against the various time intervals involved

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Abstract

This study was undertaken to deduce the supply of phosphorous-phosphates from low grade Rock phosphates in aquatic media and to ascertain the best pH range out of several pH ranges so as to apply this research further on fish growths in ponds environment. In this regard, an attempt was made to study the efficiency of phosphorus released from Rock Phosphate at various temperatures and various pH ranges, i.e., 6-7, 7-8 and 8-9. The experiments were conducted during winter and summer season for a 96 hourly and then five weeks duration period. The phosphorus released concentrations were measured spectrophotometrically by ascorbic acid method. The results incurred, from the summer as well as from the winter experiments, revealed a maximum release of phosphorus from T₄ treatments indicating that the higher pH (alkaline) range: 8-9 increased the rate of phosphorus release from Rock phosphate. The phosphate ranged between 0.06 to 0.40 mgL⁻¹ values from all treatments during the study period with the highest at high temperature during summer season. Hence, Rock phosphate enriched soils could be an alternative and cheaper source of phosphorus fertilizer to utilize low-grade Rock phosphates efficiently for enhancing fish production for alkaline soils/ waters available all over the Punjab.

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Introduction

Phosphorus is generally the most important nutrient controlling the plant growth (Rosen and White, 1999; Boyd, 2000). It is a key metabolic nutrient and its supply often regulates the productivity of natural waters (Boyd, 1982). It plays a role in photosynthesis, respiration, energy storage and transfer, cell division and enlargement and several other processes. It is necessary for skeletal formation, muscular and neural activity and is also a constituent of blood plasma. Phosphate (PO_4^{3-}) can be found as a free ion in water systems, as a salt in terrestrial environments, used in detergents as water softeners, or can be found in rock deposits.

Phosphorus occurs naturally as mineral deposits in rocks and is gradually released during natural weathering processes. Rock phosphate is the principal source of phosphorus for fertilizer manufacturing (Boyd, 2009). It is mainly cycled and sequenced through weathering, disintegration and decomposition of phosphate rocks in very small quantities in nature, then transported and deposited into aquatic systems (Chen *et al.*, 2008). The anthropogenic actions have significantly accelerated natural phosphorus cycling and intensified its mobilization resulting in its losses into water bodies and causing eutrophication of freshwater systems (Smil, 2000; Liu *et al.*, 2008; Cordell, *et al.*, 2009). The phosphate identified in these sources is referred to as inorganic phosphate because it has not been incorporated into biological tissue. Inorganic phosphate, which is typically limiting, is one of the three necessary nutrients used for primary production by terrestrial and aquatic plants. It is used in fertilizers to enhance agricultural growth and production and when introduced into aquatic systems can cause algal blooms. Its proper application poses no threats; however, its misuse and misapplication can lead to lakes pollution (Rosen and White, 1999). Soil pH greatly influences the solubility and ratio of different phosphate compounds taken up by the plants. Under high pH, hydroxide ions compete with phosphate ions for adsorption sites on iron hydroxides, thereby releasing phosphate ions into the water column (Kann, 1998).

Phosphate exchange reactions taking place between the liquid and solid phases influence the concentration of dissolved phosphate in waters having a high suspended particulate matters (Mayer *et al.*, 1980). These reactions may involve adsorption and desorption, precipitation and dissolution and they are collectively referred as phosphate "Buffering" (Frolich, 1988). These all reactions are influenced by pH. Phosphate is retained in a soil by a complex system of biological up take adsorption and mineralization the relationship between the type of clay and soil, pH is important. Soil dominated by 2:1 clays (e.g., cracking clay or versol) do not have a reactive surface and retain modest amount of phosphorus on the clay surface. In these soils pH greatly influences phosphate availability. Lower the pH causes the release of Iron and aluminum phosphate, which are insoluble compounds making phosphorus less available (Carignan and Vaithyanathan, 1999).

This study was carried out to reveal the efficiency of rock phosphate as an alternate and cheaper source of phosphorus with reference to its solubility availability at different pH levels.

Materials and methods

Experimental site

The layout and all the four phases in the research undertaken have been depicted in Table 1 & 2. The experimentation was carried out in glass aquaria placed in chemistry lab at FR&TI, Lahore. Twelve (12) glass aquaria having dimensions 1x1.8x1.25 cubic feet, each with 40L filled water capacity were used for this purpose.

Experimental layout

There were four treatments (three replicates for each treatment) for each of the four experiments with each in turn having three different pH ranges (Table 1) as follows.

All the four experiments followed the following pattern.

Phosphorous release experiments

As is evident from above tables that the investigations were carried out in two different phases i.e., during winter (at low temperature) and

summer seasons (at high temperature) to find out the efficiency of phosphorous release at different temperatures with respect to different pH ranges. The research was further segregated into two different experiments i.e., firstly an 96 hourly and secondly five weeks period experiment to find out the efficiency of phosphate release at different pH ranges against the time factor involved.

Each aquarium was added with soil up to 4 inches, which was collected from Central Fish Seed Hatchery Ponds, Manawan, Lahore. Rock Phosphate, commercially available as apatite rock, used for this purpose was obtained from District Chakwal. RP dose was constantly applied on weekly basis @ 4gm/40 liter for all four treatments. The pH was kept constant within three different pH ranges, i.e., 6-7, 7-8 and 8-9 for treatments T₂, T₃&T₄, respectively and was constantly maintained through the addition of requisite quantities of 1N HCl in T₂ and T₃ glass aquaria and of 1N NaOH in T₄ glass aquaria, respectively as per requirement. Treatment 1 was kept as control without introducing any additives for controlling pH of the medium. The concentration of total phosphate released in water was determined by the spectrophotometer model no. U2020 at 880 nm following protocols of A. P. H. A. (2012).

Table 1. Treatments Layout.

Replicates	Treatments Detail			
	T ₁ (control)	T ₂ (pH=6-7)	T ₃ (pH=7-8)	T ₄ (pH=8-9)
R ₁	T ₁ R ₁	T ₂ R ₁	T ₃ R ₁	T ₄ R ₁
R ₂	T ₁ R ₂	T ₂ R ₂	T ₃ R ₂	T ₄ R ₂
R ₃	T ₁ R ₃	T ₂ R ₃	T ₃ R ₃	T ₄ R ₃

Phase 2- Phosphate release patterns

Fig. 2 for five weeks winter experiment shows maximum increase in PO₄³⁻ release in T₄ followed by T₃, T₂ & T₁ respectively.

Phase 3- Phosphate release patterns

Fig. 3 depicts the PO₄³⁻ release over a period of 96 hours during summer days.

Physico-chemical parameters studies

Water samples from each of the glass aquaria were also monitored for physico-chemical parameters on daily/weekly basis. The pH and temperature were monitored daily by using digital meter i.e., YSI pH 100. Alkalinity and hardness were monitored on weekly basis following protocols of A.P.H.A. (2012).

Statistical analysis

The phosphate contents obtained from different treatments were compared statistically following Steel *et al.*,1996. The level of statistical significance was alpha = 0.05. The SPSS software 16 was used for statistical analysis.

Results and discussion

Phase 1- Phosphate release patterns

Fig.1 represents the winter 96 hours experiment showing an overlap of lines for all four treatments up till 48 hours. Then there is maximum increase in PO₄³⁻ release for T₃ followed by T₂ treatment, with a marked difference of PO₄³⁻ release in T₄ having very low PO₄³⁻ released and lastly the lowest release in the T₁.

As is evident from the graph that PO₄³⁻ release increases in all four treatments i.e. T₁, T₂, T₃ & T₄ within the first 24 hours and then slightly decreases over the next 72 hours and finally all comes to a stable position/constant up till 96 hours. The maximum PO₄³⁻ release is from T₄ having pH 8-9, secondly, from T₃ (pH 7-8), then from the control T₁ (pH 7) and lastly from T₂ (pH 6-7) respectively.

Table 2. Experimental pattern.

	Phases	Time Period	Treatments
1 st	Winter hours	96 hours	T ₁ , T ₂ , T ₃ , T ₄
2 nd	Winter season	Five weeks	T ₁ , T ₂ , T ₃ , T ₄
3 rd	Summer hours	96 hours	T ₁ , T ₂ , T ₃ , T ₄
4 th	Summer season	Five weeks	T ₁ , T ₂ , T ₃ , T ₄

Phase 4- Phosphate release patterns

Fig.4 represents the five weeks summer experiment. In this case, the maximum PO₄³⁻ release is in T₁ followed by T₃, T₁ and T₂ respectively which correlates completely with the summer hour's experiment following the same sequence/pattern.

Phase 1 & 3 (Winter and Summer hours) comparison

However, it is worth mentioning that by comparing Fig. 1 & 3, it is revealed that there is maximum PO₄³⁻ release in T₄ treatment for summer hours and minimum in T₂ treatment while for winter hours experiment maximum in T₃ treatment and minimum in T₁. However, T₄ while placed in the 3rd position shows maximum release of PO₄³⁻ with the passage of time.

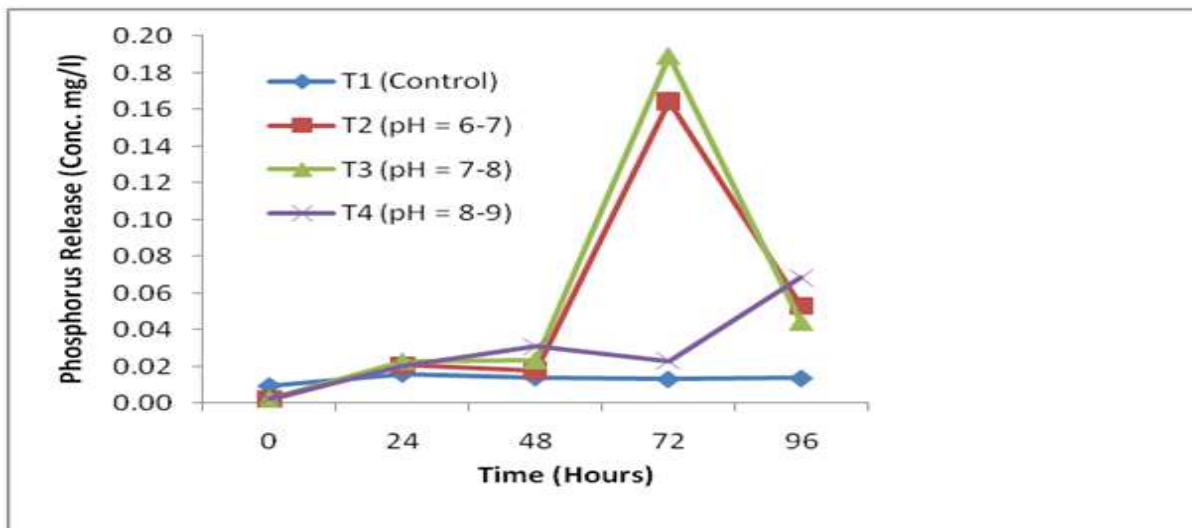


Fig. 1. Winter 96 hours experiment.

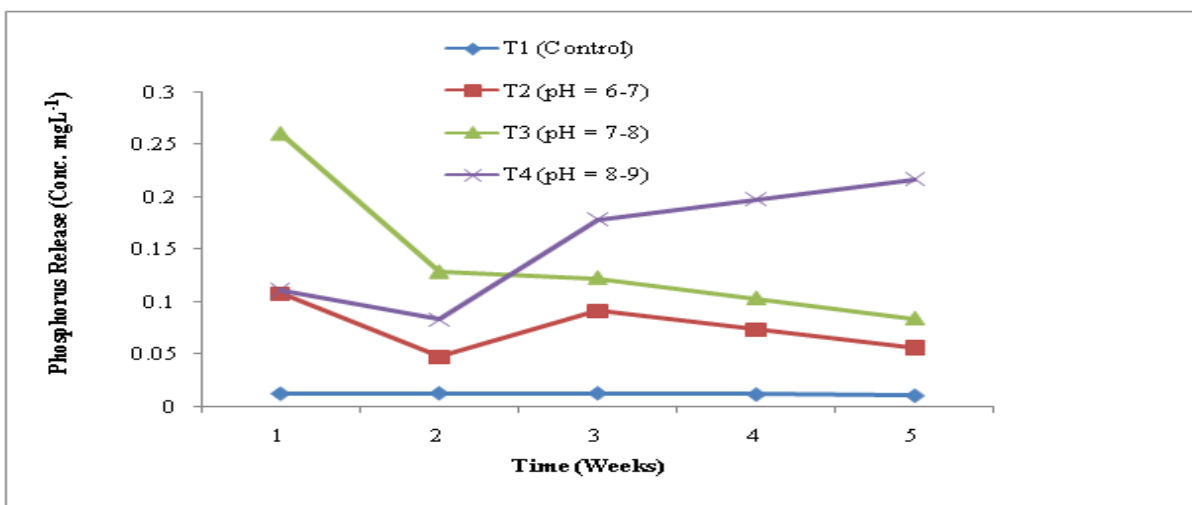


Fig. 2. Winter weeks experiment

Phase 2 & 4 (Winter and Summer weeks) comparison

Comparing Fig.2 with Fig.4 for summer and winter weeks indicates almost the same pattern in release of PO_4^{3-} during winter experiment except only for T_2 & T_1 which are vice versa in results. T_4 is maximum (0.22 mgL^{-1} in winter and 0.37 mgL^{-1} in summer) in both five weeks experiments.

The overall result by considering all the four experiment i.e. 96 hours summer and winter experiments and one month during summer and winter experiments indicates the following pattern for PO_4^{3-} release by rock phosphate.

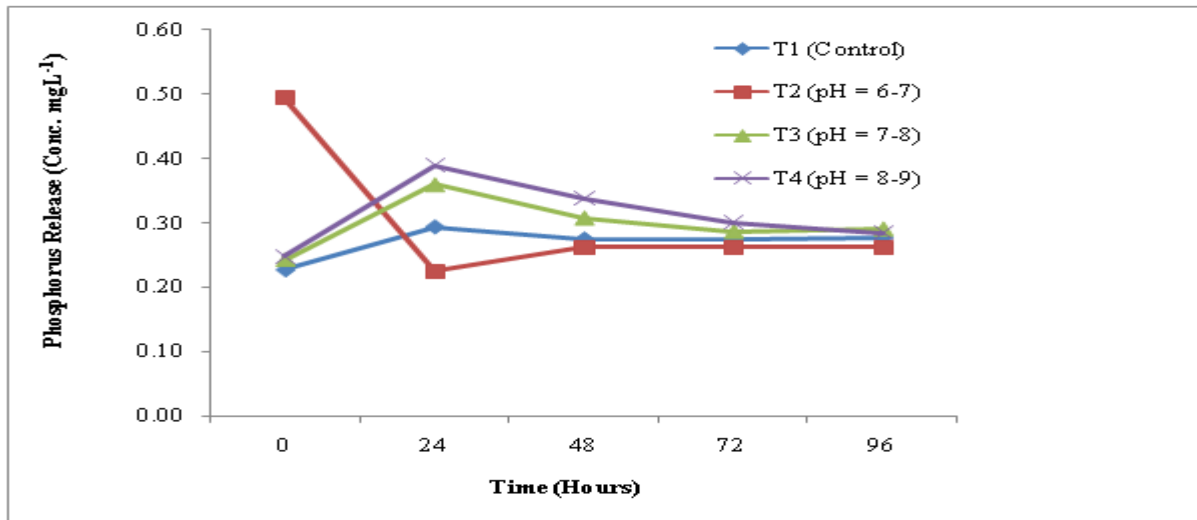


Fig. 3. Summer 96 hours experiment.

Phase 1 & 2 (Winter hours and weeks) comparison

On comparison of both Fig.1 with 2 for winter hours and weeks, it is revealed that in this case pattern is not the same i.e., $T_3 > T_2 > T_4 > T_1$ and

$T_4 > T_3 > T_2 > T_1$, respectively. Moreover, the results showed that due to low temperature release of phosphorus was less as compared to release of phosphorus at high temperature.

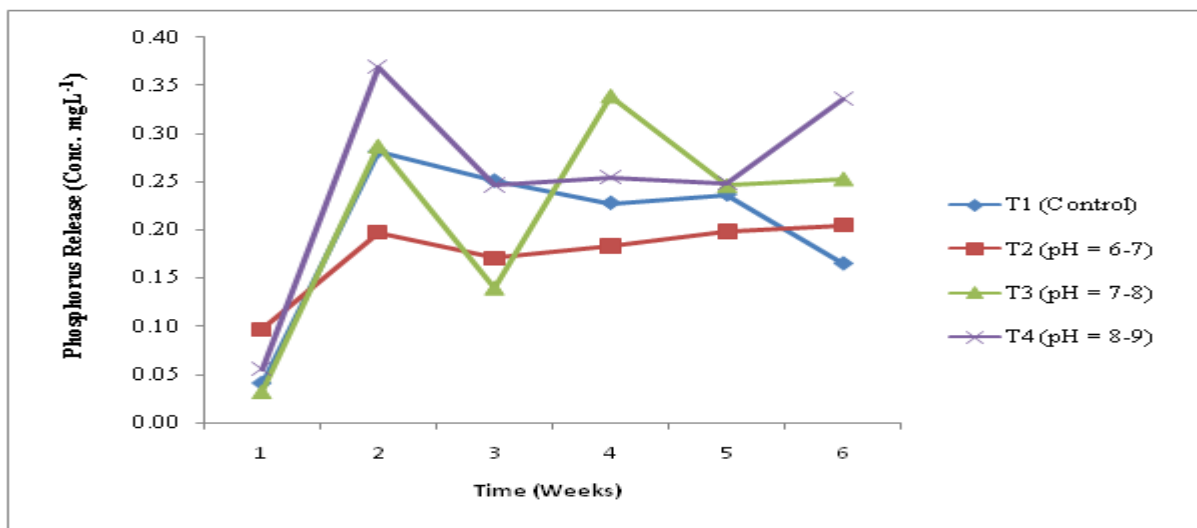


Fig. 4. Summer weeks experiment.

Phase 3 & 4 (Summer hours and weeks) comparison

On comparison of both Fig.3 with Fig.4 for summer hours and weeks, it is revealed that there is 100% correlation between the results

i.e., T_4 being maximum is followed by T_3 , T_1 & T_2 , respectively. Similarly, the higher the temperature factor, higher was the PO_4^{3-} release in summer.

Physico-chemical results

Fig 5 and 6 shows the physico-chemical parameters comparison in both winter and summer studies. It is evident from both phases that all the parameters

remained within the suitable ranges though the final results were always a bit higher than the initial values. Moreover, all the individual parameters in all the treatments did not differ appreciably.

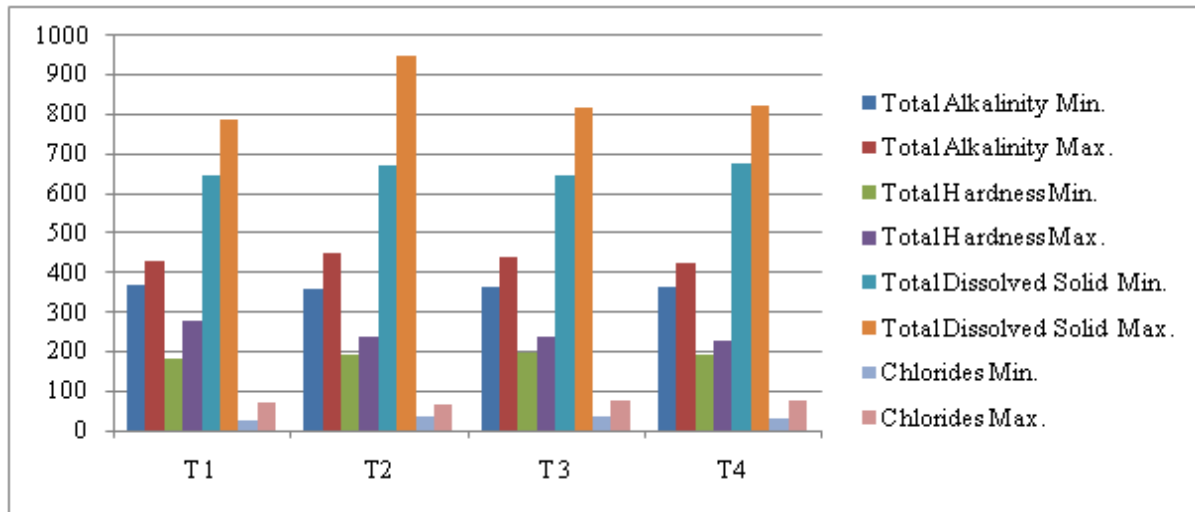


Fig. 5. Winter results.

The study revealed that addition of low-grade rock phosphate helped to enhance the mobilization of unavailable phosphorus in rock phosphate to available forms of phosphorus which in turn helped in supplying phosphorus to the experimental aqua-medium. The critical examination of the data obtained from T₁ & T₂ experiments having pH range nearly 7 and 6-7, respectively showed that there was no significant release of phosphorus in these aquaria both at low and high temperatures with only few exceptions. It can also be concluded from the above mentioned results that maximum PO₄³⁻ release from RP was at the pH range 8-9 followed by pH 7-8.

Phase1	T ₄ >T ₃ >T ₁ >T ₂
Phase2	T ₃ >T ₂ >T ₄ >T ₁
Phase3	T ₄ >T ₃ >T ₁ >T ₂
Phase4	T ₄ >T ₃ >T ₂ >T ₁

During the investigation it was revealed that the higher the temperature factor, higher was the PO₄³⁻ release as is evident from Figure 1 and 3. Furthermore, the results inferred from the time factor favored the pH range 8-9 for maximum release of PO₄³⁻ from RP. The phosphate levels for T₄ were always higher with values

ranging from 0.06 to 0.33 mgL⁻¹ and appreciably lower in the T₁ control series of water with values ranging from 0.01 to 0.04 mg L⁻¹ in glass Aquaria.

Our studies are in accordance with the research of Chakrabarty, 2007 who proved that sedimentary phosphate rock is environment friendly fertilizer, cheap fertilizer and can be used as a direct application in fish farming ponds. He showed that MPR, a Carbonate apatite is more responsive to natural dissolution than PPR, a fluorapatite being identified through X- ray diffraction studies. Jana and Sahu, 1994 research is also in accordance with our experiments that utilized Rock Phosphate in Carp Culture and found it very beneficial.

Thus, addition of Rock phosphate could be an alternative and viable technology to utilize low-grade RPs efficiently and could be used successfully as a cheaper source of phosphorus fertilizer for fertilizing fish water ponds for enhancing fish production for alkaline soils/waters available all over the Punjab in place of costly water soluble phosphorus like traditionally used commercial phosphate fertilizers sources i.e., DAP, SSP and NP, etc.

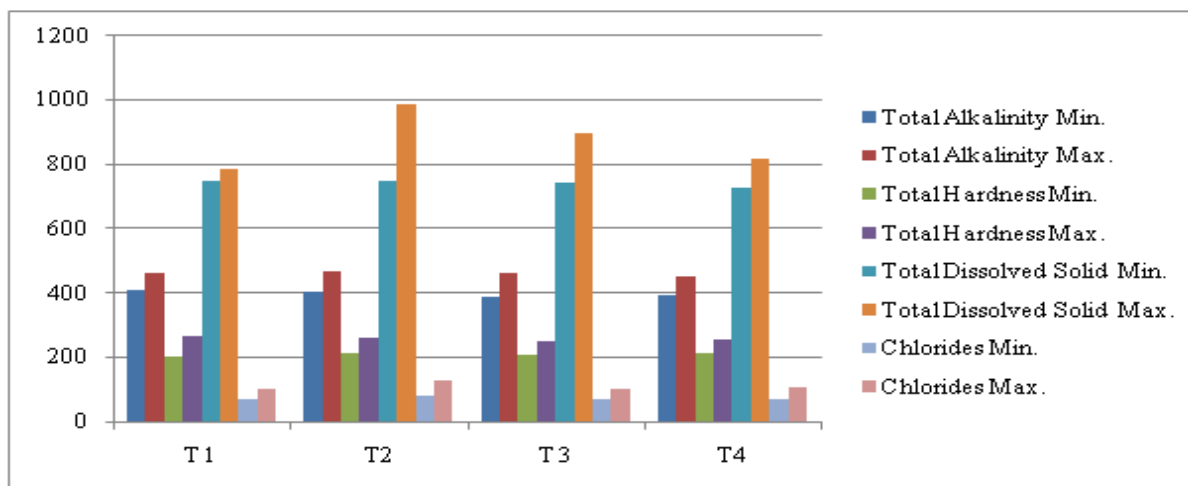


Fig. 6. Summer results.

Conclusion

The inferred results favored the alkaline pH range 8-9 for maximum release of PO_4^{3-} from RP as compared to the neutral and acidic ranges. Furthermore, the research concluded that low-grade Rock Phosphate released phosphates at higher levels as the temperature factor was increased since the phosphate release levels for summer hours and weeks were always higher with values maximum at 0.37 & 0.40 mgL^{-1} in comparison with winter hours and weeks at 0.20 & 0.25 mgL^{-1} while appreciably lower release was observed in the control series of water with values ranging only from 0.01 to 0.04 mg L^{-1} .

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