Chapter 1

Introduction

Imagine a day without petrol in a petrol pump next to your house or without electricity supply from a coal-fired thermal power station. It would be hard and even harder would be a day without food. According to UN, currently there are over 800 million people without sufficient access to food (UN, 2005), raising a fundamental question about food security. Food security, as defined by FAO, exists when all people, at all times, have access to sufficient, safe and nutritious food to meet dietary needs for an active and healthy life (FAO, 2005b). Although it is an issue subjected to myriad variabilities, one thing that remains crucial for ensuring the agricultural prosperity both in terms of quality and quantity is phosphorus.

Water and energy will always remain critical for meeting the future food grain demand but the quantitative enrichment has been achieved only through application of fertilizers supplying nitrogen and phosphorus to crops. Although these nutrients are essential for the growth of plants and for a higher crop yield, phosphorus is particularly important for root (both lateral roots and fibrous rootlets) growth and for strengthening tissues found in stems or stalks. The advantage with nitrogen is that it can be fixed from atmosphere through chemical and biological means but phosphorus remains limiting as it is to be supplied only from roots through soils. As the soils of India are thought to be generally P deficient (FAI, 1989), its limitation bears even harsh consequences, leaving only fertilizer application as the only source of P to the plants.

The reasons for the P deficiency in soil are many (Brady and Weil, 2002), as described further. Firstly, the total P level in soils is low, which is no more than $\frac{1}{10^6}$ to $\frac{1}{4}$ of N, $\frac{1}{20}$ of K in upper 15 cm of soil. Secondly, P compounds commonly found in soils are not available for plant uptake as they are highly insoluble. Thirdly, even when available forms are added to the soil they readily change to insoluble unavailable forms. This fixation reaction allows only 10-15% of the P applied to be absorbed by the plants. Also, phosphorus is not easily lost from the soil in gaseous form because soluble inorganic forms are readily absorbed by the mineral surfaces.

The prime source of phosphorus in fertilizers is rocks rich in phosphates. About 90% of the world wide demand for rock phosphate is for food production (Smil, 2002;
USGS, 2008) through fertilisers. The rock phosphates have been used as external source of P since the beginning of the 20th century. The existing rate of population growth and the increasing food demand exerts immense pressure on the phosphate rock reserves. With the present rate of consumption the current rock phosphate reserves are expected to last for another 50-100 years (Steen, 1998; Smil, 2000b; Gunther, 1997). Since the time of commercial exploitation of rock phosphates for the production of fertilizers, i.e. in the middle of 19th century, USA has been the world’s largest producer of phosphate rock (Smil, 2000b). According to a survey by USGS in 2005, the present remaining reserves are with China (17%), USA (27%), and Morocco (17%) (Soon, 2008).

The demand will continue to increase for the developing world in the time to come whereas the agricultural soils in developed countries have already crossed the ‘critical’ levels of P and require only lighter applications (Cordell, 2009). Also the soils are naturally low in P in the developing countries like India and Africa and are subjected to over application of P fertilizers resulting in its accumulation in soils and water bodies leading to eutrophication (Steen, 1998; Gunther, 1997). With about 55% of the phosphorus being lost between ‘farm and fork’ (Smil, 2000a), five times more phosphorus is mined than what is actually consumed by the humans in food. This further enhances the threat to a sustainable use of phosphate rock. An important issue concerning the extraction of phosphate from open land mining is that some of the natural phosphate rocks have elevated concentrations of Cd, As, and certain radionuclides, especially the high concentration of Cd in sedimentary phosphates (Mortvedt & Beaton, 1996). Furthermore, the processing of phosphate rocks require large amount of water, acids and in turn produces large amount of mineral residues in the sands and clays (Straaten, 2008).

Phosphorus is important because it is required by all living organisms in quantities, large or small. The very presence and indispensable nature of P for life sustaining processes make it all the more essential. Phosphoglycerate molecule trapping carbon in Calvin cycle, structural components like phospholipids in cell membrane, hydroxyapatite in bones, with fluoride in teeth (Ruttenberg, 2007), as energy transfer medium in high energy bonds in Adenosine Triphospahte (ATP) (Corbridge, 1990), as genetic material in double helix DNA structure, are just a few examples to substantiate
its importance for life sustaining processes. No wonder, approximately 1% of human body is P by weight corresponding to about 650 g of phosphorus or 1500 g of P₂O₅; 86% of which is in bones and teeth (Slansky, 1980). Therefore, for the optimum utilization of resources and reserves, understanding natural existence and cycling of P is essential, particularly, the interaction between geological and biological systems for P transformations.

1.1. Phosphorus in nature

Phosphorus with atomic number 15 and atomic weight 31 is the tenth most abundant element on earth with an average crustal abundance of 0.1%. (Nriagu and Moore, 1984; Slansky, 1986). Like other essential nutrients, P cycles itself in nature, but differing from biogeochemical cycles of C, N and S in many ways. For C, N and S cycles, the gaseous phase is the main component and atmosphere is one of the major reservoirs while for the P, the existence of gaseous phase is minimal and P containing rocks are the major reservoirs making the phosphorus cycle geological in nature (Fig. 1.1). Table 1.1 gives distribution of phosphorus concentration amongst the major reservoirs.

Table 1.1: Major reservoirs active in the global phosphorus cycle (after Ruttenberg, 2008).

<table>
<thead>
<tr>
<th>Reservoir description</th>
<th>Reservoir size Moles P X 10¹²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sediments (Crustal rocks and soil&gt;60 cm deep and marine sediments)</td>
<td>0.27 x 10⁻⁸ - 1.3 x 10⁰</td>
</tr>
<tr>
<td>Land (total soil&lt;60 cm deep: organic+ inorganic)</td>
<td>3,100-6,450</td>
</tr>
<tr>
<td>Land biota</td>
<td>83.9-96.8</td>
</tr>
<tr>
<td>Surface Ocean (total dissolved phosphorus)</td>
<td>87.4</td>
</tr>
<tr>
<td>Deep sea (total dissolved phosphorus)</td>
<td>2,810</td>
</tr>
<tr>
<td>Oceanic biota</td>
<td>1.61-4.45</td>
</tr>
<tr>
<td>Minable phosphorus</td>
<td>323-645</td>
</tr>
<tr>
<td>Atmospheric phosphorus</td>
<td>0.0009</td>
</tr>
</tbody>
</table>

P is most commonly found in +V oxidation state in combination with oxygen as [PO₄]³⁻ ion. The oxidation and reduction reactions play a minor role in controlling the reactivity and distribution of P in the environment. Nearly all dissolved and particulate forms of P are combined, complexed or slightly modified form of this ion (Jahnke, 2000). When compared with other biogeochemical cycles, the time taken for one complete phosphorus cycle is very long, and in the order of 120 Giga years (Gy)
(Slansky, 1980). It is this long duration of cycling that makes the flow of phosphorus unidirectional from rock phosphates to the ocean for all practical purposes, making phosphate reserve a non-renewable resource of importance, nothing less than that of petroleum. During its movement from land to the ocean P undergoes biogeochemical transformations and fractionation, binding/unbinding before finally settling down with sediments on the ocean floor.

Figure 1.1: Diagrammatic representation of Phosphorus cycle. Source: Ruttenberg 2008.

The flow of phosphorus in nature can be described in many ways; based on its chemical speciation as organic and inorganic (Martens & Rotman, 1999), or on the components of environment involved in cycling as terrestrial, aquatic and oceanic (Jahnke, 2000), or the natural environmental processes phosphorus undergoes, like tectonic uplift of P bearing rock and exposure to weathering, riverine transport to lakes and oceans, sedimentation and uplift of sediments into the weathering regime. The cycle
begins afresh with the exposure of sediments to the weathering regime (Ruttenberg, 2007). The phosphorus cycle also can conveniently be explained and divided based on the major processes influencing its distribution and fractionation in different phases that make P available or non-available to life forms in all the spheres of environment. Such processes include a. physical and chemical weathering of P containing rocks, b. fractionation of phosphorus leading to incorporation of P into terrestrial biomass and its return to the soil system, c. movement through the aquatic system (lakes and rivers) in particulate and dissolved form to the oceans and d. the circulation of P within the ocean constituting the marine P cycle.

1.2. Weathering and phosphorus cycling
The only natural process that makes phosphorus available for the terrestrial ecosystems including humans is the weathering of phosphate minerals in the rocks. In the mineral form, P is primarily found in combination with Ca in the mineral known as apatite (Table 1.2). Apatite accounts up to 95% of the total P on earth (Jahnke, 2000). Most of the phosphate deposits found in nature are sedimentary in origin and provide 82% of the world's phosphate production and 95% of the remaining reserves (Howard, 1979). The major sedimentary deposits are marine in origin with the authigenic apatite being primarily formed by the organic material at the sea floor (Follmi, 1996). The other minor reserves include the guano deposits, the droppings of seabirds, bats and seals. Weathering accounts for the link connecting phosphorites (apatite rich sedimentary rocks) with soil and mantle derived rocks (Trudinger and Swaine, 1979).

Table 1.2: The chemistry of apatite minerals (after Jahnke, 2000).

<table>
<thead>
<tr>
<th>General formula: Ca₁₀(PO₄)₆X₂</th>
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<tbody>
<tr>
<td>X= F: Fluorapatite</td>
</tr>
<tr>
<td>OH: Hydroxyapatite</td>
</tr>
<tr>
<td>Cl: Chlorapatite</td>
</tr>
<tr>
<td>Possible substitute for Ca⁺⁺: Na⁺, K⁺, Ag⁺, Sr²⁺, Mn³⁺, Mg²⁺, Zn²⁺, Cd²⁺, Ba²⁺, Sc³⁺, Y³⁺, rare earth elements, Bi³⁺, U⁴⁺</td>
</tr>
<tr>
<td>Possible substitutes for PO₄³⁻: CO₃²⁻, SO₄²⁻, CrO₄²⁻, AsO₄³⁻, F⁻, CO₂⁻, OH⁻, CO₃⁻, SiO₄⁻²</td>
</tr>
<tr>
<td>Phosphate minerals like vivianite, Fe₃(PO₄)₂·H₂O and struvite NH₄MgPO₄·6H₂O are also known to be formed in sediments under different conditions.</td>
</tr>
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</table>

Weathering makes the bulk unavailable P (apatite) locked up in bedrock in the form of dissolved phosphate (Nezat et al, 2007) available for biological systems. The
availability of phosphorus in biomass production is mediated by micro organisms in soils and sediments.

The reaction for weathering of apatite occurring in nature is as follows:

$$\text{Ca}_5(\text{PO}_4)_3\text{OH} + 4\text{CO}_2 + 3\text{H}_2\text{O} \rightarrow 5 \text{Ca}^{2+} + 3\text{HPO}_4^{2-} + 4\text{HCO}_3^-$$

Terrestrial plants take up this solubilised phosphorus which circulates thereafter in the living system by the decomposition of organic matter. During this process, a part of the solid phase P released during weathering goes into the bioreactive phase in the terrestrial cycles and it is this form that dominates in the later stages of soil development. The process of soil stabilization prevents the loss of P from the system (Filippelli and Souch, 1999).

The conversion of the unavailable form to available one occurs on a scale of thousands of years. The systematic partitioning and changes that occur in the forms of P during rock weathering and soil development is very well explained in a model by Walker and Syers in 1976 (Fig. 1.2).

Based on the model, describing the fractionation of P in a weathering profile/soil development process, namely the occluded, non-occluded and organic fractions were distinctly recognized and have been described by different authors (Nezat et al, 2007; Turner, 2008). According to Filippelli (2002), P bound to Fe and Mn

![Figure 1.2: The mobilisation and transformation of phosphorus in a soil development profile. (Walkers and Syers, 1976).](image)
oxyhydroxides is rendered occluded or non available because of their large surface area and the overall positive charge while Ruttenberg (2008) refers to phosphorus present within the mineral matrix of discrete mineral phases as occluded one and the available fraction as the phosphate sorbed to surfaces of hydrous oxides of iron and aluminium and calcium carbonate. On the other hand Filippelli (2008) described the available or the non occluded fraction as the P in pore spaces as dissolved phosphate ion, adsorbed onto soil particles, and the P in the soil organic matter. The third important fraction is the organic fraction which is the P absorbed by the terrestrial plants and is bound to different biochemicals used for life sustaining processes. To comprehend, the fate of phosphorus during soil formation can be viewed as the progressive dissolution of primary phosphorus mineral (dominantly apatite) some of which is lost in leaching (decrease in total P) and some of which is reincorporated into non-occluded, occluded and organic fractions within the soil (Ruttenberg, 2007).

According to the Walkers and Syers (1976) model, the initial build up in organic P results from organic matter return to soil from vegetation supported by the soil. The subsequent decline in P organic is due to progressive mineralization and soil leaching. The time scale over which these transformations occur depends upon the initial soil composition, topographic and climatic factors.

1.3. Terrestrial phosphorus cycle

The importance of phosphorus as a productivity determining nutrient in the ecosystem development is described in various studies (Stevens and Walker, 1970; Walker and Syers, 1976; Schindler, 1977; Vitousek et al. 1993; Schimel et al., 1994; Herbert and Fownes, 1995; Parfitt et al, 2005). At any point of time, the quantity and availability of nutrients determine the plant productivity and other aspects of ecosystem.

New soils and ecosystems are generally rich in rock derived nutrients such as Ca, Mg, K and P, their growth is limited by the atmospherically generated nutrients like N and C. In the long term, they become rich/ or adapt with some atmospheric nutrient fixing mechanisms and geologically derived nutrients like P, becomes limiting (Chadwick et al. 1999). The total P is usually low in weathered and leached soils. In new or freshly formed soils the highest value is associated with the parent material formed from igneous rocks and soils with high organic matter content (Soon, 2008).
The quantity and availability of nutrients in soil also control plant productivity and other aspects of ecosystem functioning.

The average concentration of P in soil is 0.09% (Nezat et al, 2007) or 380-1330 mg/Kg in upper 15 cm of soil (Soon, 2008), and the amount of P available to plants from soil solution is even smaller, which is not more than 0.01% of the total soil P. As phosphorus fractionates itself in a soil system, the availability of P for uptake depends on the form it is present in the soil solution. In the terrestrial ecosystems, plant roots absorb P dissolved in soil solution as phosphate ions ($\text{HPO}_4^{2-}$ and $\text{H}_2\text{PO}_4^-$) and some soluble organic compounds are taken up. The chemical species available for uptake is determined by the pH of the solution. The phosphorus after entering the biological system pathway is being recycled over and over again because of its limiting nature and the conservative strategy adopted by the plants (Fig. 1.3). In the life system it is present in fundamental biochemicals required for life sustaining processes signifying a close connection between P cycle and biological processes. The exchange of phosphorus between Biota and soils occur over a relatively shorter timescale of 13 years, with the average residence time of phosphorus in soils being 600 years (Filippelli, 2009).

As suggested by Brady and Weil (2002) the bulk of soil P exists in three major forms: a) Organic P bound in active, slow and passive organic fraction, b) Ca bound inorganic phosphorus and c) Fe/Al bound inorganic P. In warm, humid and sub humid climates there is extensive weathering leading to lower availability of P due to its association with Fe and Al. Erosion tends to transport mainly the clay and organic matter fractions of the soil, that are rich in phosphorus, such that eroded material is often rich in phosphorus than the original soil. In surface soil horizons Organic P constitutes 20-80% of the total P, while the deeper horizons may have large amount of inorganic P especially in arid and semi-arid regions.

The limiting nature of P in terrestrial ecosystems is attributed primarily to two phenomenon controlling the concentration and mobility of P in soil. The first is the solubility of phosphorus containing minerals and secondly the fixation or adsorption of phosphate ions on the surface soil particles (Brady and Weil, 2002).
When the soluble phosphorus is added to the soil in the form of fertilisers, a rapid reaction removes phosphorus or it is fixed in the matter of first few hours. The Phosphorus fixation reactions is a series of reactions that tend to remove phosphate ions from the soil solution and produce P compounds of lesser and lesser solubility. These reactions occur in a stepwise manner leading to decrease in availability with time. Beginning with the “precipitation” reaction where the phosphate ions are loosely bound to other ions and are readily available for uptake. The second step is the “Anion Exchange Reactions” (outer sphere) where \((\text{H}_2\text{PO}_4^-)\) may be attracted to the positive charges under acidic conditions on the surface of Fe and Al oxides and the broken edges of kaolinite clays (Fig. 1.4). They form outer sphere complexes and are subjected to the exchanges by other anions. Since this is reversible, phosphate ions may be available for the uptake by plants. With time, formation of “Inner sphere complex” occurs where the phosphate ion may also replace a structural hydroxyl to form an inner sphere complex with the oxide or clay surface. The binding is very tight and the availability of such P is
very low (Froelich et al, 1988). The last step that renders P completely unavailable under normal conditions is the formation of “binuclear bridge”. Over time, in the above mentioned reaction, second oxygen in phosphate ion may replace a second hydroxyl so that the phosphate is bound to two adjacent Al. And as more time passes phosphate is buried deeper and deeper inside the molecule and is occluded to be not taken up by the plants. The remaining P continues to get less and less soluble.

To tackle with lower soil P concentrations, plants adopt different physiological strategies like increasing root volume and surface area, secretion of chelating agents by the roots and the associated fungi. Plants also conserve P by resorption of P during senescence and the efficient recycling mechanism from the litter decomposition (Trudinger and Swaine, 1979).

**Figure 1.4**: Different reactions by which phosphorus becomes occluded i.e. removed from soil solution and fixed by reaction with Fe and Al in various hydroxides. (Source: Brady and Weil, 2002).
1.4. Phosphorus in aquatic systems
There are three routes by which phosphate migrates from terrestrial zone to hydrosphere, i.e. mainly lake or river; 1) leaching of soils 2) soil erosion and 3) harvesting of crops (through waste water) (Martens and Rotmans, 1999). The behaviour of phosphorus differs in lacustrine and river systems due to their stagnant and fluvial nature respectively. Figure 1.5 gives the transformation processes in the terrestrial and aquatic ecosystems.

1.4.a. Rivers
Rivers act as the most important carrier of P from continent to the oceans. Apart from being a transportation medium, they make into themselves a complete ecosystem wherein a lot of transformations occur having an impact on the bioavailability and biological productivity of the flood plain coming on its way. Weathering of continental rocks is the main source of P to rivers and it controls the sediment load and the dissolved load of P in rivers (Meybeck, 1987).

Figure 1.5: Phosphorus transformations during transfer form terrestrial to aquatic ecosystems (after Tiessen, 1996).

The transfer of P from terrestrial to aquatic ecosystems can occur in soluble and particulate forms (Froelich, 1982). Jahnke (2000) gives an approximation of the fractions in which the P is mobilized and released where he suggested that around 5% of the mobilized P is in the dissolved form, readily available to enter the biological
system while a majority (95%) of P in rivers remains in the particulate form, with approximately 40% in the organic phases and the remainder in the mineral lattices of the particulate matter or sorbed particle surfaces such as FeOOH, coating mineral grains or as colloids. Much of the P is transported in this manner to the estuaries and to the oceans without ever being entering the biological systems. (Conley et al., 1995; Chambers et al., 1995). The chemical form of phosphorus associated with riverine particles is variable and depends upon the geology of drainage basin, extent of weathering of substrate and on the nature of river itself. Data suggests that 20-40% of P in suspended particulate matter is organic and inorganic forms are mainly partitioned between ferric oxyhydroxides and apatite. (Bluth and Kump, 1991; 1994, Berner & Rao, 1994; Lebo, 1991).

The soluble phosphorus (SP) consists of inorganic orthophosphate, soluble reactive phosphorus (SRP) and organic phosphorus compounds and complexes, soluble organic complexes (SOP) (Tiessen, 1996). Because of high particle reactivity of Phosphorus, almost 90% of the P in rivers is in particulate form and sorption being the primary process holding it (Froelich et al., 1988). The Particulate phosphorus (PP) consists of all primary and secondary mineral P forms and organic phosphorus which includes P sorbed by mineral and organic particle eroded during runoff (Tiessen, 1996). The phosphorus associated with deposited sediments is potentially bioavailable for a longer period of time as compared to suspended sediments, as P rich detrital material is thought to be incorporated in the bed sediments (Li et al. 1972).

The partition between particulate (PP) and dissolved forms (SRP) is not hard and fast. The two forms may interchange by selective transport of fine particles which have different sorption and desorption capacity. The factors affecting this interchangeability include the discharge rate accompanied with seasonal variation, soil tillage in the watershed and the aerial transfers through precipitation of aerosols with rain water (Tiessen, 1996). The major transformation reactions between soils, plant material, rain leading to transport of SRP is given in figure 1.6.
Figure 1.6: Transformation reactions between soil, plant material and rainwater (after Tiessen, 1996).

The loading from terrestrial to aquatic ecosystems is variable and depends on many factors like the vegetation of the source area. The forests are known to conserve phosphorus (Taylor et al., 1971) whereas the loss of P from agricultural land is more. The loss of P from a watershed increases with discharge. Discharge not only influences the amount of P lost, but also the extent to which the transformations occur during a stream or river flow. The rainfall pattern and its distribution through the year also affect the P load in water bodies.

Within the river, there are many factors that describe P loading in sediments like sorption, precipitation and biological uptake whereas release is governed by changes in solution chemistry, release from biomass, hydrolysis of organic P and reduction of iron oxy hydroxides under anaerobic conditions (Baldwin et al., 2001). According to House (2003) there are three different classes of processes that determine P loading in a system. These are physically dominated processes that include remobilisation of P rich sediment and associated release of P from pore water in bed, deposition of sediment-associated P in the main channel under stable and falling river discharge and storage of sediment-associated P in flood plain deposits. The chemical and biochemical dominated processes include, net uptake of Soluble Reactive Phosphorus (SRP) and Total Dissolved Phosphorus (TDP) by sediment through sorption process, desorption of P from sediments as the SRP in the water decreases, conversion of TDP to SRP. And there are combinations of physical and chemical processes that include erosion of P
deficient minerals from river bank and their interaction with SRP in the water column, infiltration of flood waters through the floodplain and the retention of SRP within alluvial deposits.

All these processes make the biogeochemical cycling of phosphorus in a large river a complex phenomenon that largely depends on lithology, climate, relief, weathering conditions and biological activities. The present study is aimed to understand the fractionation and mobility of P during weathering and sediment generation processes in the Kaveri river catchment area.

1.4.b. Lakes

Lakes constitute an important component of the terrestrial phosphorus system and have been extensively studied (Melack, 1995; Kaiserli et al, 2002; Filippelli et al, 2006, Schauer & Chorus, 2009). Lakes offer a perfect environment for studying the different aspects of P cycle like fractionation, coupling-decoupling of P with other elements, microbial and phytoplankton adsorption and desorption reactions as they are a confined ecosystem for understanding nutrient limitation in case of N and P (Ruttenberg, 2008). The lake system extends the understanding of terrestrial P cycle to alpine and glaciated systems which is not possible in a soil chronosequence (Filippelli, 2009).

The cycling of P in lakes is even more stressed because of the anthropogenic inputs of P leading to cultural eutrophication and degradation of water bodies (Vollenweider et al, 1992). The state of sensitivity can be imagined by the concentration of P capable of causing eutrophication which is only 0.03mg/L of available P and 0.1mg/L of total P (Gibson, 1997; Brady & Weil, 2002). The P transported from agricultural land in the particulate form when reaches the base of lake may be released and become available for the living system under anoxic conditions by the reductive dissolution of Fe oxyhydroxide and the bound P can be made bioavailable (Miller, 2001). It is not only the P loading from land that determines the eutrophic status of a lake but the proneness to eutrophication depends on the average retention time of imported nutrients, quotient of mean depth and hydraulic residence time (Vollenweider, 1976).
1.4.c. Marine phosphorus cycle

The average global concentration of Soluble Reactive Phosphorus in the oceans is 2.3 micromoles/litre and this pool is by far the largest reservoir of dissolved P (Nelson, 2000). The distribution of phosphorus is stratified in ocean i.e. the variation is found in both, horizontal and vertical profiles of the ocean (Fig. 1.1). The consumption of phosphorus in its simplest composition as orthophosphate by the phytoplanktons creates a differentiation in vertical profile. For defining the optimum productivity, Alfred Redfield (1963) has identified the molar ratio of C:N:P as 106C:16N:1P to understand the ideal system and nutrient limitation. The ratio would depend on the nutrient availability and the nutritive state of the phytoplankton. When compared with the inorganic C:N:P ratio of the sea water which is 1000:15:1(HCO₃⁻, NO₃⁻, HPO₄²⁻) reflects that the nitrogen and phosphorus are limiting the productivity. In the absence of orthophosphate the planktons break down other complex forms, hence removing P from the upper layers while there is a build up of P in the deeper layers. The respiration of the biogenic particles, microbial activity during diagenesis causes this buildup in sediment pore waters. The role of phytoplankton and distribution of P into different pools is discussed at length by Nelson (2000).

Horizontally, the variation in P distribution is dependent on the distance from the continents. Continental shelf and slope sediments vary from the deep sea. The productivity is higher in the continent shelf and slope as it receives higher P, Si, N and Fe and other continent derived nutrients via rivers, accompanied by the retention of sedimentary P. Therefore, the shelf and abyssal sediments have completely different P distribution. But the common thing is that both are dominated by Ca-P (mostly authigenic apatite). This comprises the larger fraction of total P in pelagic sediments. In the hemipelagic sediments, the remaining P is partitioned between iron bound P (mostly Fe oxyhydroxides), detrital apatite and organic apatite, while the organic and detrital fractions are insignificant in the pelagic sediments (Ruttenberg, 2007). Marine phosphate deposition or phosphorus removal mechanisms are discussed by Follmi (1996), Delaney (1998) and Rao (1998). The only major P removal mechanism is through burial in sediments that includes organic matter burial (Mach et al, 1987), P
sorption and precipitation with clays and iron oxyhydroxides (Delaney 1998), phosphorite burial (Tribble et al. 1995) and hydrothermal processes (Froelich 1982).

P removal rate from the oceans is controlled by the burial of sediments with organic matter as their primary content. Upon subduction of the oceanic plate, the P is recycled into the mantle with carbon and nitrogen. Sedimentary organic phosphorus, on subduction is likely to be incorporated into the crystalline apatite during subduction zone metamorphism. The result is that subducted organic P does not return to the earth’s surface at the same rate as carbon and nitrogen and thus the Phosphorus cycle is decoupled from that of carbon and nitrogen during subduction and metamorphism. This crystallized mass upon exposure gets weathered to produce bioavailable phosphorus (Ruttenberg, 2007; Guidry et al., 2000).

P is considered limiting in marine ecosystems on a geological time scale. Some authors (Ruttenberg, 2007; Compton et al., 2000; Filippelli & Delaney, 1996) consider the weathering controlled input of phosphorus to be responsible for its limiting nature on geological time scales, while others owe it to the long residence time for its limiting nature. Contemporary studies do focus on the limiting nature of P not only on geological scales but also in modern oceans (Tyrell, 1999).

The estimates of residence time of Phosphorus in oceans are variable and are based on difference in calculation of P flux from rivers and atmospheric sources. It may vary from 10,000-80,000 years. Considering the increase in rate of burial of phosphorus, the residence time may further decrease (Nelson, 2000). It is this long residence time of phosphorus in deep water sediments as compared to other potentially bio-limiting nutrients such as Fe and Si accompanied by the vast atmospheric reserve for nitrogen that makes P the ultimate nutrient limiting biological productivity (Redfield, 1958; Howarth, 1995; Tyrell, 1999). The P supply to the oceans is constrained by the input of weathered geological material transported via rivers and a small atmospheric component indicating the link between continental weathering and oceanic supply of P. The anthropogenic interferences can significantly alter the amount of P transported to the sea (Ruttenberg, 2007).
1.5. Atmospheric phosphorus cycle

During discussions on phosphorus cycle, the atmospheric component is usually overlooked because of its smaller scale contribution as compared to other reservoirs. Though its contribution can be crucial in nutrient deficient ecosystems and oceanic productivity on the surface where the systems are P limited (Wu et al., 2000; Mills et al., 2004; Krishnamurthy et al., 2007). The main difference that separates its biogeochemical cycling from other nutrients like C and S is the lack of a stable gaseous phase in the Earth’s atmosphere and its presence in the form of aerosols (Graham and Duce, 1979; Jahnke, 2000; Mahowald, 2008).

The source of phosphorus in atmosphere is mainly terrestrial. It can be soil particles (agricultural and construction) through wind erosion, in the spores, fungi and pollen that results from biological activity and as emissions from industrial and anthropological activities as ash particles from burning of coal, fuel oils, timber and agricultural refuse (Anderson, 2009). A significant portion of the P mass is also provided by the sea-salt particles in the particulate matter (~33 X 10^10 g/yr). Magnitude wise, crustal material P input to atmosphere (~400 X 10^10 g/yr) is most important, whereas anthropogenic (~26 X 10^10 g/yr) and oceanic inputs (~100 X 10^10 g/yr) are much less important on a global basis (Graham and Duce, 1979).

Atmosphere, acting as a transfer medium transports the aerosol particles of crustal origin to the ocean and other parts of continents of which Sahara dust plume constitutes a major portion (Graham and Duce, 1979). A study conducted by Vitousek et al. (1995) describes the development of ecosystem in Hawaiian Islands of different ages varying from 0.3 K yrs – 4100 K yrs. They found that new soils are deficient in atmospherically derived nutrients like N, whereas rock derived nutrients like phosphorus becomes limiting in mature chronosequences. In such cases the contribution by atmospheric deposition of phosphorus has become important to mature soils (Swap et al, 1992; Hedin et al, 1994; Newman, 1995). Atmospheric component of P can be a significant source for the upper ocean irrespective of its overall magnitude (Nelson 2000; Chadwick 1999). Short term inputs of P in nutrient deficient systems are known to increase the biological productivity over short time scale (Migon and Sandroni, 1999).
The residence time of continental and oceanic aerosol P is found to be 3 days and 1 day, respectively (Nelson, 2000).

1.6. Phosphorus and climate change

It is imperative to understand the cycling of any nutrient in an ecosystem if the control of primary production and particulate carbon transportation is to be understood (Nelson 2000). Phosphorus, being no exception, has been linked to climate change in several studies, although indirectly. Raymo & Rudiman (1992) tried to link the rise of Himalayan-Tibetan Plateau leading to dramatic increase in chemical weathering bringing the CO₂ level down, resulting in global cooling. Following this, Filippelli (1997) and Filippelli and Souch (1999), tried to establish a relationship between the oceanic productivity and the glacial time scales. In oceanic context, P being the limiting nutrient will determine the surface ocean productivity and in turn the carbon dioxide sequestration that will occur by biomass production (Boyle, 1990; Bakun, 1990; Ruttenberg, 1993; Follmi, 1996). Geologically, Cambrian explosion supposedly resulted in excess of phosphorus in environment and as an adaptation life forms with hard body parts appeared to convert excess P into apatite (Narbonne et al, 1994; Morris, 2000).

On the other hand, studies are conducted where climate change is known to effect the phosphorus loading from terrestrial ecosystems to lakes and streams (Mackenzie et al, 2002; Malmaeus et al. 2006; Jeppesen, et al., 2008). The effects of climate change can be manifested by change in the pattern of evaporation and precipitation leading to changes in hydrology and the warmer temperatures that are of greater importance in case of lake systems altering the circulation pattern of nutrients and sometimes increasing the eutrophication (Clair and Ehrman, 1996).

1.7. Phosphorus resources and sustainable agriculture

1.7.a. International scenario

Internationally, phosphorus utilization, mining, consumption, its side effects (eutrophication), and now recycling have been become a matter of interest since the beginning of nineteenth century (Smil, 2000a). The one factor that seems to govern the aforesaid processes is the divide between the developed and developing countries
Developed nations like US and European countries have attained a critical level of phosphorus required to sustain the agricultural productivity, hence limiting the consumption; whereas, in developing nations like India, China and Africa the demand and consumption is expected to increase at least for another 50 years (Cordell et al, 2009).

The Countries like China and Africa have phosphate reserves (Fig. 1.7) to sustain themselves but other countries would depend entirely on the imports to keep up with the requirements. With the background of non-renewable nature of the phosphate rock reserves, unidirectional consumption is not everlasting. Like petroleum, phosphorus use is to be regulated. P recycling from the human waste and wastewater treatment plants is a current issue (Steen, 1998). The concern for phosphate requirement similar to that of petroleum is highlighted by Gilbert (2009). With no substitute for it, phosphate is next to get attention after petroleum. Therefore, a better understanding is required for the biogeochemistry of P in the soil and weathering systems for the proper use and reuse for the sustainable agricultural production and to feed the increasing population.

1.7.b. Indian perspective

Indian society is primarily an agrarian society with agriculture contributing 22% to its GDP and providing livelihood to two-third of its population. With increasing population, the pressure to enhance the productivity per unit of land is increasing. Of the total irrigated land area, food crops occupy 69% while the remaining 31% by the non-food crops (FAO, 2005a). Crop yield from land can be improved when the nutrient status of the field is optimum. India suffers from land degradation of different levels due to deficiency of nutrients. In general, the soils of India are deficient in P (FAI, 1989). To fill that gap, fertilizers have to be applied to support the nutrient status of crops.

As discussed earlier, the developed nations have attained the critical levels of phosphorus in their agricultural soils hence stabilizing further application of fertilizers. India, however, being a developing nation is in the process of increasing crop yield along with adopting good agricultural practices. The critical level of nutrients in soils is
yet to reach. Therefore the demand for phosphate and other fertilizers is expected to increase in the times to come. As the current level of phosphate resources and reserves with India are not sufficient to fulfill its demands (Fig. 1.7), India relies on imports from other countries (Fig. 1.8).

**Figure 1.7:** Based on accessibility of resources the figure gives the resource availability in the world. (after Vuuren et al., 2010).

**Figure 1.8:** Expected trend of net import and exports of phosphorus in India along with different world regions (after Vuuren et al., 2010).
With the high subsidy provided by the Indian Government on import of fertilizers over application of particular fertilizers is encouraged leaving more space for leakages and deterioration of water bodies. The consumption, imports and production of fertilizers in India is variable and dependent on many factors. Table 1.3 gives the production, consumption and importation pattern of NPK fertilizers in India.

Table 1.3: Production, Importation and Consumption of fertilizers. Source FAI, 2003/04

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<tr>
<td></td>
<td></td>
<td>Year</td>
<td>000 tonnes</td>
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<tr>
<td>N</td>
<td>Production</td>
<td>10873</td>
<td>10943</td>
<td>10690</td>
<td>10508</td>
<td>10557</td>
<td></td>
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<tr>
<td></td>
<td>Importation</td>
<td>856</td>
<td>164</td>
<td>283</td>
<td>135</td>
<td>205</td>
<td></td>
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<tr>
<td></td>
<td>Consumption</td>
<td>11593</td>
<td>10920</td>
<td>11310</td>
<td>10474</td>
<td>11076</td>
<td></td>
</tr>
<tr>
<td>P2O5</td>
<td>Production</td>
<td>3448</td>
<td>3743</td>
<td>3837</td>
<td>3904</td>
<td>3617</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Importation</td>
<td>1534</td>
<td>437</td>
<td>494</td>
<td>228</td>
<td>372</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Consumption</td>
<td>4798</td>
<td>4215</td>
<td>4382</td>
<td>1019</td>
<td>4123</td>
<td></td>
</tr>
<tr>
<td>K2O</td>
<td>Importation</td>
<td>1774</td>
<td>1594</td>
<td>1697</td>
<td>1568</td>
<td>1553</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Consumption</td>
<td>1678</td>
<td>1568</td>
<td>1667</td>
<td>1601</td>
<td>1598</td>
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63% of P2O5 consumption is di-ammonium phosphate (DAP), 27% other complex fertilizers and the remaining 10% is the Single super phosphate. (SSP)

The main reason behind the land degradation and water body deterioration is the gap that exists between the application of nutrients (NPK) and their removal by the crops. Also the application of fertilizers is imbalanced in terms of requirement by the crops (FAO, 2005a). The transfer of fertilizer from agricultural to aquatic ecosystems can be reduced by fertilizer management, erosion and collection control measures. Under the circumstances where P is considered a resource no less important than petroleum (Derry, 2007; Cordell et al, 2009; Gilbert, 2009; Lott et al, 2009), it becomes all the more essential to estimate the natural level of nutrients and to understand P mobility and mineralization processes in soils so that they can be better utilized for enhancing crop production and minimizing the wastages.

As weathering is known to be the major natural process of P mobilisation from the source rocks, its importance is well recognized in controlling the sediment load of rivers. The floodplains naturally fertilized by the sediments (produced after weathering) through flooding, still makes most of the fertile farmlands in India (Rajamani, 2002). Understanding the natural nutrient concentrations and partitioning in different fractions
of floodplain sediment and source sediments and rocks can help optimize the nutrient conditions and sustainable farmland production.

1.8. Importance of phosphorus fractionation study in the Kaveri catchment

The current research aims to understand the distribution and fractionation of phosphorus in the weathering profile of the catchment area of Kaveri river and its distribution in sediments and floodplains impacting the farmland formation and hence the productivity of the agricultural systems. To comprehend, the research attempts to investigate the distribution of P in a soil development profile in the catchment area of Kaveri River contributing to the sediments and henceforth the distribution and fractionation of P in sediments.

The study would help in exploring the weathering processes and sediment production in the distribution of P and its availability in sediments for the growth of plants. Although the controls on sediment yield in rivers are no doubt, complex in detail, it seems logical to suppose that a first order relationship should exist between weathering history and erosion of a given area (McLennan, 1993).

The factors controlling the distribution of P are to be understood to optimise the conditions for its maximum availability for plant growth and minimum losses to the environment. The problem identified here addresses bigger issues like nutrient availability for the plants in the Kaveri catchment region and food security; and indirectly the eutrophication. A good understanding of different fractions of phosphorus (chemical species) in natural sources and of factors making different species would help in developing the correct methodology and quantities of fertilizers to be applied externally for the growth of crops. This in turn would reduce the excess of P entering into water bodies inducing eutrophication.

Therefore, this research aims to study the phosphorus fractionation in soils and sediments and their most likely sources, the major rock types and the role of weathering in primary fractionation of phosphorus in the upper catchment of Kaveri River. The major aspects of this study include:

- Determination of chemical distribution pattern of P on two different abundant rock types of the Kaveri catchment area and their weathering products in weathering profiles under humid and semi-arid conditions.
• To determine the elemental composition of sediments including phosphorus across the selected stretch of Kaveri and its tributaries, the Harangi and Kabini river. This is to understand the contribution of P through erosion from different lithologies to the bulk sediment.

• To study the sedimentary (textural) redistribution, mixing and its effect on P distribution downstream.