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Phosphorus Recovery from the Bottom Sediments of a Lake

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<p>Phosphorus (P) is a crucial nutrient to enhance agricultural productivity and a pollutant which impairs water quality of the lake. P losses from various fields such as industrial runoff, surface runoff, agricultural runoff, landfill leachate, runoff from oil fields, mine drainage, construction sites runoff, untreated sewage, runoff from livestock feedlots, runoff from grazing land, atmospheric depositions, septic tank leakage deposit in lake bottom sediments which boost lake eutrophication. Phosphorus extraction from the bottom sediments of a lake is long-term goal of modern society to meet global P demand and restore lake quality. Over exploitation of phosphate rock, a critical raw material can be replaced by recovering P from the lake bottom sediments for both P sustainability and environmental sustainability.</p> <p>The purpose of this thesis was to find possible techniques to recover P from lakes bottom sediments. Various in situ phosphorus trapping techniques such as phoslock, modified zeolite, alum treatment, calcite, aeration and hypolimnetic withdrawal are discussed. These techniques play a significant role to restore the lakes water quality by reducing internal P-cycling. The qualitative analysis of different P-forms by sequential extraction (SEDEX), P-extraction from sediments by perchloric acid method and ignition method, and comparison of P-recovery from sewage sludge ashes and bottom sediments ashes are discussed.</p> <p>Bottom sediment is considered as a sink where P is stored. Thus, dredging of the bottom sediments by using mechanical and hydraulic dredgers can help to remove P from lakes. Sediments contain various organic and inorganic contaminants. Sediment treatment techniques and possibilities of using dredged sediments in various sectors are discussed. Disposal of dredged sediments in a landfill is not a sustainable solution. Dredged sediments after treatment can be used as a P-resource. Dredging can be considered as indirect P-recovery.</p>	
Keywords	phosphorus, recovery, dredging, extraction, bottom sediments, restoration, contaminants, fertilizers, sustainability

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I am solely responsible for any flaws and disparities found in this thesis.

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List of Abbreviations

P	Phosphorus
N	Nitrogen
TP	Total Phosphorus
FRP	Free Reactive Phosphorus
ATP	Adenosine Triphosphate
DNA	Deoxyribonucleic Acid
RNA	Ribonucleic Acid
BTEX	Benzene, Toluene, Ethylbenzene, and Xylene
PAHs	Polycyclic Aromatic Hydrocarbons
PCBs	Polychlorinated Biphenyls
VOCs	Volatile Organic Compounds
SVOCs	Semi Volatile Organic Compounds
TNT	Trinitrotoluene
RDX	Research Department Explosive
HMX	Higher Melting Explosive
CDB	Citrate-Dithionite-Bicarbonate
DO	Dissolved Oxygen
CFAP	Carbonate Fluorapatite
FAP	Fluorapatite
M	Molar
SEDEX	Sequential Extraction Method
EDTA	Ethylenediaminetetraacetic Acid
DTPA	Diethyl Triamine Penta-Acid
TEDTA	Ethylenediaminetetraacetic Acid
EDDA	Ethylenediamine-N,N'-Diacetic Acid
NTA	Nitrilo Triacetic Acid
NTTA	Nitrilotris(methylene) Triphosphonic Acid
IDA	Iminodiacetic Acid

List of Symbols

KMnO_4	potassium permanganate
H_3PO_4	phosphoric acid
$\text{C}_6\text{H}_{18}\text{O}_{24}\text{P}_6$	phytic acid
$\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$	Vivianite
LaPO_4	lanthanum phosphate
$\text{Al}_2(\text{SO}_4)_3$	aluminum sulphate
AlPO_4	aluminum phosphate
CaCO_3	calcium carbonate
$\text{Ca}(\text{OH})_2$	calcium hydroxide
$\text{Ca}_5(\text{PO}_4)_3(\text{OH})$	hydroxide apatite
MgCl_2	magnesium chloride
CH_3COOH	acetic acid
HClO_4	perchloric acid
CaO	calcium oxide
K_2O	potassium oxide
MgO	magnesium oxide
P_2O_5	phosphorus pentoxide
Hg	Mercury
As	Arsenic
Cd	Cadmium
Ni	Nickel
Pb	Lead
HNO_3	nitric acid
HCl	hydrochloric

1 Introduction

The sustainable use of phosphorus is an emerging goal of modern society to secure food demand, and water bodies. Phosphorus is both an essential element and a pollutant. Inefficient use of phosphorus diminishes environmental quality. Eutrophication is one major problem due to an excess availability of phosphorus in water bodies. Phosphate rock is a critical raw material which contains large amount of phosphate minerals. Phosphorus uses in various sectors should have economic, environmental, and ethical justifications which help to enhance phosphorus sustainability, secure raw materials (phosphate rock), and the environment for the future generations. Maximum recovery and recycling of phosphorus from various secondary phosphorus resources help to meet global P demand and enhance environmental sustainability. The precise use, recycling, reusing, and possible recovery approaches of phosphorus are current critical issues to fulfil the future demand of phosphorus for agricultural productivity, human life, and other living beings. Thus, phosphorus is important resource which could be handled, applied and utilized precisely based in a concept of circular economy to enhance food security and environmental sustainability (Withers, et al., 2015).

Phosphorus is a crucial chemical element. It exists in the Earth's crust for about 0.1% by weight. Generally, it occurs in lithosphere as orthophosphate (PO_4^{3-}) producing more than 300 minerals. It is found predominantly in a mineral named apatite ($\text{Ca}_5[\text{PO}_4]_3(\text{F}, \text{Cl}, \text{OH})$). It is also available in vivianite, variscite, wavellite, monazite, and xenotime. Largely, phosphorus amount is contained in apatite and struvite ($\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$) (Bojakowska, 2016). It is a crucial nutrient for the progress and development of all living creatures. Phosphorus availability plays an important role to enhance agricultural productivity. Proper use of phosphorus is necessary to satisfy the global food demand. The over exploitation of this non-renewable resource to fulfil the current demand is not sustainable (Johnston & Steen, 2000).

Researchers have reported the availability of phosphorus in lake sediments in various forms. It has been recognized as the key factor which affects lake water quality. The excessive concentration of phosphorus in lake water plays a vital role in eutrophication. Sediments function as a sink where P is stored. The amount of phosphorus in lake water depends upon the external P loading, its release, and its retention in the bottom sediments (Wang & Liang, 2015). The high loading of phosphorus causes high phytoplankton

biomass, turbidity, and unwanted biological changes in lake. Even though, external loading has been reduced, lake water quality can be affected by internal loading. Redox sensitive iron compounds play an important role in binding significant phosphorus amount in lake sediments or P occurs in labile organic forms which have potential to move and finally release to the lake water. Various aspects are involved to affect the phosphorus loading in bottom sediments and its release (Søndergaard, et al., 2001).

Recovering phosphorus from lake bottom sediments is an important issue nowadays. Recovered P can be used for various purposes, which helps to meet the current high demand of phosphorus. It is also important for the effective management of lake. In order to reverse the effect of eutrophication, various mitigation efforts, and preventive strategies should be required. These include permanent P removal, P extraction, P inactivation etc. Sequential extraction of phosphorus from lake bottom sediments has been discovered to recover P however this procedure has certain limitations, and varies from country to country. Sufficient researches about recovery techniques have not been done yet.

This thesis represents general review of phosphorus recovery from the lake bottom sediments, P accumulation in lake sediments and its removal and treatment procedures. Moreover, P recovery from the lake bottom sediments is compared with P recovery from sewage sludge, is also discussed in this thesis.

2 Objective of the Research

The main aim of this research was to study the availability of phosphorus in lake bottom sediments and potential recovering techniques which enhance the phosphorus availability for global consumption since phosphorus is an essential nutrient. Recovering phosphorus from lake sediments is essential to control eutrophication. It helps to maintain the lake water quality. There is problem in lake management nowadays due to excessive release of phosphorus in lake water through various means. Excessive use of synthetic fertilizers for agricultural productivity contributes to phosphorus accumulated runoff entering the lake water bodies and phosphorus finally settling in the bottom sediments. Soil erosion, landslide, and surface runoff may also contribute to phosphorus accumulation in lake sediments because sufficient phosphorus is found in soil and surface water. Phosphorus recovery from lake sediments helps the effective management of lake and meets

the continuous demand of phosphorus to ensure the worldwide food security. It helps in sustainable use of phosphorus. The sustainable use of phosphorus is important for worldwide food security and helps to reduce environmental deterioration.

Effective methods of controlling phosphorus release in lake from bottom sediments are also discussed in this thesis as they are quite essential for proper lake management. This thesis is a theoretical review of available techniques, and methods of recovering phosphorus from lake sediments. No experimental analysis was conducted during this thesis project. Above mentioned objectives show the justification and importance of this thesis. Moreover, comparison of phosphorus recovery from sewage sludge ashes, and bottom sediments ashes is also discussed in this thesis which helps to enhance the knowledge of overall possibilities of phosphorus recovery. Extracted phosphorus can be used as agricultural fertilizers and for various other purposes such as feed additives, soaps and detergents.

3 Literature Review

This section comprises the background for this thesis, as the related terms are described in more detail. It includes the presence of phosphorus, its sources, its accumulation and release in lake water. The cause of eutrophication due to phosphorus accumulation and release from lake sediments are described. Moreover, it also contains the types of eutrophication, its causes, effects and risks. The details of phosphorus in lake water are principally described in this chapter to enhance the knowledge of sedimentary phosphorus in lake.

3.1 Phosphorus and its Cycle

Phosphorus is a vital element for all living beings and is deposited basically in soil, water and sediments. It is crucial component of ATP which is considered as energy currency of life (i.e. uptake and transport of essential nutrients), DNA which contains genetic information of all living organisms, and RNA. It is essential to all vertebrates. The human teeth and bones comprise phosphorus. It is essential for all photosynthetic organisms to form their tissues. Its availability is necessary for biological productivity which creates the foundation of both aquatic and terrestrial food chain (Lenntech, n.d.).

The movement of phosphorus occurs in a cycle through rocks, water, soil, sediments, and organisms. Most of the biogeochemical cycles such as water, carbon, nitrogen, and sulphur cycles include gas phase, but phosphorus cycle does not contain gas phase; although small quantities of phosphoric acid (H_3PO_4) releases into atmosphere which may contribute to acid rain. The atmosphere does not play a significant role in phosphorus cycle because phosphorus and its compounds are in solids states at Earth's regular temperature and pressure. Largely, phosphorus accumulates in sedimentary rocks.

Generally, the phosphorus cycle commences in sedimentary rocks. The weathering of sedimentary rocks by rain water causes removal of phosphates from the rocks in to soils, and water. Plants consume phosphate ions from the soil. Phosphate transfers to animals as herbivores and omnivores use vegetations for their food. It then returns in to the soils through animal excreta and urine. Finally, the decomposition of plants and animals after death releases phosphates in to soil.

Similar process occurs in lake and other aquatic ecosystems. The phosphorus in soil particles is transported in to water bodies through various point and non-point sources. Then, it gravitates to settle on lake bottoms and ocean floors. Phosphate releases and enters in to the phosphorus cycle from the bottom when the sediments are stirred. The release phosphates are available for aquatic organisms and waterborne phosphates are taken by aquatic plants and moves through sequential steps of the aquatic food chain (The Environmental Literacy Council, n.d.).

The main components of phosphorus cycle are tectonic uplift and weathering of phosphorus-bearing rocks, physical destruction and chemical weathering of rocks which produce soils containing dissolved and particulate phosphorus, phosphorus transportation by river to lakes and the ocean, and sedimentation of organic and mineral constituents. Phosphorus containing in soils, sediments, and bedrock is not readily available to organisms. Geochemical and biochemical reactions help in the formation of dissolved orthophosphate which is readily available to organisms. Various microbial activities in soils, and sediments also affect the concentration and chemical configuration of phosphorus (Ruttenberg, 2001). The phosphorus cycle is shown in the Figure 1 below:

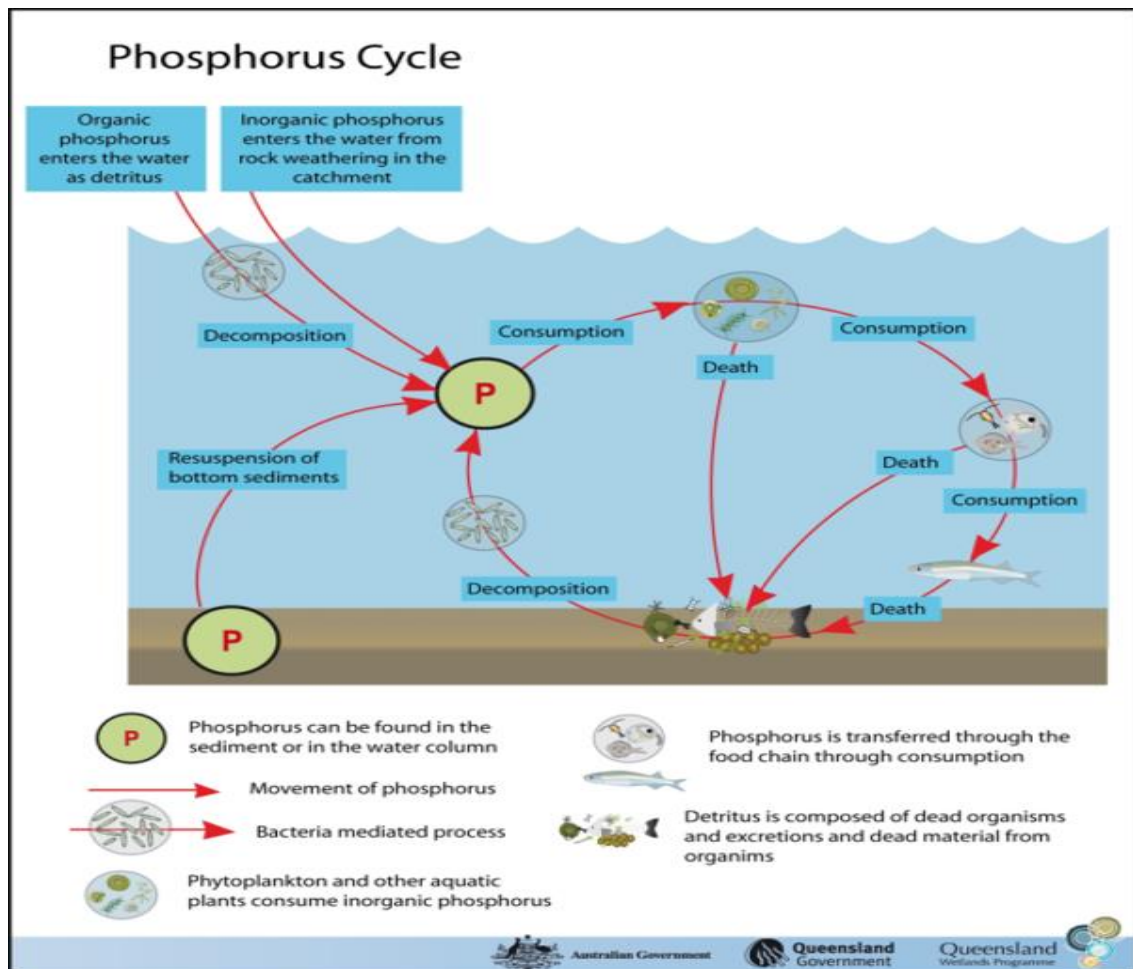


Figure 1. Phosphorus Cycle (Queensland Government, n.d.)

3.1.1 Phosphorus Sources for Lake Water

External sources of phosphorus for lake water are categorized into point, and nonpoint sources. Various point sources comprise urban and industrial waste water discharge, surface runoff and landfill leachate, runoff from oil fields, mine drainage, construction sites runoff, untreated sewage, runoff from livestock feedlots etc. Nonpoint sources include agricultural field runoff, runoff from grazing land, atmospheric depositions, septic tank leakage, runoff from unused mines etc (Hung, 2015). Phosphorus is either attached with sediment particles or dissolved with runoff water and carried towards the nearest lake. Rainfall and irrigation play an important role to transport sediments/soils containing significant amount of phosphorus into the nearest water body which causes phosphorus accumulation in water body. Various phosphorus sources for lake water are shown in the Figure 2 below:

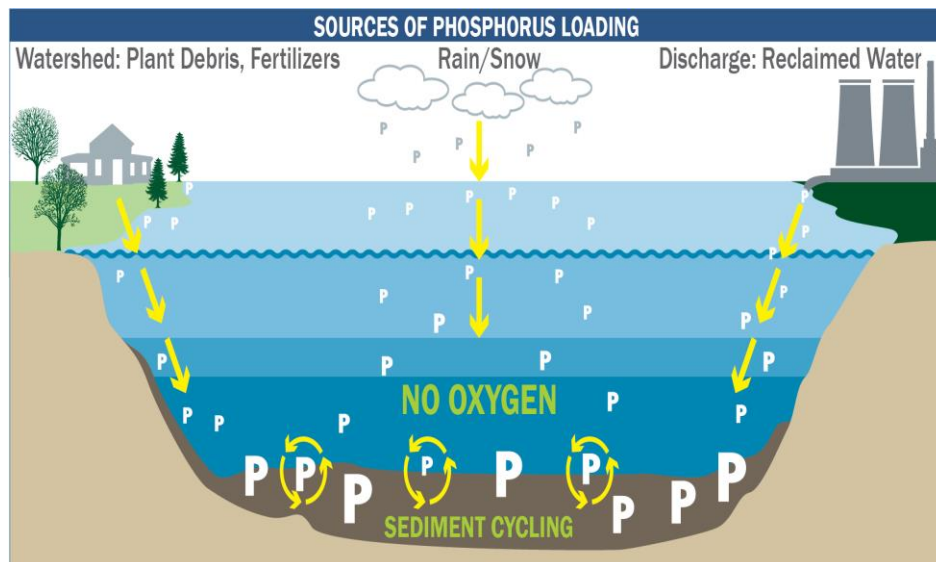


Figure 2. Phosphorus sources for lake water (Aquatic Systems, Lakes and Wetland Service, n.d.)

3.1.2 Phosphorus in Lake Sediments

Lake sediments are the materials situated at the bottom/floor of the lake. Lake sediment comprises mixture of various detrital sediment particles, organic components of algae or other terrestrial matters, and various fossils constituents. Saline and carbonate minerals precipitated inorganically are also found in lake sediments (Schnurrenberger, et al., 2003).

There are various forms of phosphorus exists in lake sediments. These are adsorbed, apatite, organic, and inorganic non-apatite forms. Adsorbed phosphorus can be released easily from lake sediments and easily available for plants and other microorganisms. Inorganic form is most sensitive to change the redox conditions. Inorganic form is co-precipitated with manganese, aluminium hydroxide and amorphous iron. In the sediments organic phosphorus exists as phytic acid ($C_6H_{18}O_{24}P_6$). The gradual decomposition of organic compounds by bacteria is a source of organic phosphorus in lake sediments. Apatite is inert phosphorus form which is stable and generally found in surface sediments in lake. Vivianite is one of the most important non-apatite mineral associated with organic remains in iron rich sediments. The chemical composition of vivianite is $Fe_3(PO_4)_2 \cdot 8H_2O$ (Bojakowska, 2016).

3.1.3 Phosphorus Retention in Lake Sediments

Phosphorus accumulates in lake as particulate or dissolved forms. Particulate form of phosphorus is deposited in lake sediments whereas dissolved form is incorporated with organic matter and finally sink to the bottom as organic form. The sedimentation happens through co-precipitation with calcium carbonate, formation of iron hydroxides, or adsorption of phosphorus by iron hydroxides. After then, phosphorus is integral part of various biological, and chemical processes in lake sediments and eventually deposited in bottom sediments. It releases and returns to the water column through interstitial water. Phosphorus retention in lake depends upon the flushing rate of the lake. Lake with high flushing rate has tendency of lower phosphorus retention than that of lower flushing rate lake.

Flushing rate is average duration of time where water spends in lake. It is calculated dividing total volume of lake by inflow from all sources. The relation between flushing rate and phosphorus retention is demonstrated by simple model of Vollenweider type:

$$P_{\text{lake}} = L_p / (Z^*(\sigma + \rho_w))$$

Here, P_{lake} is P in lake, L_p is specific loading, Z is lake mean depth, σ is sedimentary loss, ρ_w is flushing rate. This model gives sedimentation rate based on the relations of hydraulic retention time. The Figure 3 shows the input, output and forms of phosphorus in lake sediments.

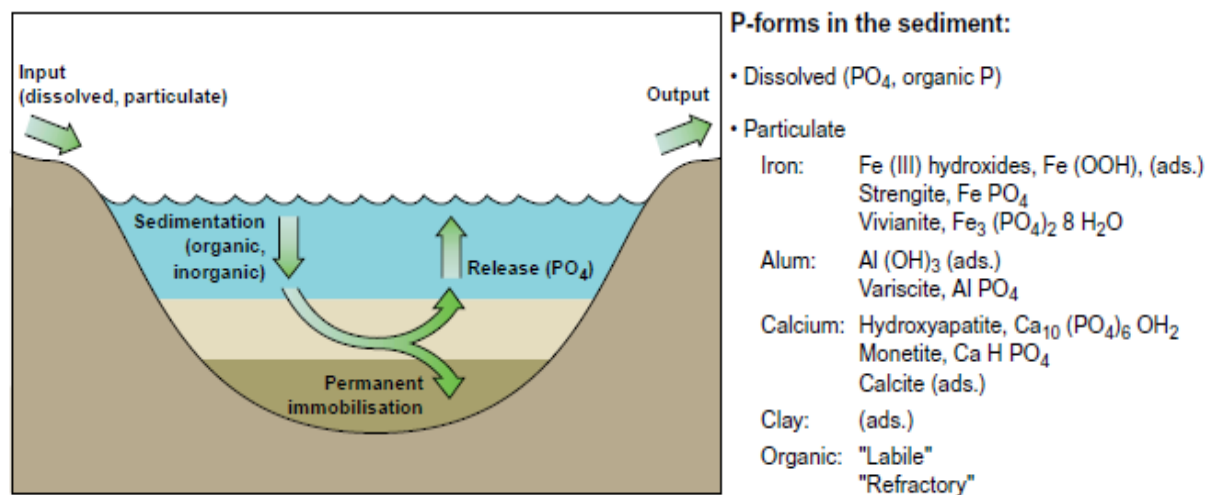


Figure 3. Diagrammatic Representation of Input/output of Phosphorus and P-forms in Lake Sediments (Søndergaard, et al., 2001)

The availability of ferric oxides and hydroxides in lake sediments play an important role to bind phosphorus and form a stable compound called Vivianite (Søndergaard, et al., 2001).

3.1.4 Phosphorus Releases from Lake Sediments

Various factors play an important role to release phosphorus from sediments. They are biological, physical, and chemical factors. Biological factor includes bacterial activity, bioturbation, and mineralization. Physical factor includes sediment mixing, and resuspension. Chemical factor includes pH, ratio of iron and phosphorus, redox status, and the availability of nitrate.

The overall P discharges from lake sediments is the difference of downward flux generated largely by the particles sedimentation occurred in water bodies (algae, debris, dregs, and other remains) and upward flux. The decomposition of organic matter releases phosphorus in lake water. The phosphorus transportation between lake water, and sediments is carried by interstitial water (Søndergaard, et al., 2001).

Sediments play a vital role in phosphorus accumulation and release in lakes. The remarkable accumulation of phosphorus in lake bottom sediments has occurred by excessive external P loading. The phosphorus release from bottom sediments, due to factors mentioned above boosts eutrophication. Phosphorus releases from bottom sediments under anaerobic condition is higher because of iron and manganese mineral reductions.

Various microbial activities in bottom and hypolimnion sediments have large tendency of using all the dissolved oxygen which cause anoxic and reducing situations. Mn (IV) reduces to Mn(II) and Fe(III) to Fe(II) which are more soluble forms. Thus, phosphorus combined with these minerals releases. Temperature of lake water is another important factor. Higher temperature activates microbial activities to decompose organic matters which releases dissolved phosphorus in overlying water (Sen, et al., 2006).

Laboratory experiment was performed to assess the effect of temperature, pH, and dissolved oxygen (DO) on P release in lake Xuanwu, China. It is favourable to release excess P in alkaline condition than that of acidic condition, whereas very small amount of P releases in neutral condition. More P releases at increasing temperature and more time to accomplish equilibrium between P in overlying water and P release from the sediments. The anaerobic situation was more favourable to release phosphorus than that of aerobic situation (Wu, et al., 2014).

3.2 Effect of Phosphorus

Lake eutrophication is one of the major effects of phosphorus. The large amount of phosphorus accumulation in lake can cause harmful cyanobacteria blooms. The over enrichment of phosphorus in lake water is due to various human activities, sewage sludge, industrial discharges, agricultural runoff, surface runoff, runoff from construction sites etc. Globally, the use of phosphorus as a fertilizer is increasing for agricultural productions which causes phosphorus to gather in soils. Phosphorus-rich soils are carried in to aquatic ecosystems which stimulate the growth of phytoplankton and other aquatic plants. Harmful phytoplankton also produces toxins and changes food web dynamics. Impacts such as human illness, economic losses to coastal societies and commercial fisheries, and death of fishes, birds, and mammals occur after the consumption or exposure to toxins. Turbidity increases due to excessive growth of phytoplankton, which decreases the penetration of light in to lower depth of the lakes, rivers or other water columns. Thus, the growth and development of submerged aquatic plants can be inhibited. Algal blooms also include marine seaweeds. Hydrogen sulphide (H_2S) is toxic gas which can be released after the decomposition of seaweeds by bacteria. Algal toxins are dangerous to human health. Fishes and other sea foods accumulate algal toxins, which are dangerous to human and animal health. Socio-economic impacts include aesthetic impacts because of algal colonies in lakes, and all other aquatic ecosystems. Shellfish, commercial fishes and other sea foods are unsafe to consume due to harmful algal toxins. Thus, fish industries are suffering from various financial problems. Many beaches are closed due to the occurrence of toxic algal blooms which create obstacle for recreation and economic activities (MarBEF, n.d.).

3.2.1 Eutrophication

According to the European Commission (EC) UWWT Directives, eutrophication is defined as “the enrichment of water by nutrients, especially nitrogen and/ or phosphorus, causing an accelerated growth of algae and higher forms of plant life to produce an undesirable disturbance to the balance of organisms present in the water and to the quality

of water concerned” (Andersen, et al., 2006). Lakes and estuaries collecting large quantities of plant nutrients are known as ‘eutrophic’ (in Greek ‘eu’ means ‘well’ and ‘trophe’ means ‘nourishment’). Due to rapid urbanization, industrialization, and excessive agricultural productions, the nutrients input in lake and other aquatic ecosystems is accelerating which causes eutrophication. Eutrophication is the over-enrichment of nutrients in aquatic ecosystems which promotes algae blooms and depletion in the level of oxygen. The stability of aquatic ecosystem is reduced due to large productions of primary producers. Lake eutrophication is enhanced not only by external loading of phosphorus but also by internal loading (P releases from sediments). Lake sediments are responsible for phosphorus metabolism. Even after the reduction of external P loading, eutrophication status is determined by internal P loading. Various studies suggest that uptake, storage, and release of phosphorus are performed by sediment bacteria. Lake eutrophication persists longer duration of time because of internal recycling of sediment phosphorus (Pettersson, 1998; Carpenter, 2005).

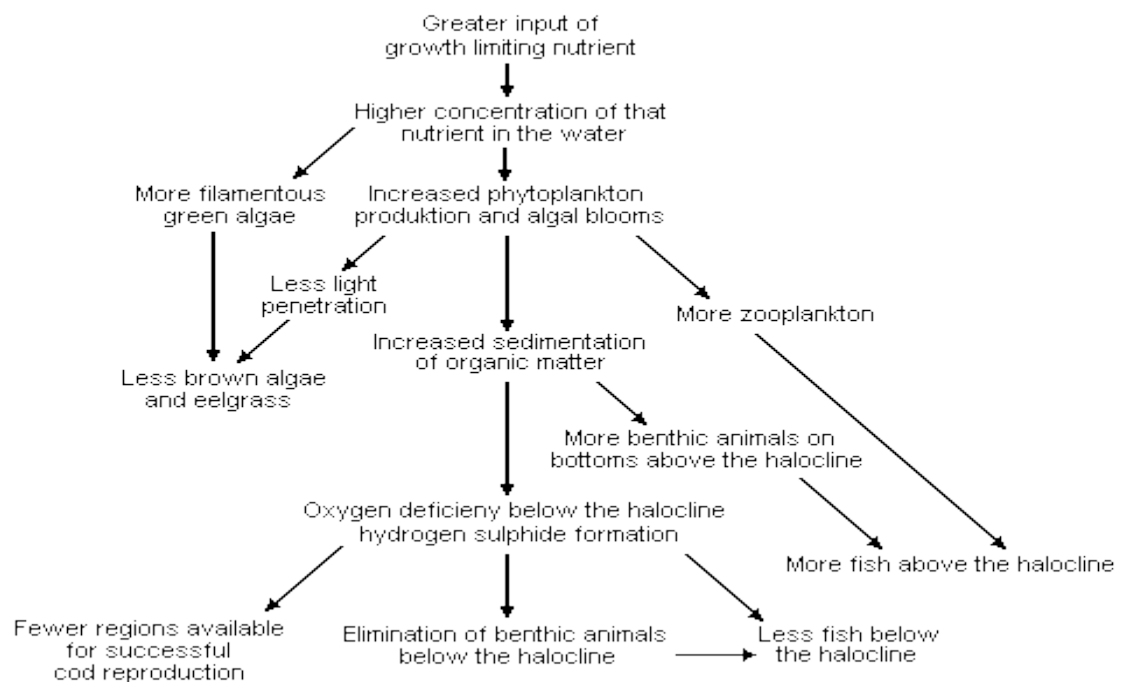


Figure 4. Eutrophication Process (Barrow, n.d.)

3.2.2 Types of Eutrophication

Eutrophication is mainly classified in to two types. They are natural eutrophication and artificial or cultural eutrophication.

The gradual aging of lake due to the enrichment of nutrients is known as natural eutrophication. In this process oligotrophic lake is transformed in to eutrophic lake. This process is slow and natural aging of lake. Nutrients, sediments, and organic matters gradually settle in lake bottom, and eutrophication occurs. Artificial eutrophication is the process which is accelerated by human activities. It is the rapid process. Cultural eutrophication is mainly associated with phosphorus found in fertilizers, sewage sludge, and other organic waste. Human activities such as deforestation which causes soil erosion, excessive use of fertilizers, pesticides etc. are responsible for rapid eutrophication (Bennett, 2017). Figure 5 illustrates a general diagram of cultural eutrophication

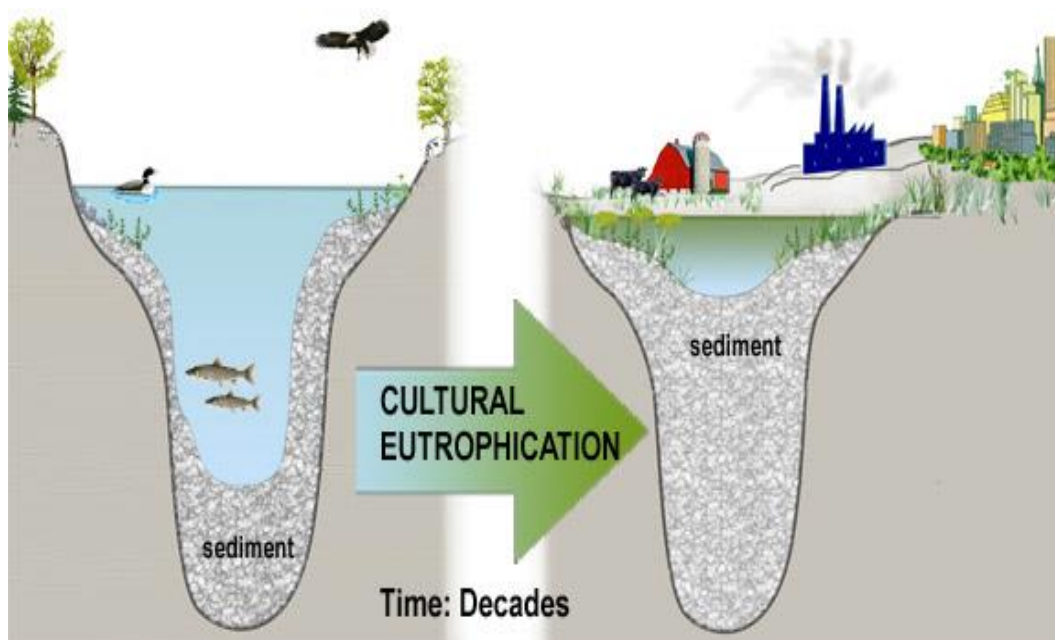


Figure 5. Cultural Eutrophication (Creeklife (Articles for the Environment), 2015)

3.2.3 Effect of Eutrophication and Risk

The intrinsic equilibrium of aquatic ecosystem is interrupted by eutrophication. It damages the water ecosystem and gradually deteriorates its functions and capacities. Water transparency and quality are extremely degraded. Eutrophication also causes lack of dissolved oxygen or supersaturation in water bodies which is unfavourable to aquatic animals. The biochemical composition of organic matter is altered because of excessive accumulation of organic carbon by eutrophic water bodies. It causes algal bloom and,

form dense layer on water surface and releases harmful toxins. It can cause drinking water crisis by damaging water quality. Algal toxin is produced after the death of blooming algae which is injurious to human and animal health. Cyanobacteria toxins (Cyanotoxins) contain cytotoxins and biotoxins which are lethal to animals and humans (Yang, et al., 2008).

The effects of eutrophication are listed as follows:

- Rapid growth in plant and animal biomass
- Excessive algal blooms
- Increase in growth and development of rooted vegetations
- Deterioration in species diversity
- Turbidity increases, and water transparency decreases
- Red tides and discoloration of water
- Modification in predominant biota
- Occurrence of hypoxia and anoxic situations which cause asphyxia and suffocation (Shinde & Gawande, 2016)

3.2.4 Lake Types and Eutrophication.

On the basis of nutrient existence, lakes are classified in to oligotrophic mesotrophic, and eutrophic lakes.

Oligotrophic lakes

There is very low nutrients concentration (N and P) in this type of lake. Minimal growth of organic matters in oligotrophic lake such as; zooplanktons, phytoplankton, algae, macrophytes, bacteria, and other aquatic animals. This type of lake bottom is associated with sand and rock particle with very low amount of phosphorus and nitrogen. Organic sediments accumulation in the bottom of lake is very low. This type of lake is generally deep and clear. Very little phosphorus accumulation in sediments of this type of lake.

Eutrophic lakes

This type of lake contains excessive nutrients (N and P). Large number of zooplankton, phytoplankton, and other organic matter grows in this type of lake. Excessive nutrients cause algal bloom which cloud the water of eutrophic lake. Large production of organic matter occurs and finally deposited in the bottom as organic sediments. Bacteria use all oxygen for the decomposition of organic matters and there is oxygen depletion at the bottom of the eutrophic lake. Generally, eutrophic lakes are shallow. The tendency of phosphorus accumulation in eutrophic lake is high (Kevern, et al.).

Mesotrophic lakes

The amount of nutrients (N and P) in this type of lakes are medium i.e. neither very high nor very low. Phosphorus accumulation in this type of lake can contribute eutrophication. Generally, this type of lake has clear water with sufficient availabilities of submerged plants.

Phosphorus recovering from shallow eutrophic lake is essential to eradicate the global eutrophication problem. Substantial amount of P extraction from eutrophic lake helps in lake recovery. Table 1 illustrates the basic differences between these three types of lake (Martinez, 2016).

Table 1. Differences between three types of trophic lakes

Oligotrophic Lake	Mesotrophic Lake	Eutrophic Lake
Transparent and clear water	Cloudy, murky water	Cloudy, turbid water
Low nutrients availability (N, P)	Higher availability of nutrients	Over nutrients availability
Excessive oxygen concentration	Sufficient/ good oxygen concentration	Low oxygen concentration
Proper penetration of light	Adequate penetration of light	Very low or no penetration of light
Not productive for aquatic plants	Fairly productive for aquatic plants	Very productive for aquatic plants i.e. Excessive growth of aquatic plants

4 Phosphorus Treatment Techniques for Lake Restoration

This chapter comprises lake restoration techniques. Due to an excessive anthropogenic impact, the lakes are suffering from various problems such as eutrophication, acidification, oxygen depletion, and hazardous substances contamination. Lakes need to be restored using viable techniques, and strategies to return in their natural status.

4.1 Physical Techniques

Techniques like aeration and hypolimnetic withdrawal are oldest mechanical restoration techniques which have been used for decades to upgrade the lake quality.

4.1.1 Aeration

The lower layers of lakes deteriorate remarkably due to the depletion of dissolve oxygen. The excessive consumption of dissolved oxygen is not replenished by photosynthesis and natural aeration. Thermal stratification of lakes (especially in summer) causes hypolimnetic oxygen depletion which have negative impacts on many aquatic habitats including cold-water fisheries. Aeration can be done either by mixing entire lakes with oxygen or injecting oxygen in hypolimnetic layer. It helps to protect the lake from thermal stratification. The artificial oxygenation in hypolimnetic layer helps in the phosphorus oxidation and locked in the sediments. Mainly, iron-rich sediments in the bottom of the lake lock the phosphorus in the presence of oxygen. The absence of oxygen in the lake bottom causes phosphorus release from the bottom sediments in the overlying water and lake quality is deteriorated. Thus, artificial aeration is needed for the proper functioning of the lake (Mostefa & Ahmed, 2012).

The proper implementation of this technique helps to control aquatic weed, maintain water quality and minimize organic muck, odour, nutrients and toxic gases. It also helps to reduce coliform bacteria, and nuisance algal growth. It enhances lake performance by providing suitable environment for beneficial aerobic bacteria and micro-organisms (CLEAN FLO Cleaning Water Biologically, n.d.). Lake aeration can be done as shown in Figure 6 below.

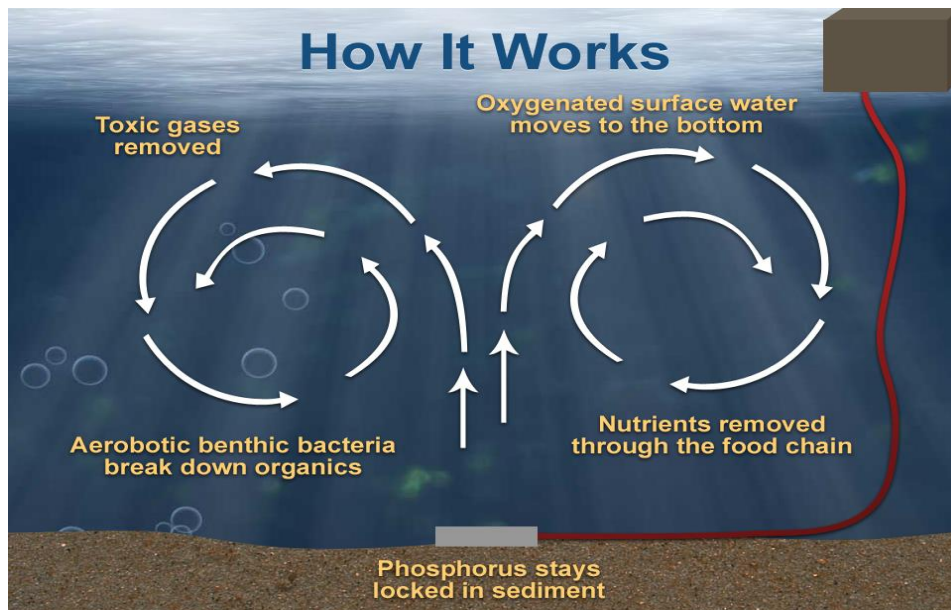


Figure 6. Lake Aeration (Lake Savers, n.d.)

4.1.2 Hypolimnetic withdrawal

It is one of the lake restoration technique based on withdrawal of anoxic, nutrient-rich, and toxic hypolimnetic water. The epilimnion water rich in dissolved oxygen is retained in the lakes. The removal of anoxic hypolimnetic water plays a significant role to limit the release of P from bottom sediments. Thus, it helps to reduce the P-cycling to the epilimnion which controls eutrophication. Maintaining thermal stability and natural level of lakes are critical challenges during the implementation of this technique (Friends of Reservoirs, n.d.). Figure 7 is a general sketch of hypolimnetic withdrawal.

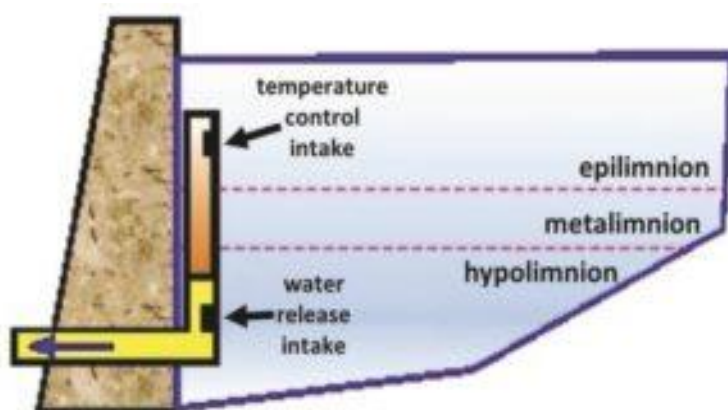


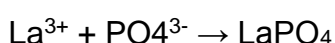
Figure 7. Sketch of Hypolimnetic Withdrawal (Friends of Reservoirs, n.d.)

4.2 Chemical Techniques

The chemical restoration techniques are implemented to reduce the P release from the bottom sediments. These techniques are applied to bind the P in sediments which help to restore eutrophic lake. These techniques help to reduce the internal P recycling. Various absorbents are used in these techniques. The mostly used viable techniques are Phoslock, modified zeolite (Z2G1), alum, and calcite.

4.2.1 Phoslock Technique

This is phosphorus locking technique to rehabilitate the lake water quality. It is one of the effective and widely applied technique which can bind free reactive phosphorus (FRP) and it does not form flocs (SEPRO, n.d.). The active component of lanthanum is used which reacts with phosphate and form an insoluble biologically inert compound. Phoslock is typically added as a slurry and it sinks through the water column and binds phosphate. It settles on the sediment by forming very thin layer and has tendency to bind phosphate releases from sediments. Phoslock contains 95% bentonite and 5% lanthanum. It is made through a controlled ion-exchange procedure through which bentonite cations exchange with lanthanum cations. Lanthanum is gripped within bentonite structure and gains its capability to bind phosphate without forming any free ions in water. The reaction that occurs in this technique is given below:



The lanthanum phosphate (LaPO_4) is the product obtained from the reaction which is insoluble in water and biologically inert or not available (Phoslock Europe GmbH, n.d.). Figure 8 shows the phoslock technique applied to trap phosphorus releases from the bottom sediments.

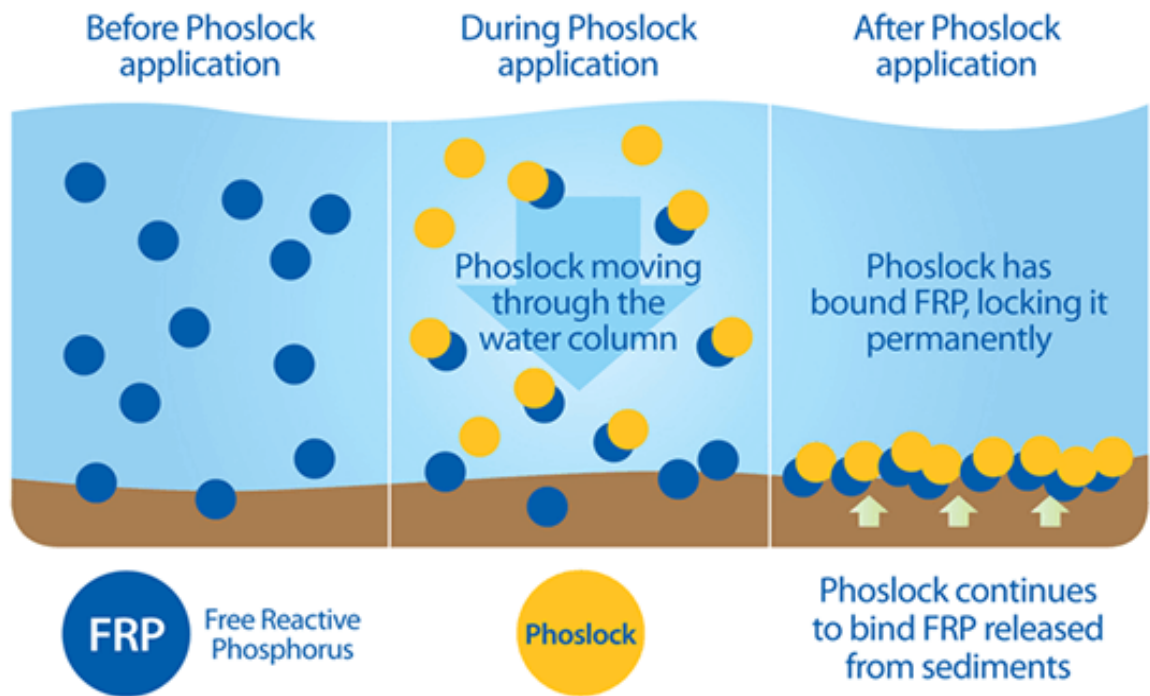
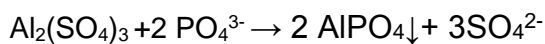


Figure 8. Phoslock Technique to restore lake quality (SEPRO, n.d.)

4.2.2 Alum Treatment Methods

Aluminium sulphate $[Al_2(SO_4)_3]$ commonly known as alum is nontoxic substance which can be used for lakes restoration. It binds P release from bottom sediments under anoxic conditions and controls internal recycling of phosphorus. Fluffy aluminium hydroxide precipitates (flocs) when alum contacts with water. Aluminium hydroxide binds with P and forms stable, insoluble compound called aluminium phosphate. Thus, on the bottom of the lake, layer is formed to bind the P releases from bottom sediments. It helps to form long-lasting sink of phosphorus in lake bottom which controls lake eutrophication (Wisconsin Dept. of Natural Resources, 2003). However, this technique is a temporary and not a sustainable solution for the lake recovery. The reaction occurs in this technique is given below:



4.2.3 Modified Zeolite

Natural zeolite is aluminosilicate porous substance. It has large surface area for maximum absorption because of its fine porous formation. It is also an excellent cation absorbent. A modified zeolite (Z2G1) is sediment capping agent. It is modified form of Al salt to enhance P uptake capability. This technique can remove both N and P without releasing Al in lake water. Various laboratory analysis suggests that its toxicity is very minimal. Phosphorus releases from bottom sediments to overlying water due to anoxic situations can be captured by using this technique. This material also absorbs cationic metals available in lake water. It absorbs NH_4^+ available in overlying water and stops the release of $\text{NH}_4\text{-N}$ from the sediments (Zamparas & Zacharias, 2014).

4.2.4 Calcite

It is calcium carbonate (CaCO_3) natural precipitation technique. This technique can be applied to clean hard water eutrophic lakes by trapping dissolved P and algal cells. The pH increases due to excessive algal growth which promotes the formation of CaCO_3 . When hydrogen carbonate anions react with calcium cations under high concentration it forms CO_2 and CaCO_3 . CaCO_3 precipitates and co-precipitates P in the sediments. Thus, in this technique, lime (Ca(OH)_2) is artificially used in lake water for the maximum precipitation of CaCO_3 for removing P and helps in algal flocculation which helps to enhance the lake water quality. In this method, the dissolved P is co-precipitated in the form of PO_4^{3-} with CaCO_3 . Finally, the complex mixture of CaCO_3 and forms of calcium phosphate is formed. The mostly occurring final form is hydroxyl apatite [$\text{Ca}_5(\text{PO}_4)_3(\text{OH})$]. It has very low solubility product (K_{sp}) (Zamparas & Zacharias, 2014). The summary of the above mentioned chemical restoration techniques is given the Table 2 below (Zamparas & Zacharias, 2014).

Table 2 Chemical Restoration Techniques

Chemical Techniques	Implemented as	Mechanisms	P adsorption capacity (mg P /g subs.)	pH range for maximum efficiency	Possible hazards
Phoslock	Slurry or granules	$\text{La}^{3+} + \text{PO}_4^{3-} \rightarrow \text{LaPO}_4$	10.5	5-8	Mostly non-poisonous
Modified Zeolite	Slurry or granules	$\text{Al}_2(\text{SO}_4)_3 + 2 \text{PO}_4^{3-} \rightarrow 2 \text{AlPO}_4 \downarrow + 3 \text{SO}_4^{2-}$ (same as alum)	12.7	5-7	Generally harmless
Alum	Liquid	$\text{Al}_2(\text{SO}_4)_3 + 2 \text{PO}_4^{3-} \rightarrow 2 \text{AlPO}_4 \downarrow + 3 \text{SO}_4^{2-}$	12-13.8	5.5-8.2	Chances of pH reductions may cause acidification, flocs may cause suffocation of the benthos
Calcite	Slurry	$3 \text{Ca}^{2+} + 2 \text{PO}_4^{3-} \rightarrow \text{Ca}_3(\text{PO}_4)_2$	6.4	5-6	-

4.3 Artificial Floating Islands (AFIs)

It is an innovative technique which comprises aquatic (sometimes terrestrial) plants growing in constructed buoyant frames hanging on the surface of lake or other water bodies. The plants roots are hydroponically buried within the water column and consume nutrients (N and P) directly from water column which enhances the accumulation of nutrients in biomass. The nutrients (N and P) concentration in water bodies is gradually decreasing which improve the water quality. It helps in the conversion of different pollutant in to readily available nourishments and various other by-products for plants growth and microbial activities. Different micro-organisms attached in AFIs help in water purification. Thus, AFIs plays a significant role to eradicate lake eutrophication by reducing the concentration of TP and TN (Li, et al., 2013; Shane, 2014) as shown in Figure 9.

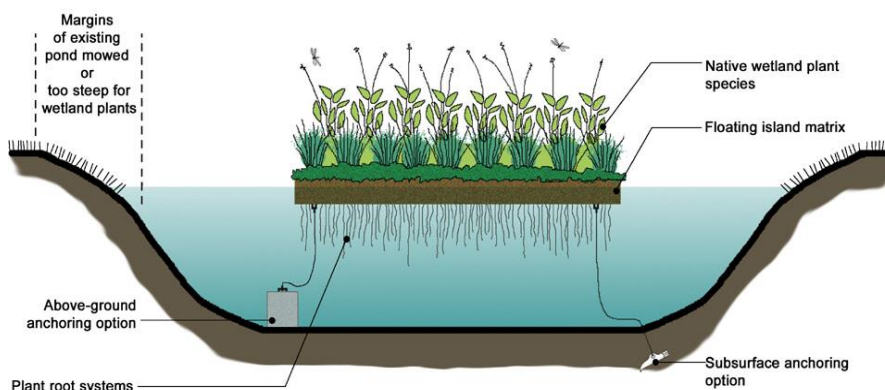


Figure 9. Artificial floating Island (Texas Community Watershed Partners, n.d.)

5 Sediments

This chapter addresses sediments compositions, dredging and sediments remediations techniques. Various possibilities of sediments use as a source of phosphorus are also discussed in this section.

5.1 Lake Sediments

Lake sediments consist allochthonous and autochthonous constituents. The allochthonous constituent is originated outside and carried to lakes by rivers, streams, runoff, wind, and underground/subsurface drainage. It contains various components such as fluvial(river) or aeolian(wind) clastic components, soluble salts, macrofossils, plant debris, pollen, charcoal. The autochthonous constituent is originated within the lake biogenically. It is also formed through inorganic precipitation within the lake water column (Bradley, 2015).

Lake sediments can be arranged into three categories based on their components. They are clastic sediments, chemical sediments, and biogenic sediments. Clastic sediments contain allochthonous components such as quartz grains, sand, clayey silt, silt, clay deposited by physical processes of sedimentation at the bottom of lakes. Various inorganic or biologically arbitrated chemical processes help in the formation of chemical sediments. Chemical sediments are formed within lake (autochthonous) by precipitation, recrystallization of detrital evaporites, siliceous and calcareous debris. The chemical constituents

are calcite, halite, pyrite, and Gypsum. The fossil remains of various former living organisms such as ostracods, diatoms frustules, molluscs or algal organic matter help in the formation of biogenic sediments. The biogenic sediments are peat, coal, diatom debris, and coquinas (detrital limestone comprises shell or shell fragments) (Schnurrenberger, et al., 2003).

5.2 Dredging

The dredging consists of four phases such as excavation, lifting, transportation, and disposal of sediments (Rajan, 2014). It is the process of removing the nutrient-rich bottom sediments from lakes or other water bodies to reduce the internal cycling of nutrients (N and P). The dredged sediments may also contain various toxic substances and heavy metals along with nutrients (P and N). These should be transported and deposited properly to other location without releasing any toxic substances. This technique is considered as one of the viable method of sediments management though it is relatively expensive. It is most useful in shallow eutrophic lakes (Jeppesen, et al., 2009).

The normal condition and operation of the lakes should not be affected during dredging. Generally, there are hydraulic and mechanical dredgers. In hydraulic dredging, sediment mixed with water is excavated and transferred to the dump sites or landfill. In mechanical dredging small buckets mounted on a chain to shove, lift, and transport the excavated sediments (Jain & Singh, 2003).

5.3 Types of Dredgers

Dredgers can be broadly classified in to two types based on the method used to transport sediments from the bottom of water bodies to the surface. These are mechanical dredging and hydraulic dredging.

5.4 Mechanical Dredgers

Mechanical dredgers dig and extract the sediments from the bottom of lakes or other water bodies by using bucket or clamshell (Airboat & Marsh Excavator Service, 2016).

There are different types of mechanical dredgers such as bucket dredger, grab dredger, and backhoe/ dipper dredger.

5.4.1 Bucket Dredger

It is also called a bucket ladder dredger. It is a stationary and one of the oldest type of dredger. This dredger contains series of buckets which are mounted to the wheel to collect the sediments by using mechanical process. The water added to the extracted sediments is very minimal in this dredger. Wide varieties of materials such as soft rock, corals can be collected and removed by using this dredger. Excessive noise pollution is the main drawback of this dredger (International Marine Consultancy, 2012; Marine Insight, 2016). The diagrammatic representation of bucket Dredger is given below in Figure 10.



Figure 10. Bucket Dredger (Demas, n.d.)

5.4.2 Grab Dredger

It is a stationary dredger which contains a revolving crane equipped with a grab, fixed on a hopper vessel or pontoon. It is useful to remove loose sand, silts, clays, rubbish, old piles, and rubble from the water bodies (International Marine Consultancy, 2012; Marine Insight, 2016). Figure 11 shows the main features of grab dredger.

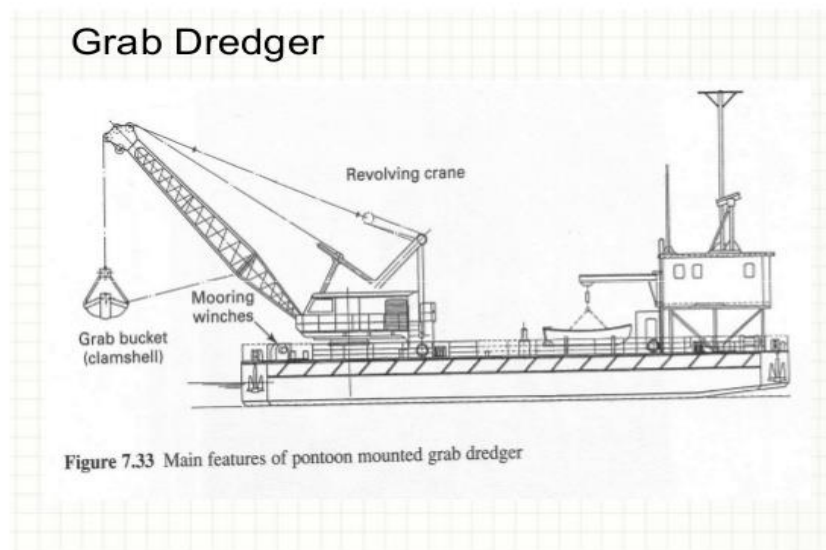


Figure 11. Grab Dredger (Rajan, 2014)

5.4.3 Backhoe Dredger

It is stationary, shelf-propelled dredger which have a digging bucket like onshore excavator which digs the sediments from the bottom and carries to the transport-barge (sediments collection place). The wide range of materials such as clay, sand, pebbles, rocks, muds, boulders can be removed from the bottom of the water bodies by using this dredger (International Marine Consultancy, 2012; Marine Insight, 2016). Figure 12 shows a diagrammatic representation of backhoe dredger.



Figure 12. Backhoe Dredger (Dharti Dredging and Infrastructure Ltd., n.d.)

5.5 Hydraulic Dredgers

Hydraulic dredger is a powerful floating machine which withdraws the bottom sediments by sucking the mixture of water and sediments (slurry) and helps to transport the slurry on shore or on board by using floating pipes. Different kinds of hydraulic dredgers are suction dredger, cutter suction dredger, and trailer suction hopper dredger (Airboat & Marsh Excavator Service, 2016).

5.5.1 Suction Dredger (SD)

It is a stationary dredger used to extract the sand from the depth of the water bodies. It consists the suction pipe which is pushed vertically in to the sand to extract the sand and collect the sand in to barges or reclamation area by sing a pipeline. Modern suction dredger helps to remove sand or other sediments from high depths up to 100m (International Marine Consultancy, 2012). Suction dredger is shown in Figure 13 below.



Figure 13. Suction Dredger (Engineers Daily , n.d.)

5.5.2 Cutter Suction Dredger (CSD)

Cutter suction dredger (CSD) is a stationary dredger. It consists a rotating cutter head at the suction inlet. A cutter head helps to break hard soils, and sediments. The water-resistance pump is used to suck the sediments or soils and discharge them by using a pipeline (International Marine Consultancy, 2012; Marine Insight, 2016). Figure 14 shows the main features of cutter suction dredger.

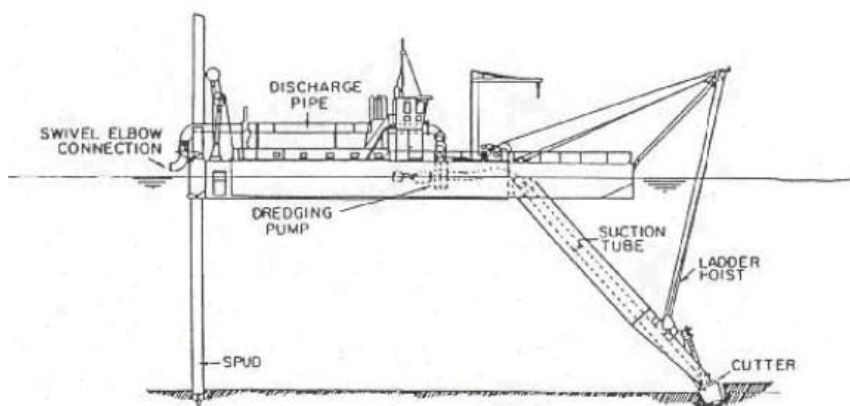


Figure 14. Cutter Section Dredger (Standards Development Branch, Ontario Ministry of the Environment, 2011)

5.5.3 Trailer Suction Hopper Dredger (TSHD)

It is a self-propelled, mobile vessel which has capacity to excavate, transport, and discharge sediments or other seabed constituents. It contains centrifugal pumps, blades in drag-head, and water jets to shave and disintegrate sediments and transport it as a slurry. This dredger is suitable for removing non-cohesive constituents like sand, and loose silts (Western Dredging Association, 2018). Figure 15 shows the main features of trailer suction hopper dredger.

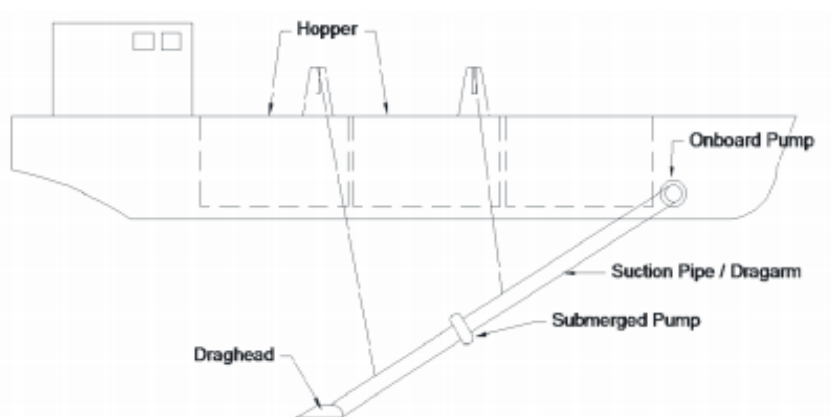


Figure 15. Trailer Suction Hoper Dredger (Western Dredging Association, 2018)

5.6 Sediment Remediation Techniques

This section contains various techniques related to sediment dewatering, and effective removal of associated contaminants. Dredged sediments contain different types of environmentally hazardous contaminants which should be removed from sediments before disposing sediments or utilizing sediments as a source of fertilizers in agricultural land.

5.6.1 Sediments Dewatering techniques

There are mechanical, physical, and chemical techniques to remove the water from sediment slurries. Dewatering helps to reduce the volume of slurry remarkably and also decreases the sediment toxicity. The different types, properties and mechanisms of these techniques are given in the Table 3 below (BCI Engineers & Scientists, Inc, 2007):

Table 3. Dredged Sediments Dewatering Techniques

Type	Classification	Explanation
Geo-textile tubes	Passive	These tubes contain highly durable polypropylene fabric filled by a system of pumping dredged slurries. Fine-grain sediments are retained in tube by releasing effluent water through the tube wall.
Polymers	Chemical assist	Polyacrylamide polymers are used to solidify or coagulate and flocculate slurries. Other chemical may be used in dewatering and settling sites.
Centrifugation	Physical	Flocculated sediments are subjected to huge centrifugal force in feed port of centrifuge. Solids are separated from liquid due to the difference in specific gravity.
Thermal dryer	Physical	Removal of water from sediment slurries by drying. 90% of solids in sediment slurries are separated. It comprises preliminary drying, essential drying and final drying to evaporate water from slurries
Filter press	Mechanical	Slurry is passed in to the filter press and at the end there is formation of filter cake.
Belt press	Mechanical	It contains gravity drain site where flocculated sediment slurry/sludge is passed and sediment slurry spins and outspreads over the belt. It helps to release liquid from the slurry and drain through the cloth and drain pan. Again, the sediments are squeezed in porous belt cloth to remove water. finally, there is formation of cake.

5.6.2 Types of Contaminant in Sediment

There are mainly two types of contaminants in sediment. They are organic and inorganic contaminants. Different types of organic and inorganic contaminants are given in the Table 4 below (Reis, et al., 2007).

Table 4. Sediment Contaminants

Organic contaminants	Inorganic contaminants
Hydrocarbons (light and heavy)	Heavy metals (Hg, As, Cd, Cu, Ni, Pb)
BTEX (benzene, toluene, ethylbenzene, and xylene)	Radionuclides
Oxygenated hydrocarbons	
Chlorinated hydrocarbons	
Halogenated and non-halogenated pesticides	
PAHs (Polycyclic Aromatic Hydrocarbons)	
PCBs (Polychlorinated Biphenyls)	
Dioxins	
Furans	

5.6.3 Contaminated Sediment Treatment Techniques

Various techniques can be used to remove the contaminants from the dredged sediments. These techniques are bio-slurry technique, composting, chelation technique, oxidation technique, incineration, and pyrolysis. The technique, its description and applicability are summarized in the Table 5 below (Reis, et al., 2007).

Table 5. Sediment Treatment Techniques

Techniques	contaminants removal	Description	Drawbacks
Bio-slurry	Pesticides, fuels, PCBs, PAHs, creosote, halogenated compounds, BTEX, hydrocarbons, halogenated and non-halogenated VOCs and SVOCs	It is biological technique to treat fine-grained contaminated sediments by using bioreactor. Convenient microorganisms are mixed in sediments. Mostly aerobic but also anaerobic treatment for	Heavy metals and chlorines available in dredged sediments can restrict microbial

		biodegradation are applied.	degradation. Low organic pollutants destruction efficiencies.
Composting	Biodegradable organic contaminants, explosives (TNT, RDX, and HMX)	It is biological treatment process. water, oxygen, and nutrients are added for bacterial growth. It degrades contaminated sediments in to less-toxic compounds.	Slow procedure, large land area needed, not effective to remove PAHs, and heavy metals
Chelation	Heavy metals	It is the process of forming stable complex. Chelating agents such as EDTA, DTPA, NTPA, TEDTA, IDA, NTA, EDDA are used to binds metals and form stable, inert complexes.	Not effective for organic compounds
Oxidation	Pesticides, PCBs, dioxins, furans, hydrocarbons, amines, phenols, cyanides	It degrades the organic contaminants in sediments in to less toxic and bioavailable forms. Oxidizing agents such as H_2O_2 , peroxone ($H_2O_2+O_3$), $KMnO_4$, $Ca(NO_3)_2$, and O_2 with or without UV light.	May need post treatment, not applicable for all PAHs
Incineration	Organic contaminants	It is organic contaminants destroying technique by burning sediments in the presence of	Not effective to remove heavy metals. Proper

		oxygen with proper emission control system	emission control challenge.
Pyrolysis	Pesticides, SVOCs	This technique involves heating the sediments in the absence of oxygen to destroy pollutants. It comprises primary and secondary combustion chamber along with pollution control devices. Hydrogen gas can be used to remove chlorine atoms from dioxins, PCBs.	Expensive technique, may require pre-treatment, emissions

5.6.4 Uses of Sediment

Sediment is a valuable resource. It can be used in various fields rather than being disposed in a landfill. Disposal of sediment into landfill is not a sustainable solution. The contaminant-free sediment after treatment is an essential nutrient resource which can be used in agricultural land to enhance agricultural productivity, parks and meadows. It can also be used as a resource in concrete production, construction industry and brick manufacturing industry. It has been reported that 50% of natural clay used in brick manufacturing can be replaced by sediments. Fine-grained sediments can be used as an alternative of sand in many construction sites (Junakova & Junak, 2017).

6 Recovering Methods of Phosphorus from Lake Sediments

Phosphorus releases from lake bottom sediments play a significant role in lake water. It contributes to higher amount of nutrient accumulation to stimulate the growth of algae which enhance the risk of eutrophication. Thus, it is necessary to extract phosphorus from sediments to improve lake water quality. The extracted phosphorus can be used in various purposes to fulfil the demand of phosphorus.

6.1 Sequential Extraction (SEDEX) of Phosphorus

This method has been developed to separate, extract or identify different types of phosphorus associated in the lake sediments, marine sediments or soils. It is one of the most promising techniques regularly used to study the availability of phosphorus in sediments, and soils. Different types of phosphorus in sediments are loosely sorbed P, P bound with ferric iron, detrital apatite P, calcium associated P, and organic P. This method is interpreted based on reactivity of a certain phase in a given extractant. It is difficult to evaluate and determine the efficiency of extractant and accuracy for a given phase. The SEDEX technique generally comprises five different steps to separate different types of sedimentary P mentioned above. The diagrammatic representation of SEDEX technique is given below. In the steps before III the solution pH of MgCl_2 and Citrate-Bicarbonate solution are adjusted to reduce dissolution/dispersal of carbonates. Detrital apatite and authigenic carbonate fluorapatite (CFAP) can be separated by adjusting PH of the acetate buffer solution. The extraction using Citrate-Dithionite-Bicarbonate (CDB) is carried out at room temperature (many other processes recommend CDB extraction at 80-97 °C) to avoid the formation of iron sulphides. The extraction steps IV and V are used to identify inorganic P and total phosphorus (TP) on two different splits of sediments. In SEDEX technique, the residue from steps I, II and III are used in steps IV and V to extract Fluorapatite (FAP) and additional inorganic P which escape to extract in previous steps. Step V directly measures the organic P. The important points of this technique are as follows:

- Authigenic Carbonate Fluorapatite (CFAP) are chemically separated from Fluorapatite (FAP). CFAP denotes reactive phosphorus in sinks of oceans or lakes.
- This technique resolves the residual redistribution of phosphorus during extraction.
- Sediment residue can be used again and again (from step I to V) in this technique by washing it with MgCl_2 between extraction steps.
- This technique can measure very low concentration as low as 0.005 weight% P. Thus, it is suitable to extract even small amounts of phosphorus associated in lake or marine sediments.

This technique has the advantage of the aspect that various solid phases illustrate dissimilar reactivity towards various solutions. Most sensitive phases are removed first in a sequence. (Ruttenberg, 1992).

It is a well-known fact that different laboratories where sediment samples are stored for analysis have dissimilar environmental conditions. Mainly, oxygen and water content in

sediments may altered due to the laboratory environment if the samples are not preserved properly. The changes in PH and redox potential play a vital role to change the quantity of OP and Fe-P. The risk of redistribution of organic P coming from decomposition of organic matter due to adsorption onto Fe(III)-oxide -hydroxide if there is oxic environment. Golterman (1996) recommended to use fresh sediments instead of freezing or drying of sediments. Freezing or drying of sediments can change the extraction results (Wang, et al., 2013). Figure 16 illustrates the sequential extraction of different types of sedimentary P.

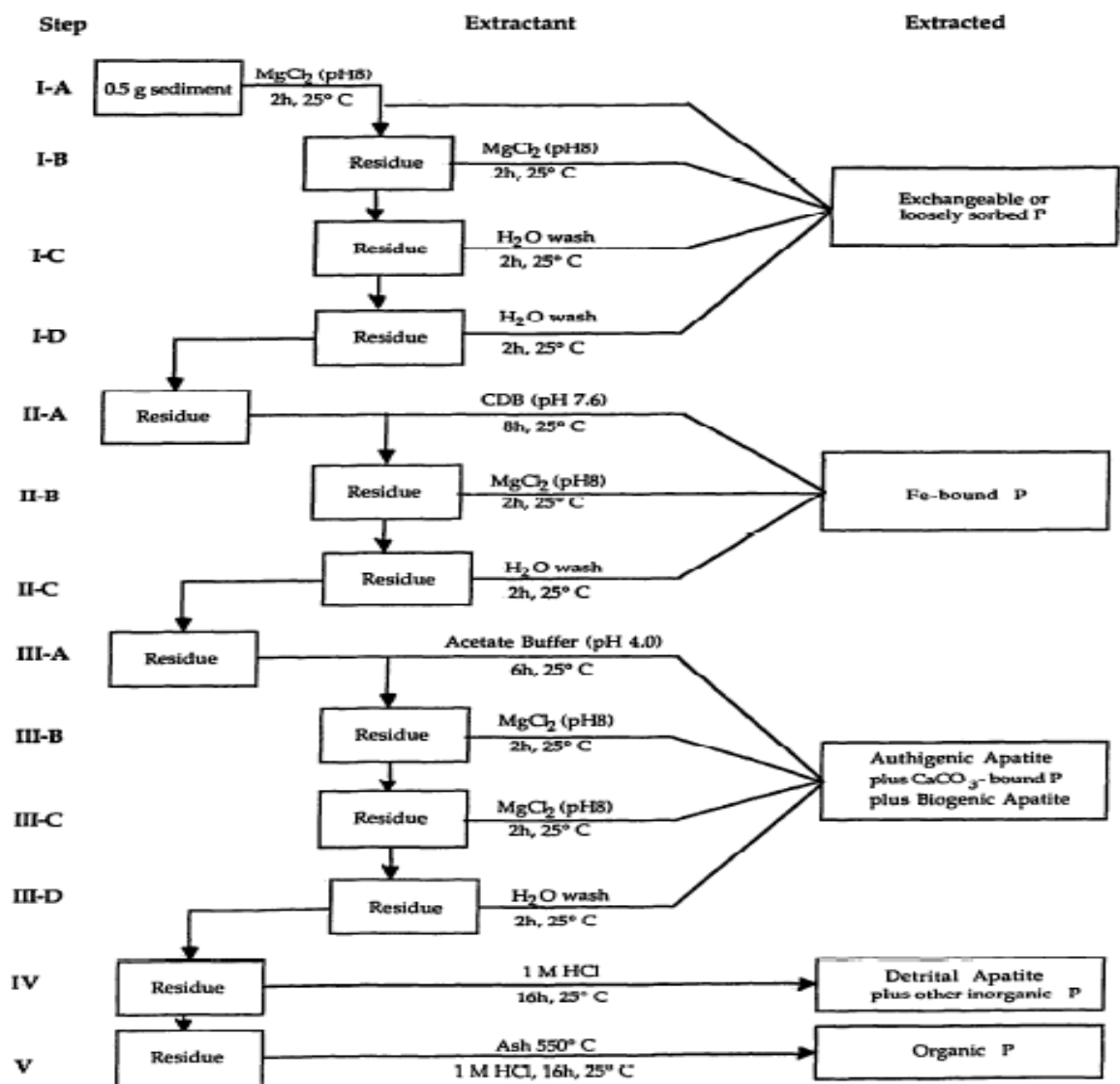


Figure 16. SEDEX Schemes for different types of Sedimentary P (Ruttenberg, 1992)

The mechanisms of various reactions in different steps are illustrated in the Table 6 given below (Ruttenberg, 1992).

Table 6 Reactions Mechanisms in SEDEX Technique

Steps	Extractant	Phase ex- tracted	Reaction
I	1M MgCl_2 (PH 8)	Exchange- a- ble/Loosely sorbed P	Forming MgPO_4^- complex and mass reaction displacement of Cl^-
II	0.3M Na_3 - citrate 1M NaHCO_3 (PH 7.6) 1.125g of Na-dithionite in 45mL of citrate bicarbonate solution	Smoothly reducible or reactive Ferric-P	Fe^{3+} reduced by dithionite and following bonding by citrate
III	1M Na-acetate buffered to PH 4 by using acetic acid (CH_3COOH)	CFAP plus biogenic hydro-apatite plus CaCO_3 -P	Occurrence of acid dissolution at moderately low PH And bonding of Ca^{2+} by acetate
IV	1M HCl	FAP	Acid dissolution
V	Ash at 550°C 1M HCl	Organic P	Dry oxidation at 550°C 1M HCl extraction of residue associated with ash

6.2 Perchloric Acid Method

In this process, dry sediment (0.15-0.20g) is taken and mix it with 10 ml deionized water and 2 ml concentrated nitric acid (HNO_3) in a 100 ml Erlenmeyer flask. Initially, there is oxidation by evaporating water and HNO_3 on a hot plate.

Then, 2 ml concentrated perchloric acid (HClO_4) is added and boiled it until it becomes completely clear. Finally, the sample is cooled and diluted up to 100 ml in a volumetric flask. The aliquot (final sample) is taken to determine orthophosphate. Here, Orthophosphate is extracted by using ascorbic acid reduction method of Murphy and Riley (1962).

6.3 Ignition Method

In this process, dry sediment sample (0.15-0.20g) is ignited by using muffle furnace in a porcelain crucible. The temperature is maintained to 550°C for 1 hour. After 1 hour, the residue is cooled and wash it with 25 ml 1 N HCl in a volumetric flask and boiled for 15min on a hot plate. Then, the sample is diluted in a 100 ml volumetric flask. Orthophosphate is extracted as in the perchloric acid method (Anderson, 1976).

One experiment was performed by collecting the sediment samples from four different types of lakes in Denmark. The upper 20 cm sediment samples were collected by using kajak bottom sampler and dried at 103°C. Then, the samples were grinded and taken it as dry sample to determine orthophosphate by using perchloric acid method and ignition method. The name of lakes and their characteristics are given in the table 3 below (Anderson, 1976).

Table 7. Lake Types and Characteristics

Lakes	Maximum depth (m) and types	sediments	Loss in ignition of dry weight (%)	Calcium dry weight (mg g ⁻¹)
Esrum	32, Eutrophic, Alkaline	Gyttja (bottom sediments rich in organic constituents)	35	98
Furesø	36, Eutrophic, Alkaline	Calcareous and Gyttja	11	176
Gribsø	11, Humic, Acidic	Mixtures of Gyttja and humic colloids	29	4
K vind sø	2.5, polluted by sewage sludge, Alkaline	Gyttja	35	6

The amount of phosphorus in dried sample after experiment by using above two methods are given in the table 8 below (Anderson, 1976).

Table 8. Phosphorus Determination from Lake Sediments

Lakes	Perchloric acid method (mg P g ⁻¹ sediment)	Ignition method (mg P g ⁻¹ sediment)
Esrum	2.109	2.061
Furesø	1.387	1.369
Gribsø	1.356	1.280
K vind sø	2.495	2.507

6.4 Bioavailable phosphorus extraction from sewage sludge ashes and from bottom sediment ashes

A research about phosphorus recovery from ashes of bottom sediments of water reservoir and municipal sewage sludge was conducted in Poland. Bottom sediments were taken from the dam of the “Jezioro Turawskie Duze” reservoir (Poland). The bottom sediment sample was ignited at 600°C for 3 hours. The sewage sludge sample was taken from municipal sewage sludge incineration plant located in Nowiny (Poland) ignited at 850°C. Total phosphorus (TP) can be extracted with ICP-MS after microwave digestion in aqua-regia. Six methods were used to assess the amount of bioavailable phosphorus in bottom sediments ashes and sewage sludge ashes. They were as follows:

- Distilled water extraction (WE method) (1:20 w/v i.e. ratio of mass and volume of ashes and extractant) in duration of 22hours. Then centrifugation was done, and Supernatant was filled with 0.2 cm³ 0.12 M MgCl₂. Again, Centrifugation was done.
- Extraction by using 2% citric acid. (CA method)
- Extraction of phosphorus by using Trough’s reagent (TS method) i.e. 0.002 N H₂SO₄ +0.3% (NH₄)₂SO₄. and it was buffered with pH 3.00. The ratio of mass volume ratio of ash and extractant was 1:200 and shaking time was 30 mins. Finally, an extract was obtained and marked calorimetrically by using the molybdate blue method.
- Egner- Rhiem (E-R) method by using 0.04 M calcium lactate along with lactic acid and maintaining pH 3.35 by buffering.
- P recovery with sodium bicarbonate. Maintaining pH 8.5 by buffering, according to the recommendation by Olsen (OLS) for alkaline soils. The ratio of ash and extractant was 1:20 and duration of shaking was 30mins.

- Golterman methods of phosphorus extraction from bottom sediments. This method is shown in the Table 9 below (Ciesielczuk, et al., 2018).

Table 9. Goltermann method of determining P-fraction

Stage	Extraction time(h)	Extractant	Fraction
G I	4	0.05 M ca-EDTA	P bound with ferric, aluminum, Manganese, and hydroxides
G II	18	0.1 M Na ₂ -EDTA	Carbonate bound P
G III	2	0.5 M H ₂ SO ₄	P from soluble compounds with organic constituents
G IV	2	2 M NaOH	Aluminosilicates bound P and residue remaining from stage III bound P

6.4.1 Results

It was found that the presence of bioavailable phosphorus in sewage sludge is comparatively higher (average over 30% of total phosphorus) while the bottom sediments also contain extractable quantities of phosphorus. The sewage sludge ashes contain 13.8-18.4% of total phosphorus whereas sewage sludge alone contain 2.97-6.64% of total phosphorus. The bottom sediments contain lower 4.6% of phosphorus although bottom sediments are still valuable for P recovery. The amount of bioavailable (P₂O₅) and total phosphorus after the experiment using above mentioned methods are given below in the Table 10 (Ciesielczuk, et al., 2018).

Table 10. P-recovery from sewage sludge and bottom sediment ashes

Methods	P in Sewage sludge ashes (g P ₂ O ₅ kg ⁻¹ d.w.)	Bottom sediment ashes (g P ₂ O ₅ kg ⁻¹ d.w.)
WE	0.002	0.002
CA	11.865	0.296
TS	3.749	0.283
E-R	4.424	0.578
OLS	0.558	0.252
G I	8.638	0.184
G II	32.07	0.176

G III	94.24	1.78
G IV	2.519	0.832
G-total	137.5	2.972
TP	184.2	4.621

6.4.2 Analysis

Sewage sludge incineration ashes were alkaline and bottom sediments ashes were neutral. Electrolytic conductivity of ashes was detected very high. Thus, ashes cannot be used as a fertilizer directly since, it could create threat to plant seedlings. In other hand, both bottom sediments and sewage sludge incineration ashes contain valuable nutrients such as calcium oxide (CaO), magnesium oxide (MgO), potassium oxide (K₂O). It proves their importance to use as a fertilizer and deacidifying agent for agricultural soils. Both bottom sediments and sewage sludge contain substantial quantity of phosphorus-rich organic constituents. Sediments can be used as natural fertilizer to enhance soil quality if the concentration of various heavy metals in sediments satisfy the legal requirements. The sewage sludge ashes generally contain high concentration of heavy metals such as zinc, cadmium, mercury, chromium, and lead. Thus, it cannot be used directly as a natural fertilizer (Ciesielczuk, et al., 2018)

7 Conclusion and Recommendation

Lake bottom sediments contain sufficient amount of phosphorus which can be extracted. However, sufficient researches about reliable, economic, and viable phosphorus recovering techniques in large scale have not been done yet. The laboratory scale experiments using perchloric acid method and ignition method as shown in Table 6 concluded that adequate amount of phosphorus is available in bottom sediments of eutrophic lakes which can be extracted and used in various fields. It has been found that phosphorus extraction from bottom sediment ashes (bottom sediments after ignition) is more convenient than that of direct extraction from bottom sediments without ignition.

Phosphorus-rich sediment dredging is a popular technique to restore lakes quality. The proper dredging techniques without disturbing an ecological environment of lakes still need to be developed. The proper utilization and management of dredged sediments are often challenging. Landfill disposal of dredged sediments should not be considered as a

solution. There are various techniques to remove inorganic and organic contaminants from dredged sediments, but they have certain limitations and high cost. The dredged sediments after treatment can be utilized as a source of phosphorus. Thus, dredging can be considered as an indirect recovery of phosphorus.

Deeper studies are recommended to develop environmentally-friendly and economically viable techniques to recover phosphorus from lake bottom sediments to enhance both phosphorus sustainability and environmental sustainability.

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