# Critical Review of Phosphorus Recovery Technologies from 'Waste' Streams

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## *Abstract*

*Phosphorus plays a vital role as a limiting nutrient for plant growth, but the majority of minable phosphate rock reserves are located in just a small handful of countries: South Africa, Jordan and Morocco. Therefore, Europe is totally dependent on imports, with phosphate rock recently being added to the EU list of critical raw materials. As result, it is necessary to immediately change our attitude towards food and 'waste' streams to assure sustainable food security for the coming generations.*

*We have analyzed different streams rich in phosphorus content and the P-recovery technologies. As from the 'simple' precipitation of struvite using the sludge liquor, to the 'chemical digestion of sludge using the Stuttgarter Verfahren technology without forgetting the more complex technologies applied to the sludge ash such as the AshDec process for P recovery that also integrates heavy metal removal and phosphate solubilization.*

***Key words:*** *Phosphorus, P-recovery technologies, sustainability, 'waste' streams, food security, emissions, fertilizers, Wastewater Treatment Plant (WWTP).*

## Introduction

Presently, we are living in an era of growing awareness, and the current way of living based on a constant depletion of fossil reserves is coming to an end.
Until recently, it was thought that phosphorus (P) reserves were not going to end. Instead of recovering phosphorus for further reuse, we have continued to mine it in other parts of the globe from non-renewable phosphate rock reserves and use it to replace the phosphorus that previously was lost or dumped as waste.
Recently, phosphate rock was added to the list of 'critical raw materials' from European Commission. Phosphorus is an essential element for the support of life on Earth; it forms part of DNA, ATP, and bones. It is impossible to synthesize in the laboratory, and it has no substitute. To maintain high agricultural yields, it is necessary to apply phosphorus based fertilizers. Therefore, to achieve food security, it is necessary to sustainably manage the phosphate rock reserves that remain.

Attention to sustainable phosphorus use is no longer singularly focused on reducing environmental impacts, but is also concerned to food security. That is, sustainable phosphorus use must ensure that all the world's farmers have sufficient access to phosphorus to produce enough food to feed humanity, whilst minimizing adverse environmental and social impacts.

### *Food Security and Fertilizers*

The use of mineral fertilizers has led to intensification and specialization of agriculture, as well as allowing the human population to grow through a more diverse and abundant diet. However, it also has led to less recycling of waste streams, which are not returned to the sites of production. Manure, for example, after the introduction of mineral fertilizers, was no longer seen as a valuable and vital resource for agriculture. Recycling, in general, and mixed farming in particular were from then on no longer a need. [1]

### *Losses*

The efficiency of mining and application of phosphorus is very low, only about one-fifth of the phosphorus mined for fertilizer production ends up being consumed by humans. Phosphorus losses occur in all stages between ‘mine to fork’, including mining losses, soil erosion (where the phosphorus eventually ends up in ocean sediments), crop losses and food losses (around 80% of the daily consumed phosphorus will be present in the excreta, making the wastewater a P-rich stream). Another important type of loss occurs in the waste sector when P-rich streams end up being locked in landfills, or in the sewage sludge.

### *Governance of Phosphorus Resources*

Phosphorus reserves are essential for food security, and their exhaustion is a possible scenario if unsustainably managed. The restrictions on fertilizers use are usually developed to avoid the impacts of excessive inputs in agriculture, which leads to eutrophication of water bodies, rather than by the fear of a possible shortage in the future. To ensure the efficient use of phosphorus, it is necessary not only to make global agriculture more sustainable, but to ensure further P recovery and reuse. Sustainability requires the prevention of direct losses, such as the losses resulting from mining and soil erosion, and the recycling of phosphorus from P-rich waste streams back to agriculture.

Sustainable management of P must map its stocks and flows to identify key points at which to minimize dissipation and increase recycling chances. [2]

### *P-Rich ‘Waste’ Streams and Recovery Technologies*

### *Meat and bone meal*

Meat and bone meal (MBM), a product from the rendering industry, can be used as a secondary resource. In the EU, USA, Australia, and New Zealand the use of animal by-products is extremely restricted due to the concern about BSE. These by-products are designated into three risk categories:

- Class 1: Must be incinerated,
- Class 2 and 3: Can be composted or digested for biogas production.

Chemical analyses of MBM indicate that the material contains substantial amounts of organic matter, nitrogen, phosphorus and calcium. The material should therefore be considered as a possible fertilizer. In order to recover its P content, the most efficient technology used is the mono-incineration, and the P is recovered from the ashes by acid digestion, or thermochemical digestion. [3]

### *Manure*

Manure is a P-rich stream, and can be used to substitute mineral fertilizers. In the event of intensive livestock farming, P is imported to the farm with animal feed. Most of the farmed animals, mainly the monogastric animals, such as chickens and pigs only use a very small part of the P present in the feed, whereas the majority is expelled in their excreta. P in the manure is mainly present in the inorganic form, meaning that is bioavailable for plant uptake. On the other hand, the use of manure represents some challenges, for instances: high transportation costs, is difficult to define the appropriate application rate, the risk of pathogen transmission, and odor effects. [4]

Although it needs to be processed, the N/P ratio is not suitable for the proper development of crops. The challenge offered by this stream is the transportation to regions that lack it. The separation between solid and liquid manure to a correct N/P ratio enables its transportation and storage. Otherwise, the local community would face a P surplus. An option to improve the transportability of P in manure can be to use it as input for energy production. Such as, anaerobic digestion systems intended for the production and combustion of methane gas ($CH_4$) as fuel for electricity generation. Anaerobic digestion does not influence the nutrients content in the manure. Yet, it reduces pathogens content, and the odors in raw manure are highly reduced in the effluent. Therefore, it improves the storage, transportation and application of manure. When of the combustion, majority of the nitrogen compounds are burnt, although P and potassium are present in the ash residues. These ashes are free from organic pollutants, and can be easily processed into P fertilizers.

***Table 1: P content in manure***

| | Liquid pig Kg P/l | Liquid dairy Kg P/l | Liquid poultry Kg P/l | Solid dairy Kg P/t | Solid beef Kg P/t | Solid poultry Kg P/t |
|---|---|---|---|---|---|---|
| Average | 1.4 | 1.0 | 1.0 | 1.4 | 1.0 | 9.0 |
| Minimum | 0.1 | 0.1 | 0.3 | 0.5 | 0.3 | 0.5 |
| Maximum | 3.8 | 10.1 | 1.7 | 7.7 | 5.9 | 25.2 |

***Wastewater***

Wastewater is an important source of P worldwide, it contains around 4.6Mt P yearly, which represents approximately 2% the world’s phosphate rock production.

It is necessary to recycle the nutrients from urban centers back to the food production areas to ensure food security for the society. Urban population is expected to each 9.6 billion by 2050. By that time, 4.7 Mt of P will be emitted to the wastewaters in urban areas, yearly. To be able to recycle P from wastewater it is fundamental to have an adequate sanitation structure- a wastewater treatment plant.

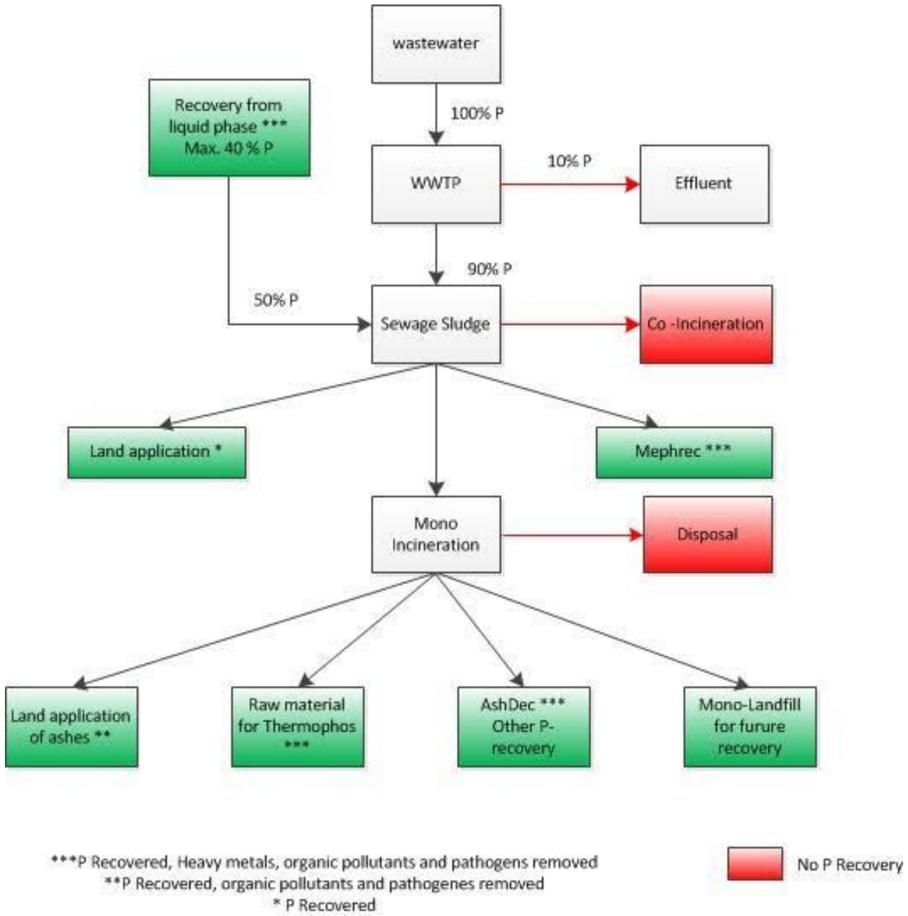


***Figure 1: Diagram of complete P recovery from sewage sludge and incineration ashes. (Source: Petzet and Cornel 2010; Petzet and Cornel 2011)***

WWTPs are important sources for the recycling and recovery of P, around 90 % of the influent P is transferred to the sludge phase by chemical precipitation or biological uptake. The chemical precipitation is less favorable for P extraction because are formed insoluble phosphate precipitates within the sludge matrix. On the other hand, biologically uptake P is released as soluble phosphate and consequently can be recovered as struvite or calcium phosphate.

P recovery from concentrated wastewater in WWTPs as struvite ($MgNH_4PO_4$) or calcium phosphate ($Ca_{10}(OH)_2(PO_4)_6$) is a simple, cost effective and proven technology. Although its potential use is limited, because it can only be applied to a certain type of wastewater treatment process, specifically to enhanced biological P removal (EBPR). P recovery it is limited to 30 %, and the remaining stays present in the sludge and in the effluent. [3]

***Sludge***

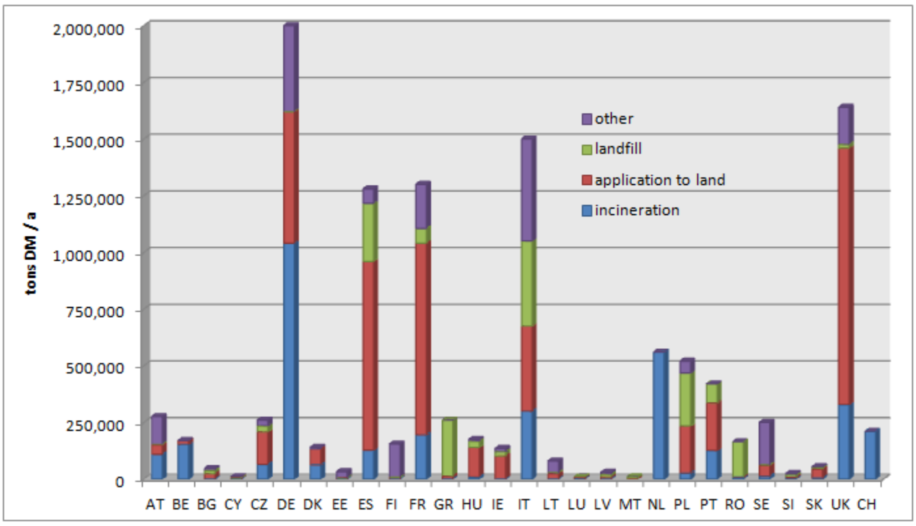


***Figure 2: Sludge valorization and disposal in Europe 2010. (Source: P-Rex, sustainable sewage sludge management fostering phosphorus recovery and energy efficiency)***

Sludge represents one of the most versatile P-rich streams. Currently, the majority of P-recovery technologies have been developed to use sludge as a secondary P-resource. These technologies can be applied to sludge liquor, dewatered sludge, as well as to sludge ashes from mono-incineration processes.

When the sludge is stabilized using anaerobic digestion it is possible to reduce its volume by methane production. The P present in sludge can be readily released from the poly-P-rich biomass to the liquid phase.
Recycling of digested and/or stabilized sludge to land is the simplest way to recycle the P present in the wastewater, although in some situations it is banned because of the environmental impacts of organic and inorganic pollutants that can be present in the sludge, or due to the lack of agricultural area near by the urban agglomeration.

By using the sludge liquor, it is possible to obtain struvite ($NH_4MgPO_4 \cdot 6H_2O$) by stripping off $CO_2$ with air from the liquor to increase the pH, and afterwards $MgCl_2$ is added to precipitate the struvite. This process has some definite advantages, for example the sludge's dewaterability is improved and problems with incrustation are avoided. On the other hand, the P-recovery efficiency is low (around 30%), and the possible present organic pollutants are not destroyed.

One of the processes applied to sludge after stabilization is acid digestion. Trial results indicate that acid digestion has higher efficiency at lower pH values. The final product is struvite, which is obtained at the pH of around 2.9 with 62% recovery efficiency.

Incineration of sludge is a practice that is often used. The sludge can be incinerated in monoincineration plants or coincinerated in power plants. When the sludge is incinerated the P is permanently tied to the resulting ashes and products, and its recovery it is not viable economically and technologically. When of monoincineration of sludge, P and non-volatile metals are concentrated in the ashes, which represent a good “source” for P recovery. Several processes exist for P recovery from ashes, which depend on the chemical composition. Contrary to sewage sludge, the organic contaminants (including pharmaceuticals and pathogens) are destroyed, and P can be solubilized by the addition of acid.

Phosphate rock can be substituted by sewage sludge ash. Although it is necessary to assure an low content of iron in the ashes, which can be accomplished by the use of aluminum instead of iron during precipitation or by the use of EBPR.

When sewage sludge and ashes from sewage sludge cannot be directly recycle to the soils, it is necessary to use technologies that will remove inorganic and organic compounds, and convert the P into a bioavailable form.  (Bellow are going to presented two technologies to recover P from sludge ashes)

The Ash-Dec process removes heavy metals by chlorides and thermochemical treatment of ashes at about 900-950ºC. An Ash-Dec plant could stand alone, but due to economical and environmental reasons makes sense to combine it with a monoincineration plant. This combination allows to feed hot ash from the monoincineration plant to the Ash-Dec facility.The flue gases can be treated at the monoincineration plant.

For this technology are necessary three raw materials: sewage sludge, dried sludge ( the reducing agent), and sodium sulphate.

Ash is directly charged (at 850ºC) from the monoincineration plant (if not, it needs to be preheated) with the preheated sodium sulfate (to 450ºC), which is separated from the off gas by a cyclone. Afterwards it is added to the kiln together with sludge and hot ash. The thermal reaction takes place in the kiln in counter flow. [5]

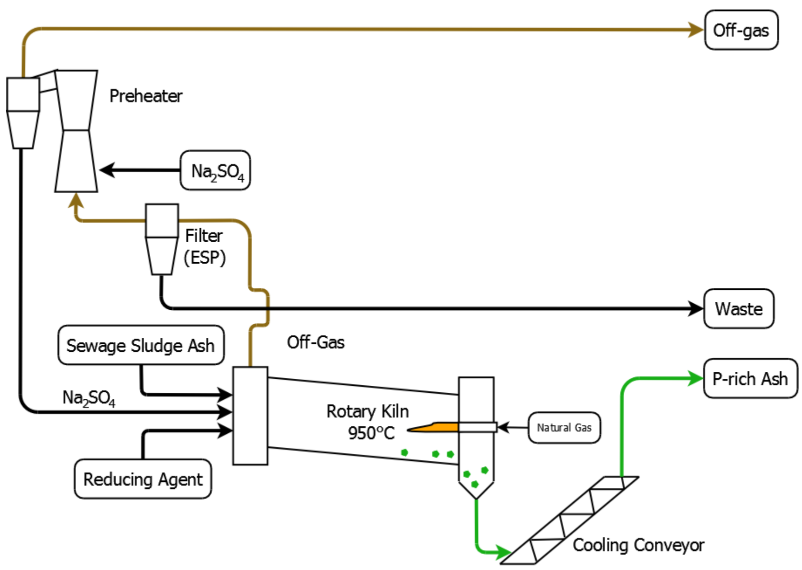


***Figure 3: Ash-Dec process Flow chart. (Source: P-Rex, sustainable sewage sludge management fostering phosphorus recovery and energy efficiency)***

Leachphos is a process that consists of a serial of leaching and precipitation steps. The first step is a leaching of sewage sludge with dilute sulphuric acid in a stirred batch reactor for 20-30 minutes. The dissolution of P and metals depends on the sulfuric acid concentration and on the solid/liquid ratio. About 70-90% of P in the ash is dissolved into the leachate. Afterwards takes place a solid/liquid separation in a vacuum belt or filter press. Consequently the sludge ash filter cake is removed from the process and must be disposed. The P containing liquid is pumped to another stirred reactor where the dissolved P precipitates due to the addition of lime (CaO) or caustic soda (NaOH). At higher pH values are obtained higher yields of P precipitated, but on the other hand are also precipitated more heavy metals. The final product has a concentration of around 30% $P_2O_5$. [5]

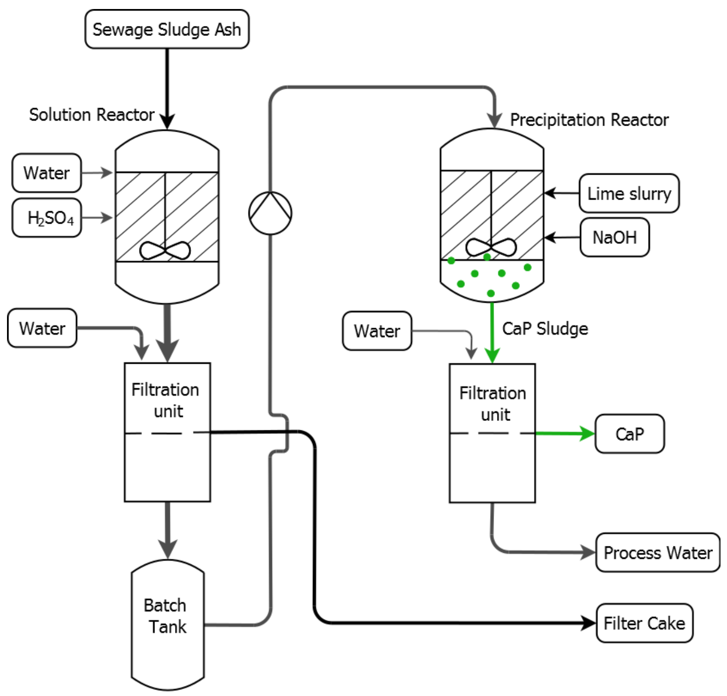


***Figure 4: Leachphos process flow chart. (Source: P-Rex, sustainable sewage sludge management fostering phosphorus recovery and energy efficiency)***

## Conclusion

*Losses of phosphorus are unavoidable in mining, processing, and use. Depending on the sink, the dissipated phosphorus can be recovered for subsequent recycling. Phosphorus recycling has diverse scales and contexts: from farms, to households, to megacities. A critical challenge for sustainable phosphorus use is to make phosphorus recovery economical, reliable, and predictable while ensuring that recycled phosphorus products will not have adverse health or environmental impacts. Therefore, it is fundamental to manage phosphorus stocks and flows, including the concepts of dissipation, eutrophication and recycling. The stakeholders involved are very diverse: industries, agricultures, NGO's, and researchers that should be working together towards sustainable phosphorus use.*

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