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Phosphorus in Water Quality and Waste Management

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1. Introduction

Phosphorus (P) is a key element for all living systems. Phosphorus is a component of DNA and RNA and indispensable for the energetic metabolism (ADP/ATP) of living beings. Phosphorus cannot be substituted in these biological functions by any other element. The tremendous growth of global population is therefore linked to a proportional increase of phosphorus requirement for the production of food, which actually to a large extent is depending on the use of mineral phosphorus fertiliser.

Many natural (aquatic) ecosystems are controlled by restricted availability of phosphorus which represents one important factor for high biodiversity. The anthropogenic increase of phosphorus flows therefore has the potential to cause severe negative effects on natural (aquatic) ecosystems (see section 2).

Roughly 80 - 90% of the extracted phosphate rock is used for food production and nutrition. Given that P is a non-renewable resource and the global reserves are limited (contrary to nitrogen another essential nutrient) the aspects of scarcity and recycling/recovery have to be considered. Today's global mine production and reserves of phosphate rock (average P_2O_5 content is 31 % (P 13.5 %), ranges from 26 - 34 % (P 11 - 15 %) (Kratz et al, 2007; Steen, 1998) are reported ca. 160 Mio t/a and 16 billion tons, respectively (USGS, 2010). This gives a static lifetime for the reserves of some 120 years, a number which has been similarly reported by several authors before (Röhling, 2007; Wagner, 2005; Rosmarin, 2004; Pradt, 2003; Steen, 1998; Herring et al., 1993), others come to lifetimes up to hundreds of years (EFMA, 2000).

Phosphate ore is produced mostly from open pit mines, resulting in dust emissions and large quantities of tailings (mining wastes). Villabla and colleagues (2008) report material and energy consumption data for the production of 1 ton of P_2O_5 (Table 1). Another major waste is produced at a later stage when wet phosphoric acid (H_3PO_4) is produced from phosphate rock concentrate using sulphuric acid. This so-called phosphogypsum (ca. 5 tons per ton of wet H_3PO_4) is normally disposed of at sea or in large-scale settling ponds. It has very little use because it contains a considerable number of impurities such as Cadmium and radioactive elements (Villabla et al., 2008).

Attention: in historic literature phosphorus content of products or minerals is mostly expressed as P_2O_5 which corresponds to 0,44 P. Actually there is a trend to relate all data to P as element.

The above mentioned coverage times show that there is no urgent scarcity problem appearing at the horizon but the following aspects are worth to be considered: First, the relevant reserves of phosphate rock are highly geographically concentrated in China, Morocco & Western Sahara, South Africa and the U.S. The world's largest producers are China, followed by the U.S., Morocco and Russia (USGS, 2010). Large economies such as Western Europe or India have virtually no domestic supply and are dependent on imports. This is one major ingredient for a geopolitically instable situation. Second, the quality of extracted phosphate rock is continuously declining, meaning that the content of hazardous substances such as Cadmium and Uranium is rising (Kratz & Schnugg, 2006; Van Kauwenbergh, 1997; Steen, 1998). This will require, e.g., the employment of costly decadmiation processes in the future if agricultural soil shall be further on protected and not be used as a sink for heavy metals. Third, population growth, nutrient conditions of soils in developing countries and changing nutrition patterns (changeover to a meat- and dairy based diet) will entail increased demand of fertilisers. The Food and Agriculture Organisation predicts annual growth rates between 0.7 to 1.3 % until 2030 (FAO, 2000) which would mean an increase of some 25 % in phosphate rock consumption compared to now. The Population Division of the Department of Economic and Social Affairs of the United Nations Secretariat predict 9.2 billion people in 2050 (+37 %) (UN, 2008). Considering these facts similar market effects and price volatility as currently are the case for crude oil have to be anticipated for phosphorous fertilisers in the future (Fig. 1).

Production Stage	Input	Output
Mining	Electricity 697 MJ	Waste 21.8 tons
	Diesel 125 MJ	Mine water
	Explosives 3,3 MJ	Diesel exhaust gases
Mineral processing	Water	Waste water
	Electricity 1,128 MJ	Tailings 6.5 tons
	Flotation reagents	
	Diesel 396 MJ	Diesel exhaust gases
Total primary, energy consumption		ca. 5,500 MJ
Total solid waste		ca. 28 tons

Table 1. Material and energy consumption for the production of 1 ton P_2O_5 (= 0.44 t P), adapted from Villabla et al. (2008).
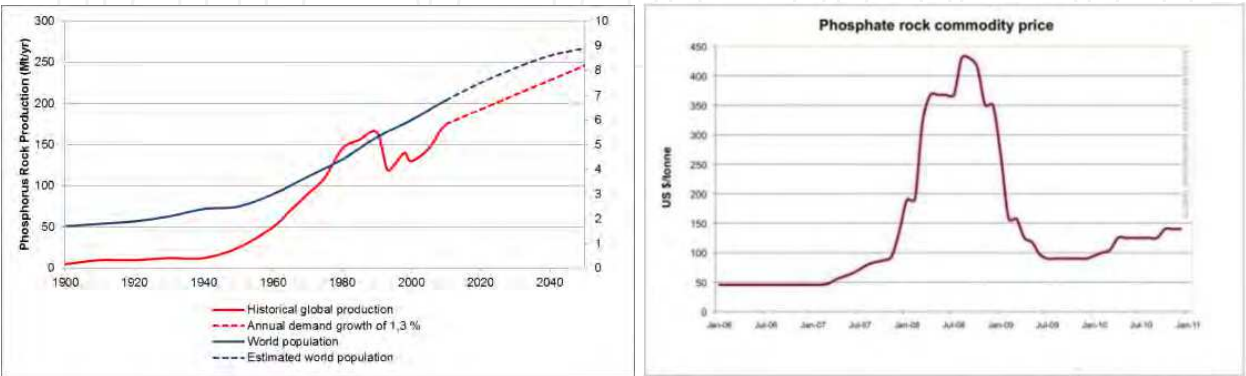

Fig. 1. a) Phosphate rock production and world population (historic situation and future trends); b) Phosphate rock commodity price 2006 – 2010

Mankind's usage of P is rather non-circular and dissipative. Bacinni & Brunner (1991) established a P-balance for the 1980ies where it is shown that the use of P is inefficient (only 10% of P employed in agriculture is contained in the food) and large losses occur to the soil and the hydrosphere. These findings still hold and today there is consensus that effective phosphorous management in agriculture and waste water is of upmost importance. Considering the above mentioned today's goals for P management in a region could be: Keeping soil fertility under minimized P fertilization, reducing surface emissions to the hydrosphere, reducing point emissions to the hydrosphere and increasing recycling.

In countries with centralised waste water infrastructure sewage sludge is a by-product a result of fulfilling a legal requirement for water protection by waste water treatment. Sewage sludge represents a relevant source for P-recycling, especially if P-removal from waste water is applied (UWWD, 1996) (see section 1.2). For example, Austria imported 31.000 t P/a in form of phosphate rock, fertilisers, food, and fodder in 2001 (Seyhan, 2006). The actual P content of sewage sludge in Austria is ca. 7,000 t P/a, which corresponds to a P-removal efficiency of ~ 85 % from waste water.

Sewage sludge is a waste according to actual legislation, as long as it cannot be marketed as a product (e.g. to phosphate industry substituting phosphate rock). The common practise to recycle the P-content of sewage sludge is its application in agriculture as fertiliser and soil conditioner. As sewage sludge also contains potentially hazardous substances (pathogens, heavy metals and organic micro-pollutants) this recycling path is subject to various legal constraints (US/EPA Biosolids Rule and NPDS, EU Sludge Directive 86/278, numerous national and regional sludge regulations, soil protection regulations) and is still a matter of controversial discussion even in the scientific community. (Engelhart et al., 2000; Brunner et al., 1988; Giger et al., 1984; Giam et al., 1984; Sjöström et al., 2008; Sandaa et al., 2001; Ghaudri et al., 2000; Giller et al., 1998)

In US and UK the main risk associated with sludge recycling is related to hygiene (pathogens) and there is a clear distinction between sludge and biosolids, the later being a market product meeting certain quality criteria. In parts of Europe the main risk is associated with soil and food protection (heavy metals and micro-pollutants). Beyond agriculture and waste water treatment plant operators and also food industry, food chain traders and retailers and numerous NGOs are stakeholders. Also the competition between sludge as P-fertiliser and manure application in countries/regions with extensive animal production has to be considered in this context.

Sludge application on land has strongly supported the reduction of emissions from point sources which was very successful for heavy metals where the concentrations in sewage sludge considerably decreased during past decades. Regarding the source control of micro-pollutants the discussion has started but as these substances to a large extent originate from market products the situation is much more complex than for heavy metals. Sewage sludge not meeting the actual quality criteria for land application or sludge produced in countries/regions where land application is banned (e.g. in Switzerland) have to be disposed of. Where landfilling of organic material, as sludge, is not allowed any more incineration has become a viable treatment option as ashes meet the criteria for landfilling.

At present sludges are incinerated in so-called mono-incinerators or co-incinerated in cement kilns, coal-fired power plants and waste incineration plants. Incineration destroys the organic sludge fraction including the micro-pollutants. Phosphorus and also most of the heavy metals are contained in the ashes. A favourable condition for P-recovery is only with mono-

incineration (maybe co-incineration with P-rich waste fractions) because only then P-rich ashes are produced which can be put to special storage sites for future recycling of P.

2. Phosphorus in water quality management

Phosphorus is the limiting nutrient for algae (autotrophic) growth in most fresh water bodies (lakes, rivers and reservoirs) and some coastal waters influenced by river discharges. The anthropogenic discharge of phosphorus to these waters therefore increases the potential for algae growth, which is the starting point of eutrophication. Eutrophication is characterised by increased availability of phosphorus for primary production (algae) which represents the basic substrate for the aquatic ecosystems. Even moderate anthropogenic increase of P availability influences the competition between the species which results in changes of the aquatic ecosystem.. Beyond certain thresholds of phosphorus discharge the ecosystems shift to a completely different status with steadily increasing deterioration of water quality.

In natural environments phosphorus is mainly present in particulate form as minerals with low solubility. The availability of phosphorus for plants and algae is therefore quite restricted. Hence in many natural aquatic ecosystems life is limited by phosphorus deficiency. The decay of the organic material produced by photosynthesis under aerobic conditions again results mainly in mineral phosphorus compounds in the sediments with low availability. Under anaerobic conditions decomposition process results in the release of phosphorus in dissolved and therefore easily accessible form.

Natural environments normally are characterised by restricted dissolved phosphorus flows. Soil erosion results in relevant phosphorus loads depending on the P-content of the particulate material either coming from natural rocks and soils or from agricultural land. As long as this material remains under aerobic conditions in the waters and their sediments, availability of phosphorus for algae growth is low. The main anthropogenic sources of phosphorus, except erosion, for the aquatic environment are (Lee et al., 1978):

- municipal and industrial waste waters
- drainage from agricultural land
- excreta from livestock
- diffuse urban drainage

Humans need a daily phosphorus uptake of 1.8 - 2 g P via their nutrition and discharge it with their excreta to the waste water. Most of this phosphorus is easily accessible for plants, in waters for algae and macrophytes. Waste water therefore has a great potential for enhancing eutrophication if not properly handled before discharge to the aquatic environment. Agriculture uses either mineral phosphorus fertilisers or manure to meet the phosphorus requirement for crop production. If correctly applied phosphorus is either taken up by the crops or retained in the topsoil. Only soils with low quality tend to release phosphorus compounds to the ground water, as e.g. at reclaimed agricultural areas from wetlands. For the assessment of the effect of phosphorus discharges to waters it is always relevant to investigate the availability of the phosphorus loads (particulate versus dissolved) and that this strongly depends on the redox conditions in the sediments.

2.1 Source of P in waste water

The main sources of phosphorus in waste water are the human excreta, phosphorus containing household detergents and some industrial and trade effluents. Precipitation runoff only little contributes to P-loads in waste water if combined sewer systems are

applied. Figure 2 shows the input and output loads of households in Austria, where P-free laundry detergents but phosphorus containing dish-wash detergents are used.

plant products 0,8 - 1,1

animal products 0,8 - 1,1

detergents ~ 0,2

households
Total waste water
1,6 - 2 g P/PE*d

urine 0,9 - 1,1
feces 0,4 - 0,6
others 0,3

waste 0,2 - 0,4

Fig. 2. Recent phosphorus loads from households (Zessner & Aichinger, 2003)

Industrial use of phosphorus is quite limited; relevant phosphorus loads in industrial effluents therefore are relatively low. P-discharges to waste water can origin from food and textile industry and from rendering plants. Industrial and trade contribution to P-loads in municipal waste water can vary in a broad range depending on local situations and is in a range of 10 to 40 %.

Historical development

In the 1970 and 80's the daily phosphorus load per inhabitant in municipal waste water was up to 5 g, the main source being the phosphorus containing laundry detergents. Due to the resulting eutrophication problems the removal of P-containing detergents from the market was achieved which resulted in the actual P-loads in municipal waste water of 1.4 - 1.6 g P/PE/d (1PE = 60 g BOD_5/d, or 120 g COD/d). Dish wash detergents still contain phosphorus and contribute to about 10% of the P-loads (ATV, 1997; ATV DVWK, 2004). This development makes P-elimination from waste water at treatment plants more economically and ecologically advantageous. Application of P containing dishwashing detergents is still increasing and therefore the development and application of P-free dish wash detergents are aimed at.

While phosphorus can be or has to be removed from municipal waste water, the biological treatment of industrial waste water often requires the addition of phosphorus As bacteria are able to store phosphorus the control of P-dosing is not easy. Low phosphorus availability favours the growth of filamentous bacteria (at activated sludge treatment plants), which results in bad settling and thickening properties of the sludge. Impairment of thickening properties of the sludge can be used as a sensible indicator of phosphorus deficiency. Severe P-deficiency strongly affects treatment efficiency. An excess dosing of phosphorus can result first in filling the P-storage capacity of the microorganisms and therefore will not immediately be detected by rising P-concentrations in the effluent. (Prendl et at., 2000; Nowak et al., 2000)

2.2 Phosphorus elimination

In most of the surface waters, availability of phosphorus limits the growth of algae and macrophytes. The discharge of P-loads contained in waste waters therefore normally results in an increased growth of algae and macrophytes which may cause reduced water quality by eutrophication. This is especially relevant for lakes and estuaries ("Sensitive Areas") but also can affect the quality of rivers. According to EU Urban Waste Water Directive (91/271/EEC) phosphorus needs to be eliminated from the waste water at treatment plants in sensitive areas.

The EU effluent standards for sensitive areas for total phosphorus (TP) are 2 mg/L for WWTP 10.000 - 100.000 PE and 1 mg/L for more than 100.000 PE or a minimum TP load reduction of 80 %. National standards can be even more restrictive especially for catchments of lakes or very sensitive coastal regions. Where environmental standards cannot be met by applying only the minimum requirements (effluent standards according to precautionary principle) much higher P-removal requirements can be prescribed for specific WWTPs (e.g. MURTHY, Chesapeake Bay, Blue Plains WWTP). Figure 3 shows a single step waste water treatment plant with its typical mechanical, biological and sludge treatment processes.
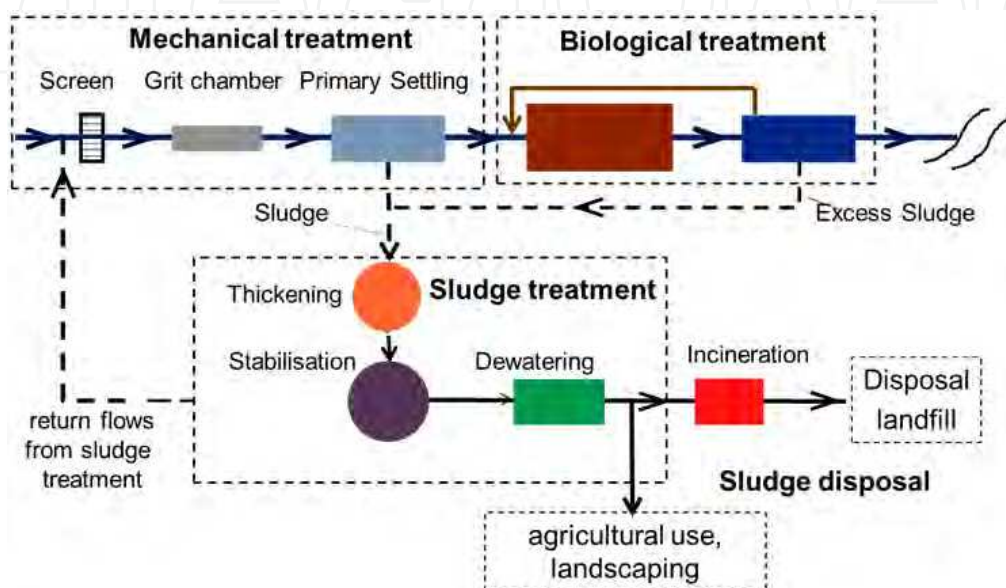
Fig. 3. Schematic of a conventional activated sludge treatment plant

2.2.1 Mechanical treatment
During mechanical treatment phosphorus contained in the particulate material is removed from the waste water together with primary sludge which results in a TP removal of 10 - 15 %. Biological incorporation, enhanced biological P-removal and chemical precipitation are state-of-the-art processes to reliably reduce P-load from waste water. The total phosphorus loads removed from the waste water in most of the processes applied in practice end up in the sludge. In principle the P-content of the sludge can be recovered and reused which is of increasing relevance for the long term availability of this limited resource.

2.2.2 Chemical-physical P-elimination
The most reliable and most frequently applied removal process is chemical phosphorus precipitation by addition of metal salts. Dissolved phosphorus is converted to solids which are removed from the waste water together with the sludge. If very low effluent concentrations < 0.5 mg TP/l) have to be achieved secondary effluents can be treated by flocculation filtration.

P-removal by precipitation is based on five processes (ATV DVWK, 2004):
1. Dosing: complete mixing of precipitants (metal cations: Fe^{3+}, Al^{3+}, Ca^{2+}) to waste water stream
2. Precipitant reaction: Formation of particular compounds as precipitant cations, phosphate anions and other anions.

3. Coagulation: destabilization of colloids in waste water and coagulation to micro-flocs
4. Co-precipitation and flocculation: Formation of separable macro-flocs. Inclusion of particulate matter, colloids as well as organic bounded phosphorus in these flocs
5. Separation: By sedimentation, filtration, flotation and a combination of these processes, macro-flocs will be separated.

The elimination of phosphorus is based on the precipitation of the negative charged dissolved phosphate (PO_4^{3-}) by a trivalent metal ion. Sources of these metals are ferric and ferrous chloride, ferrous chloride sulphate, ferrous sulphate, aluminium sulphate sodium aluminate. Except the last one which is alkaline all the other precipitants are acid. Phosphate compounds as $FePO_4$ and $AlPO_4$ with very low solubility product will be formed ($pK_L \sim 22$). Iron and aluminium have nearly the same effect, but the optimum pH for iron is about one unit lower than for aluminium. Iron-flocs have a higher density are more compact and more shear resistant than aluminium-flocs. These properties influence the separation process especially if pre- and post-precipitation processes are applied. With both metal ions PO_4-P effluent concentrations ≤ 0.1 mg/l can be achieved if dosage is sufficiently high.

$$Me^{3+} + PO_4^{3-} \rightarrow MePO_4 \qquad (1)$$

Theoretically one mole of Fe or Al is needed to precipitate one mole of P. Due to the different atomic weight of the atoms, the appropriate mass dosage needs to be calculated based on the molar weights (1 Mol P: 31 g; 1 Mol Fe: 56 g; 1 Mol Al: 27 g). The specific precipitant dosage (β-value) is the molar ratio between precipitant and phosphorus to be precipitated as e.g. described above for simultaneous precipitation.

$$\beta = \frac{mol\ phosphorus}{mol\ metal} \qquad (2)$$

But iron- and aluminium-ions also react with other compounds therefore more precipitants have to be added than theoretically necessary. With a chemical addition corresponding to a β-value of 1.5 an effluent PO4-P concentration below 0.5 mg/l (TP < 1 mg/l) can be achieved with simultaneous precipitation at activated sludge plants. Figure 4 is based on TP effluent data of full scale municipal treatment plants. It shows the relation between TP effluent concentrations and the β-factor applied for different P-removal techniques. As mentioned above satisfying P-effluent concentrations need a higher dosing of metal salts than derived from stoichiometry only. To precipitate 1 kg P theoretically 1.8 kg of iron (56/31) and 0.9 kg (27/31) aluminium are necessary (β-value of 1). For simultaneous precipitation it has to be considered that part of the phosphorus will be incorporated into the sludge and therefore needs not to be precipitated. For rough calculations it can be assumed that this incorporated phosphorus at least corresponds to ~ 1 % of the BOD_5- load in the influent to the biological treatment (e.g. 0.6 g P/PE_{60}). If enhanced biological P-removal occurs the precipitant requirement can only be derived from the operational experience on site based on effluent monitoring.

Crystallisation processes

By precipitation with calcium cations manifold reactions are known, which are hard to predict. High P-removal efficiency can be achieved at pH controlled crystallisation of calcium hydroxyapatite which has a very low solubility product ($pK_L \sim 59$). PO4-P concentrations below 0.1 mg/l can be achieved depending on the dosage.

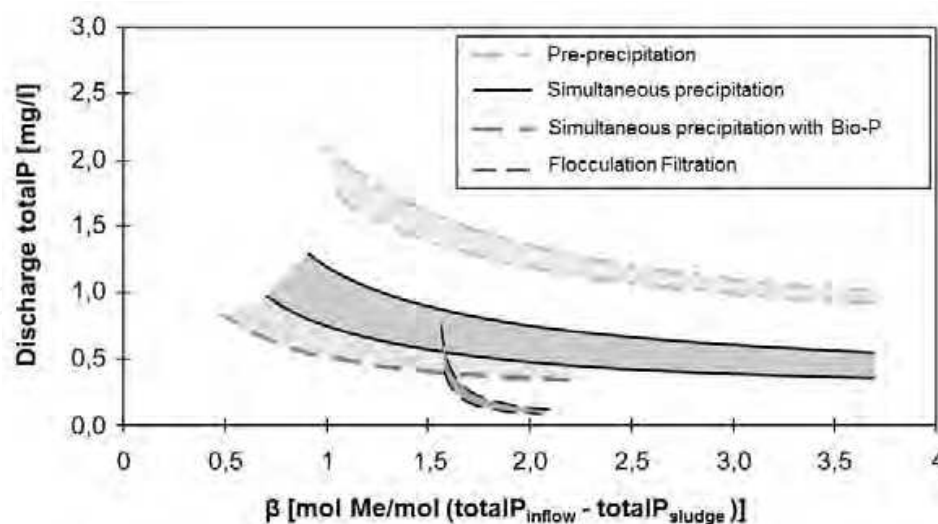$$5Ca^{2+} + 3PO_4^{3-} + OH^- \rightarrow Ca_5(PO_4)_3OH \qquad (3)$$
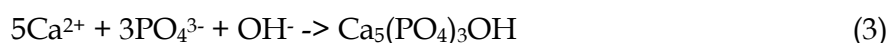
Fig. 4. P-discharge in relation to the β-factor (Nikolavcic et al., 1998)

Phosphate reacts also with magnesium and ammonium forming magnesium-ammonium-phosphate (MAP, struvite), a precipitation product with low solubility (Schulze-Rettmer, 1991). The precipitation (crystallisation) process is strongly dependent on pH. All the 3 components are present in waste water in low concentrations while in the sludge liquors after anaerobic digestion even in high concentrations. Uncontrolled MAP-precipitation can cause operational problems by incrustations of pipes and machine parts at sludge treatment plants. Normally the precipitation process is limited by the (low) Mg concentrations. Efficient MAP precipitation can be achieved in a controlled process by dosing Mg salts (see side stream and crystallisation processes). Depending on the location of the addition of the precipitants at waste water treatment plants the following techniques can be distinguished (ATV-DVWK 2004):

- Main stream processes:
  - Pre- precipitation (1),
  - Simultaneous precipitation (2),
  - Post precipitation with flocculation and sedimentation (3) and
  - Post precipitation with flocculation filtration (4)
- Side stream processes
  - Sludge liquors

Pre- precipitation (1)

The metal salts are added to the influent of grit chambers or primary clarifiers. The precipitation product can be separated together with the primary sludge. P-precipitation results also in additional removal of organic suspended solids which has to be considered for design and operation of nitrifying and denitrifying treatment plants. Pre-precipitation has to be continuously controlled according to the influent P-load and for a following biological treatment P deficiency must be avoid. Especially nitrifying bacteria are sensible to P-deficiency.

Simultaneous precipitation (2)

This is by far the most frequently applied process in full scale. Precipitants are added to the influent of the aeration tank, directly into the aeration tank, to the inflow of the secondary clarifier or to the return sludge. If enhanced biological P-removal is aimed at, the

precipitants are preferably added to the effluent of the aeration tank in order to avoid competition between biological and chemical P-removal. In such a case divalent iron salts (e.g. ferrous sulphate) cannot be used because they have to be first transformed to trivalent iron by oxidation. Divalent salts should only be added to the aerated volume of the tanks. The precipitation products are removed together with the excess sludge. The increase of the inorganic fraction of the excess sludge has to be considered for the design but this has only a low relevance if P-free detergents are applied in the catchment. With simultaneous precipitation P-effluent concentrations of ≤ 0.5 mg TP/l can be achieved if the dosage of precipitants is adequate (β-value see capita 2.2.2). At the dosing points good mixing conditions have to be ensured (high turbulence).

The access of iron salt is precipitated as $Fe(OH)_3$ and stored in the activated sludge. At higher phosphorus loads this iron storage is able to precipitate surplus phosphorus. Thus control of the dosage is much simpler than at pre or post precipitation.

Post precipitation with sedimentation (3)

This P-removal process normally is only applied as a polishing step after biological treatment with P-removal in order to achieve TP concentrations below 0.5 mg/l. All these processes have to concentrate on the retention of particulate material as bacterial flocs and fine precipitation products containing phosphorus. The dissolved P fraction in the treated effluent depends on the chemicals used, the dosage related to the P-load and the environmental conditions (pH, T). For particle separation flocculants are added which allows removing the precipitation products by sedimentation. In order to improve the removal efficiency sludge can be recycled to the flocculator where gentle mixing is applied.

Post precipitation with flocculation filtration (4)

The only important differences to the process described above consist in particle separation after flocculation by rapid sand filtration and in the future probably by membrane filtration.
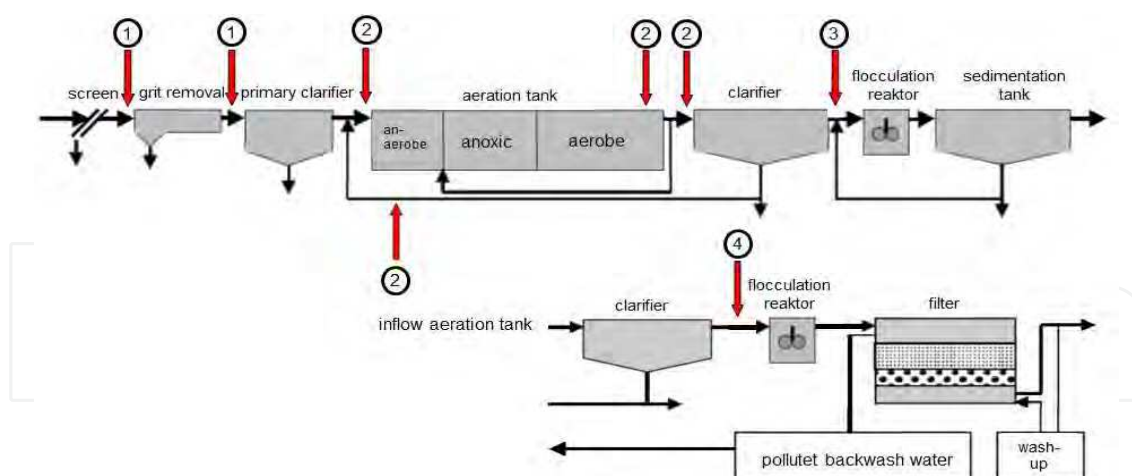

Fig. 5. Physical- chemical P-elimination

Effluent TP concentrations ≤ 0.1 mg/l can be achieved. It has to be stressed that the specific cost for the post precipitation processes (€/kg P removed) are much higher than for the in-stream processes described earlier.

For all the processes the effluent concentrations of dissolved PO_4-P are depending on type of chemicals used, β-value applied, pH and temperature. The percental removal efficiency strongly depends on the P-influent concentration. Applying the same β-value the removal efficiency will decrease with decreasing influent concentrations. For the TP effluent

concentration particle removal efficiency and the fraction of complex phosphorus compounds which cannot be precipitated (e.g. phosphonic acids) in the influent is decisive.

2.2.3 Biological phosphorus removal processes

P-removal by normal-uptake of bacteria

Microorganisms need phosphorus for their growth i.e. the excess sludge production. P-removal from the waste water therefore is a necessary side effect of conventional biological waste water treatment, depending on the specific sludge production per unit of organic pollution (e.g. population equivalent of 120g COD/(PE*d). An average P-removal of 0.6 to 1 g P/(PE*d) can be achieved with bacterial growth only. Microorganisms are able to store phosphorus in order to survive periods with phosphorus deficiency. This is not relevant in municipal waste water treatment plants, where there is a continuous excess of P in the waste water. At plants treating P-deficient industrial waste waters this ability of bacteria has to be considered for an adequate control strategy for the P-dosage (Svardal, 1998).

P-removal by luxury-uptake of bacteria

Luxury uptake is performed by phosphorus accumulating organisms (PAO) able to store phosphorus up to ≥ 5 % of their dry weight if process configurations are applied which increase the competitiveness and survival probability of PAOs in biological treatment plants. The main characteristic of this process is to subject the microorganisms to alternating anaerobic and aerobic (anoxic) conditions. With this process phosphate storing microorganisms are enriched in the system (Barnard, 1975; Ludzak, 1972; Nicolls, 1972; Levin, 1965).

Process description:

Anaerobic conditions are characterized by the absence of dissolved oxygen (DO = 0 mg/l) and oxidized forms of nitrogen (nitrate and nitrite) and the presence of biodegradable material causing an oxygen demand. Under anaerobic conditions PAOs are not able to grow but can accumulate and store organic substrate by converting organic acids to poly-hydroxy butyrate (PHB) and similar energy rich organic compounds. For this process the bacteria need energy which they gain under anaerobic conditions from the conversion of stored energy rich poly-phosphate to dissolved phosphate which is released to the water under these conditions.

The substrate storage process under anaerobic conditions is controlled by the energy stored in the bacteria in the form of polyphosphates. The "poly-phosphate energy battery" is recharged under anoxic or/and aerobic conditions where PAOs use part of the energy gained from the aerobic degradation of the organic carbonaceous pollution.

The excess sludge withdrawn from or after the aerobic (anoxic) zone contains the stored polyphosphate load which increases the P-removal from the waste water via the excess sludge. Dry solids of conventional activated sludge have a TP contents of 1 - 1.5 %, while those of enhanced biological P removal plants can achieve up to > 4 % TP.

As substrate availability in the aeration tank is low the growth rate of the bacteria is low due to substrate limitation (low effluent concentration). Under such conditions PAOs gain an increased competitiveness as they can additionally grow using the stored accumulated substrate. The best indicator for P luxury uptake in an activated sludge plant is the increase of the dissolved phosphate load in the anaerobic tank (figure 3).
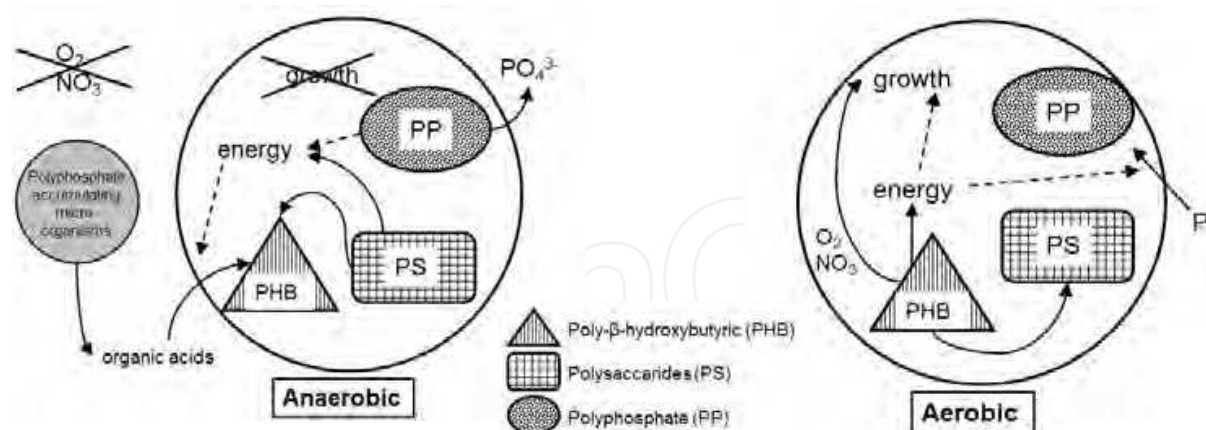
Fig. 6. Metabolism processes at luxury uptake (Henze, 2008)

Conclusion:

Enhanced bio-P removal (luxury uptake) from waste water is advantageous as it does not require chemical addition. The reliability of this process strongly depends on specific local conditions which can partly be compensated by favourable process configurations and the detention time in the anaerobic tank volume. Enhanced bio-P removal can easily be combined with the very reliable P removal by chemical precipitation. Optimization of design and operation can therefore be achieved on the basis of economic and operational considerations.

As the temperatures of the waste water strongly vary over the year it is reasonable to make optimal use of the total aeration tank volume over the whole year. E.g.: at high temperatures the anaerobic tank is used for Bio-P removal while during the lowest temperatures this tank can also be used for denitrification, while P-removal is maintained by chemical precipitation.

An important consequence of bio P removal is that the excess sludge must not be subject to anaerobic conditions during thickening. If primary and secondary sludge are thickened together, this would l result in a release of P-luxury uptake to the supernatant which returns it to the influent. Separate mechanical thickening of the excess sludge is the most common solution to avoid this effect.

During one step anaerobic sludge digestion P-release normally remains neglectable as long as the organic acid concentration is kept low, which is the case at sludge retention times > 20 days and quasi steady state conditions. Phosphorus remains bound to the solids which is favourable for sludge application in agriculture or incineration with P-recovery from the ashes.

The application of a two-step digestion process (hydrolysis + methanisation) at Bio-P removal plants would result in the release of the luxury P uptake to the supernatant (sludge liquor). In this case P crystallisation processes can be applied to the sludge liquor in order to convert the released P to a market fertiliser (Triple-phosphate) with low contamination by heavy metals and micro-pollutants. The normal P content of bacteria and the chemical precipitated phosphorus remain bound to the sludge solids. Whether such a process configuration is economically viable has to be proved in practice (Pinnekamp, 2007).

Enhanced bio-P removal technologies

There are numerous processes for enhanced biological phosphorus removal. All of them contain an anaerobic tank (cascade) and try to minimize the negative impact of oxygen and oxidized nitrogen compounds to the process. It is possible to distinguish in stream and side stream processes. All in-stream processes remove phosphorus together with the excess

sludge. Side-stream processes force the release of phosphate to the liquid phase of the return sludge or to the sludge liquors from where phosphate is precipitated (crystallised) by chemical addition. The following simplified process configurations are used in practice:

In-Stream Processes

The following in-stream processes are described by Pinnekamp (2007), Kunst (1991) and Matsché (1989).

Bardenpho (Barnard, 1974)

The Bardenpho-process consist of the anaerobic tank in front, a pre-denitrification/ nitrification step with internal recirculation followed by an anoxic tank and a final aeration step in order to avoid nitrate transfer to the anaerobic tank by the return sludge. This process achieves high P-elimination and is operated with very low loadings. Numerous WWTP of this type operate in South Africa and North America.
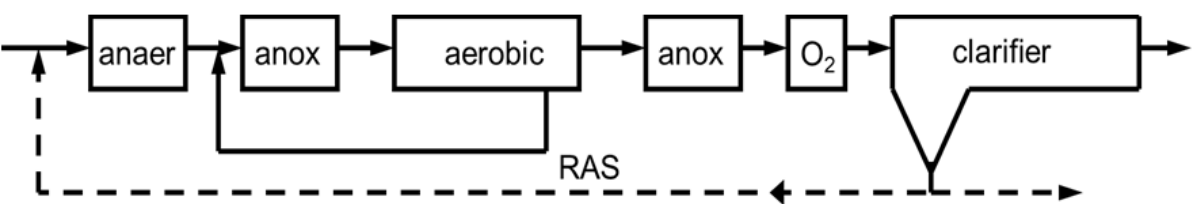

Fig. 7. Bardenpho-Process

UCT (University of Cape Town (Rabinowitz and Marais, 1980))

Because of remaining nitrate in the return sludge at the Bardenpho- and Phoredox-process release of phosphorus in the anaerobic tank can be affected. The UCT-Process was developed at the University of Capetown in order to avoid this. The main difference to the Bardenpho process is that the return sludge is fed to the anoxic pre-denitrification tank from where the denitrified activated sludge is returned to the anaerobic tank.
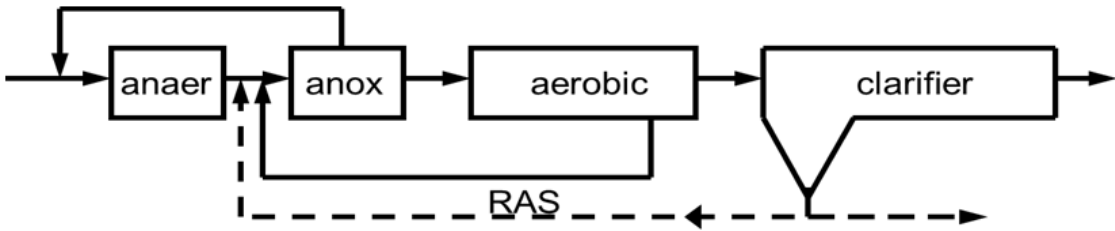

Fig. 8. UCT-Process

Phoredox (Barnard, 1976)

The Phoredox-process is a simplification of the Bardenpho-process. Because of the low reduction rate in the second anoxic tank and the aeration tank these steps were omitted.
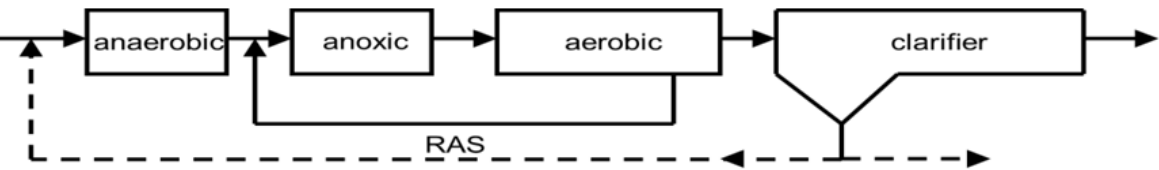

Fig. 9. Phoredox-Process

Johannesburg (JHB)-Process (Burke et al., 1986)

This process is a modification of the Phoredox-process. Return sludge will be denitrified in an anoxic tank before reaching the anaerobic step. Therefore the input of the anaerobic tank is the inflow and nitrate free return sludge. The name of this process is based on its location in Johannesburg.
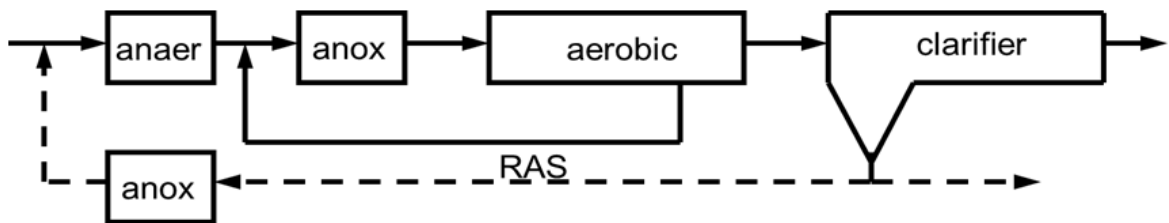
Fig. 10. Johannesburg-Process

A²/O (Barnard, 1974)

The A²/O is a modification of the Phoredox-process with nitrification and denitrification. Compared to the Phoredox-process the tanks are constructed as cascades, while the order of the tanks is identical (Figure 11). This process is operated in the US and Brazil in some plants.
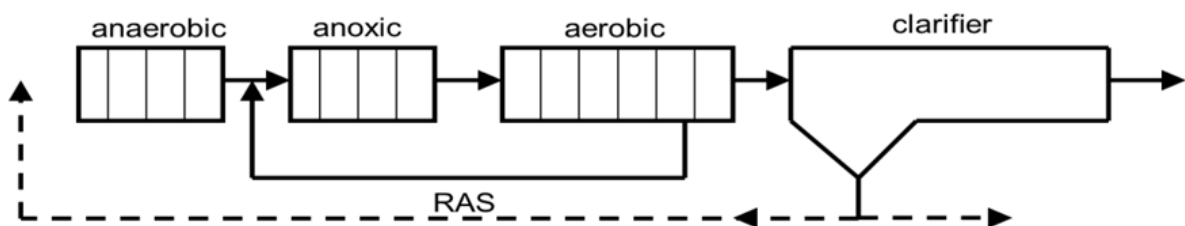
Fig. 11. A²/O

Biodenipho (Krüger, n.d.)

Two circular aeration tanks are operated with alternating nitrification and denitrification. Waste water flow is added during the periods of denitrification where aeration is stopped. Thus waste water of the first activated sludge tank will be denitrified while the second activated sludge tank will be aerated and therefore nitrification will occur. As soon as all nitrate in the not aerated tank will be denitrified, the inflow and the aeration changes. Thus the created nitrate of the aerated tank will be denitrified and the available ammonia in the aerobic tank will be oxidized. An upstream situated anaerobic tank enables a biological P-elimination.
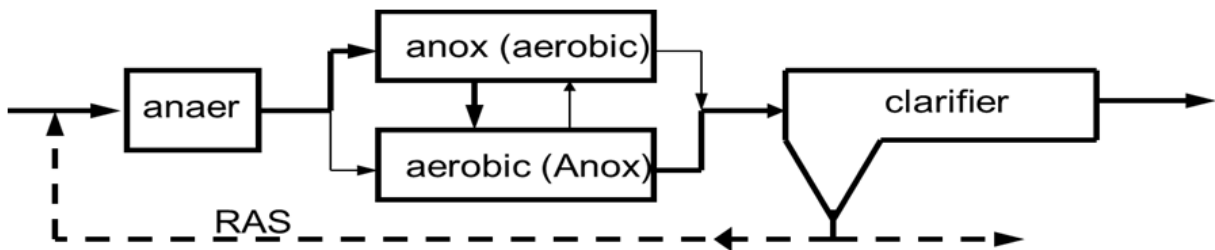
Fig. 12. Biodenipho-Process

Extended Anaerobic Sludge Contact (EASC) (Schoenberger, 1989)

This process was developed to implement biological P-elimination to existing WWTP. The primary sedimentation tank is used as an anaerobic reactor. Return sludge is fed to the sedimentation tank where anaerobic conditions enable sedimentation of primary sludge and RAS (Return activated sludge). Therefore the residence time of the sludge extends and leads to an acidification of the raw water. This acidification leads to improvement of the substrate quality for P-storing microorganisms. The runoff of the sedimentation tank and settled sludge will be fed to the anoxic tank together with the sludge recycled from the aerated nitrification tank.
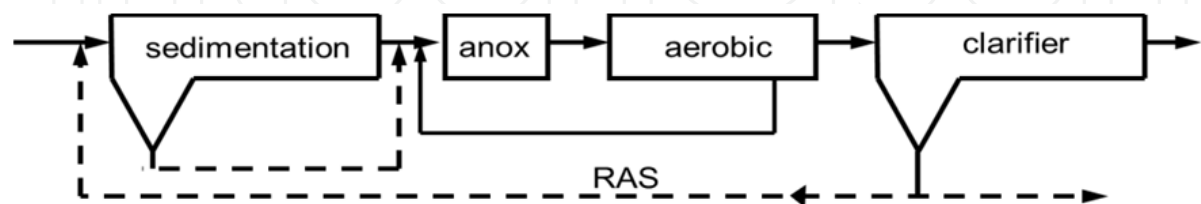
Fig. 13. Extended Anaerobic Sludge Contact (EASC) Process

ISAH (Austermann-Haun, 1998)

The ISAH is an approved process under unfavourable conditions (low temperature, dilution by external water or low substrate concentrations). RAS will be denitrified in a separate anoxic tank, which inhibits a possible disturbance of phosphate re-dissolution. Thus the easy degradable waste water inflow is fully available to phosphate-rich microorganisms.
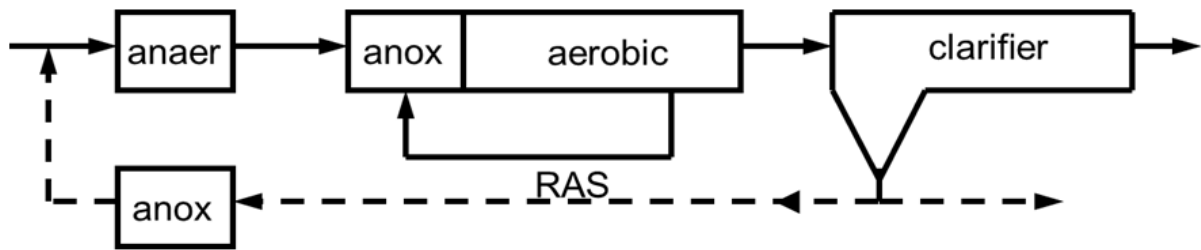
Fig. 14. ISAH-Process

Sequencing Batch Reactor (SBR) (ATV, 1997)

Compared to the continual flow processes, SBR works with only one tank in time sequences. One cycle passes the steps of filling (anoxic), filling and mixing (anaerobic), aeration (aerobic), sedimentation and removal of the treated effluent (Fig. 15).
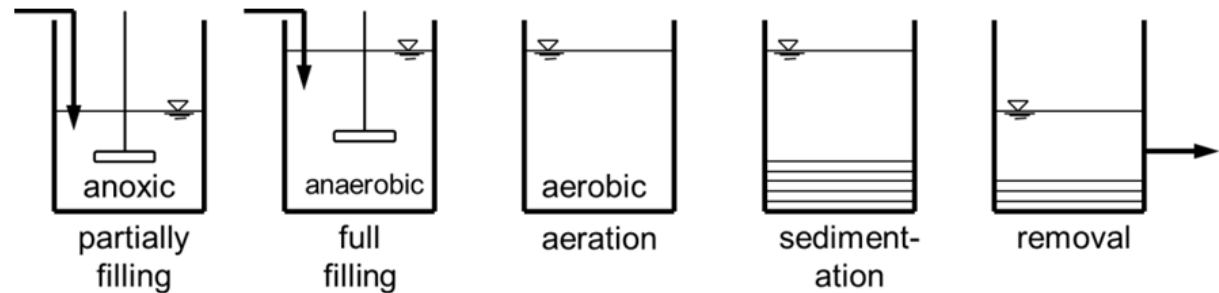
Fig. 15. Sequencing Batch Reactor (SBR)

Full scale experience shows that Bio P-removal can be achieved with many aeration tank configurations where anaerobic zones or cascades occur and irrespective whether the treatment efficiency is high i.e. with nitrification or only BOD-removal is achieved. Typical reports on these full scale investigations can be found in (Spatzierer et al., 1985) and for Berlin (Peter et al., 1991). Especially for treatment plants with low treatment efficiency (low sludge age) it has to be considered that in secondary clarifiers anaerobic conditions can occur which will cause a release of stored phosphate to the effluent.

Side stream processes

Phostrip (Levin, 1965)

In contrast to the in stream processes the anaerobic phase is situated in the return sludge cycle. Core of this process is the stripping tank which works similar to a common sludge thickener. The steps in this tank are:

- Separation of sludge and waste water by sedimentation
- Sludge thickening up to 4 % dry matter
- Anaerobic storage of the sludge
- Hydrolysis of particular COD or activated sludge to easy degradable organic substrate
- *P-release*

In this sludge-water phase concentrations up to 50 mg L^{-1} PO_4-P are possible. The actual practical relevance of this process is low.
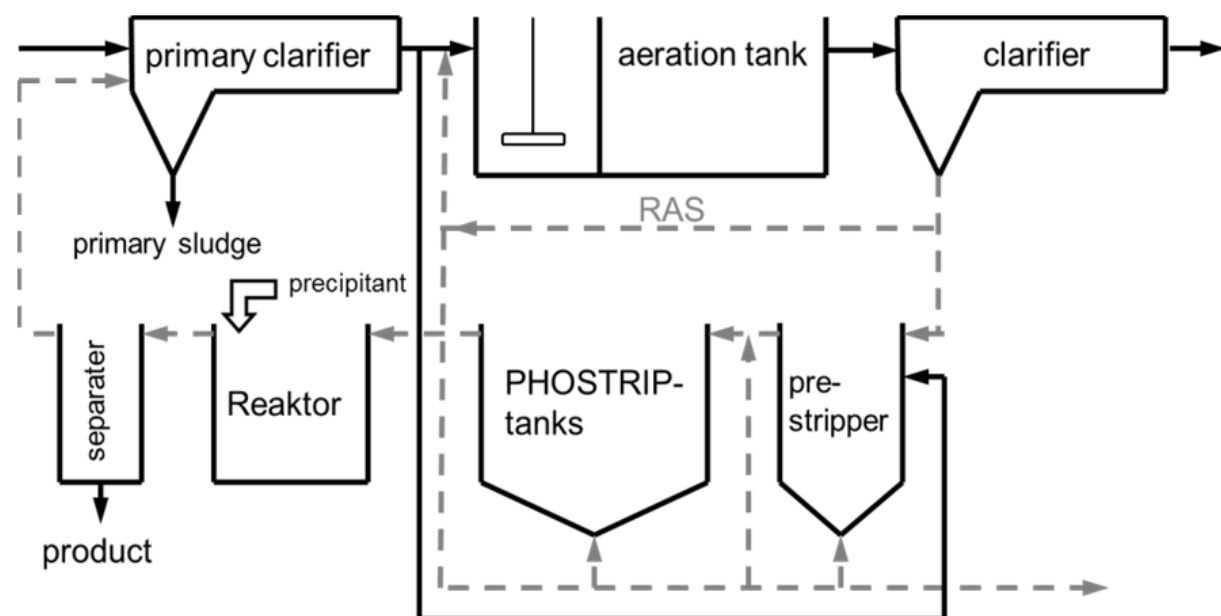

Fig. 16. PHOSTRIP-Process

2.2.4 Crystallisation processes

Crystallisation precipitation) processes are mainly applied to remove phosphorus from sludge liquors and from urine if separately collected. These processes are easy to integrate in to consisting WWTP. By adding different chemicals as calcium hydroxide ($Ca(OH)_2$),

calcium chloride (CaCl$_2$), magnesium hydroxide (Mg(OH)$_2$) or magnesium chloride (MgCl$_2$) to crystallisation reactors, calcium phosphate (Ca$_3$(PO$_4$)$_2$) and magnesium-ammonium-phosphate (MAP -> NH$_4$MgPO$_4$ x H$_2$O) will be formed. This product can be used directly in agriculture. Following to the P-recovery, the pH of the purified water needs to be lowered because of the alkaline chemicals in the reactor. With this process only ≤ 45 % of the P load of the raw waste water can be recovered. Worldwide there are few different large scale realisations but also numerous attempts to implement this technology successfully at waste water treatment plants especially to sludge liquors with high phosphate and ammonia concentrations. These are namely:

DHV Crystalactor ®	Netherlands	Giesen (2002)
WASSTRIP	US	Ostara (2008)
Unitaka Phosnix	Japan	Ueno et al. (2001)
Nishihara Reactor	Japan	Petruzzelli et al. (2003)
WWTP Trevisio	Italy	Cecchi et al. (2003)
PRISA	Germany	Montag (2008)

Table 2. Crystallisation processes worldwide

2.2.5 Urine separation

The daily amount of urine per person of 1.5 to 2 litres offers a highly concentrated dissolved phosphate mass flow. The following Table 3shows the distribution of nitrogen and phosphorus in urine and faeces (Vinneras, 2004).

	Unit	**Urine**	Faeces	**Urine (%)**	Faeces (%)
N	g/(PE*a)	**4000**	550	**88**	12
P	g/(PE*a)	**365**	183	**67**	33

Table 3. Distribution of nitrogen and phosphorus in human excretions

Dry toilets, vacuum toilets, separation toilets or waterless urinals are necessary to separate urine. Afterwards the phosphorus and part of the ammonia can be recovered by MAP-precipitation, resulting in a market fertiliser (Bischof, n.d.).

MAP-precipitation

MAP (Struvite) is produced when ammonium, phosphate and magnesium ions react in a stoichiometric molar ration of 1:1:1. By adding MgO or MgCl to the urine with a minimum pH of 9, MAP can be precipitated. If a complete ammonium recovery is aimed, phosphate and additional magnesium have to be added (Sreeramachandran, 2006). The

final product MAP is low in heavy metals and micro-pollutants and represents a valuable market fertiliser. Figure 17 shows the multi-stage process developed by Hans Huber AG with ammonia recovery by stripping.
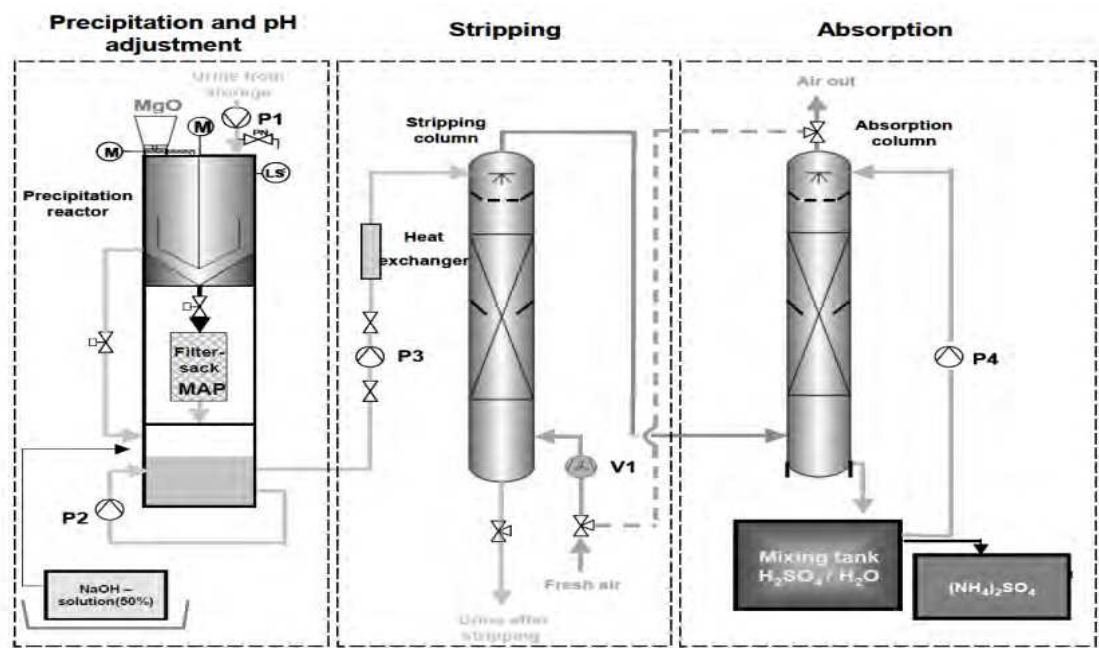

Fig. 17. Multi-stage MAP-Precipitation with ammonia recovery by stripping (Bischof, n.d.)

2.2.6 Cost estimation
The costs of P-elimination are subjected to regional and temporal variations. They include WWTP operational costs for the P-removal (chemical cost) and have to reflect the influence on sludge treatment and disposal. Therefore reported costs strongly depend on specific local situation, assumptions made and cost calculation method applied. Table 4 shows costs for P-elimination derived from literature (EAWAG, 2008, Baumann, 2003).

Treatment	Costs
Biological P-elimination	3,5 €/(PE*a)
	2,5 - 9 €/kg P$_{eliminated}$
Chemical P-elimination	4 - 9 €/(PE*a)
	6 - 14 €/(kg P$_{eliminated}$)

Table 4. Specific costs for P-elimination

The specific costs of new recycling technologies from sewage sludge and sewage sludge ash are 1.5 - 5 €/(inhabitant*year) or 5 - 20 €/kg P$_{recycled}$. Recycling directly from waste water is most expensive due the low recycling rates and high investment cost. The actual market price for 1 kg P$_{recycled}$ is about 0.5 - 1 €. Therefore these technologies are presently not cost efficient (Pinnekamp, 2007).

2.3 Sewage sludge

Sewage sludge is a necessary by- product of waste water treatment and is a mixture of water and solids. It consists of primary sludge from primarily setting tank, excess sludge form the biological treatment step and precipitants from chemical P-precipitation. Because sludge production cannot be avoided the operator of a waste water treatment plant needs a technologically and legally reliable sludge disposal method at any time. This has to be considered especially for all marketing strategies for sludge or products from sludge.

2.3.1 Quantities

Due to increasing capacity of waste water treatment in EU the quantity of sewage sludge is increasing, too. In Europe (EU 15) the actual sludge production is about 10 Mio tons dry matter per year which corresponds to about 22 kg per capita (EUROSTAT, 2010). North America (USA and Canada) produces about 7.7 Mio tons of municipal wastewater sewage sludge every year. Calculated with a P concentration of 2.5 to 3 %/t DM the theoretical P-recovery potential in Europe and North America is up to 0.5 Mio tons every year. This corresponds to ~ 3 % of the annual phosphorus fertilisers sourced from mining phosphate rock (15 Mio tons P (Jasinksi, 2010)).

2.3.2 Composition of sewage sludge

Nutrients

Depending on the origin of waste water the composition of sewage sludge can vary in a wide range. Nutrients in sewage sludge originate mainly from human excreta but also from detergents and different industrial effluents (food, pulp and paper, chemical industry). Typical concentrations of valuable sludge compounds are shown in Table 5.

oDM % DM	N g/kg DM	NH_4-N g/kg DM	P_2O_5* g/kg DM	K_2O g/kg DM	CaO g/kg DM	MgO g/kg DM	S g/kg DM	Na g/kg DM
35 - 60	**13 – 65**	0,6 - 13	**20 - 45**	1 - 8	60 - 130	5 - 16	5 - 10	1 - 3

Table 5. Nutrient concentrations in sewage sludge (Zessner & Aichberger, 2003)

Sludge application has to be integrated into agricultural fertiliser management. For this goal availability of the P content of the sludge has to be considered. Enhanced biological P-elimination without or little use of precipitants during the waste water treatment process is favourable for agricultural use of sewage sludge, as the availability for the plants is high. Phosphorus availability is lower with alum precipitation and even more restricted with iron precipitation. P-precipitation as MAP results in full availability of the phosphorus and contains also ammonia as a fertiliser but is normally not applied for pre- and simultaneous P-removal.

Literature reports regarding plant availability of phosphorus compounds in sewage sludge in agriculture, widely differ depending on the investigation methods, the sludge applied, and whether lab-scale tests or full scale experience have been used. The availability not only depends on the P removal process applied (biological/chemical, chemicals used) but also on the soil properties (pH, redox potential, type of soil, content of humus, organic substance and nutritional status) as well as on sewage sludge stabilization process applied

(anaerobic/aerobic). Also the test procedure for the determination of plant availability can be of substantial influence. There is consent that short term P-availability of iron or aluminium precipitated phosphorus in sewage sludge is restricted (Krogstad et al., 2005; Henke, 2000; Jokinen, 1990). Biological treatment with lime addition for P-removal resulted in sewage sludge with a P fertilisation effect comparable to inorganic P fertilisers as investigated in pot trials. The application of sewage sludge to pot experiments also resulted in low concentrations of water extractable P, which is positive. They caused a considerable accumulation of P with low plant availability in soil (50 - 95 % increase) which represents a potential environmental risk due to the transport of erosion products by surface runoff to receiving waters (Krogstad et al., 2005). This also stressed the importance of inclusion of sludge application into fertiliser management as reported by Krogstad et al. (2005).

Plant roots absorb exclusively dissolved inorganic phosphate, but its concentration in soil solution is low (Blume et al., 2010). Especially during the growing phase the need of dissolved P is markedly increasing. By desorption of adsorbed P, dissolution of Ca-phosphate and mineralization of organic P the need of dissolved phosphate will be satisfied (Blume et al., 2010) Most market fertilisers contain phosphorus compounds which are immediately and at least easily available to plants. Nutrients included in organic fertilisers mineralise slowly to plant available substances. It therefore can be recommended to combine mineral fertiliser application with organic fertilisers as sewage sludge. The characteristic of P compounds in sewage sludge is shown in Table 6.

Inorganic phosphorus	60 - 90 %, depending on P-precipitation (chemical or biological) and sludge treatment (anaerobic/aerobic)
Water soluble Citric acid soluble	<1 - 38 % 60 - 90 % only biological treatment (Gutser, 1996) Clearly lower after chemical precipitation
Inorganic compounds	Octacalcium phosphate ($Ca_8H_2(PO_4)_6 \times 5H_2O$) Dicalcium phosphate (-dihydrate) Fe- and al-phosphate (vavianite and wavellite)
Organic compounds	Monoester Diester Phosphorus lipids

Table 6. Characteristic of P in sewage sludge (Frossard, 1996)

Where P removal from waste water is required, normally the area specific application of sewage sludge is limited by the phosphorus addition, which should be adapted to the crop uptake in order to avoid unwanted P-accumulation in top-soils (eutrophication abatement from erosion). Guidelines on application of sewage sludge in agriculture in regard to phosphorus fertiliser and heavy metal management are available (e.g. ÖWAV Regelblatt 14,

2004). Sludge from treatment plants with enhanced P-removal requirements can be classified as a phosphorus fertiliser. Normally phosphorus content limits the mean area specific application of sludge to1 - 2t DM/ha/year.

Metals and heavy metals

Heavy metal loads in waste water and hence in sewage sludge varies in a broad range depending on industrial and trade discharges, surface runoff, sewer system, household infrastructure, waste water treatment system and geogenic background. Typical metal concentrations (mg/kg DM) in Central Europe sludges are shown in Table 7. The heavy metals used for sludge quality characterisation in sludge regulations are marked in bolt.

As	Be	Br	**Cd**	**Cr**	Co	**Cu**	Fe	**Pb**
4 - 10	0,2	37	**0,6 - 3**	**3 - 54**	5 - 11	**120 - 300**	11800 - 17000	**37 - 145**

Mn	**Hg**	Mo	**Ni**	Se	V	Sn	**Zn**
220 - 320	**0,5 - 2,3**	3,9 - 14	**17 - 37**	1,8	15	32	**700 - 1320**

Table 7. Heavy metal concentrations in sewage sludge (Zessner & Aichberger, 2003)

Metals as boron, iron, copper, zinc, molybdenum, manganese or selenium are essential trace elements for plants and living organisms, but too high concentration can be harmful and toxic. Heavy metal as cadmium, lead and mercury do not have proved functions in living organisms and can be toxic and harmful beyond threshold concentration or doses. Therefore the area specific application of sewage sludge to agricultural area is strictly regulated in order to avoid an enrichment of heavy metals in soil or plants (Phatak et al., 2009; Gaskin et al., 2003; LFU, 2003). The standards for the heavy metal concentrations can be either expressed as mg/kg DM or as mg/g P, the latter is especially relevant for sludge with high P-content up to 35 g P/kg DM from P-removal treatment plants.

Pathogens

Sewage sludge contains pathogens as bacteria's, viruses, protozoas and worm eggs which stem mainly from human excreta but also from animals. Anaerobic mesophilic stabilisation and low temperature drying do not achieve the required reduction and inactivation of those pathogens. Especially for salmonella, enteroviruses, roundworm eggs, cryptosporidium, multi-resistant enterococcus and staphylococcus (Böhm, 2006). This means that sewage sludge has a potential to transfer infectious pathogens to animals and humans. Depending on the application of the sludge and the infection potential different hygienic quality criteria can be derived. Appropriate processes to minimize the hygienic risk of sludge application are sludge pasteurisation, thermophilic treatment, quicklime addition, composting and long term storage. The highest hygienic risk is at the farm level, where a close contact of animals and humans with sludge can occur. Furthermore sludge application is restricted to specific production areas.

Micro-pollutants

Micro-pollutants are ubiquitous in the aquatic environment even the concentrations of only a very limited number is monitored. Their effects on organisms differ widely and are often

insufficiently investigated. Depending on their properties the substances can have genotoxic/immunotoxic/neurotoxic, carcinogenic and endocrine impact on living organisms (Gangl, 2001). Table 8 shows different micro-pollutants of concern:

Organic pollutants	AOX, LAS, PAH, PCB, PCDD/F, DEHP, HC, NPE
Pharmaceutical substances	Antibiotics, endocrine hormonal drugs, psychotropic drugs, cytostatic

Table 8. Micro-pollutants in waste water and sewage sludge

Up to now there are no scientific reports on negative effects on agriculture and food if controlled sludge application on land is used even for decades in several regions. Whether they represent a long term risk for humans and the environment it is still a matter of scientific research and discussion.

2.4 Recovery, treatment and disposal of sewage sludge
The following figure shows the current situation of sewage sludge recovery, treatment and disposal in Europe and North America (Emscher Lippe, 2006; WEF, 2011; CCME, 2011).
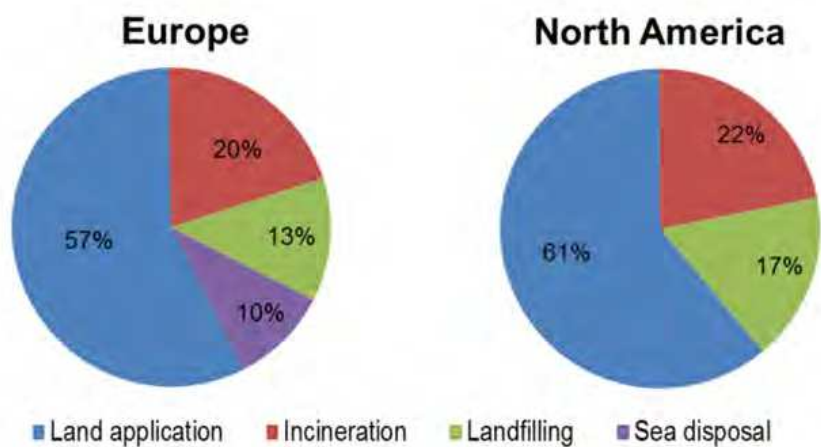

Fig. 18. Sewage sludge recovery, treatment and disposal in the EU and North America

2.4.1 Direct land application
Direct application of sludge in agriculture is closing the nutrient cycle especially for phosphorus. Sewage sludge contains also valuable other nutrients (nitrogen), organic matter and many macro- and micronutrients which are essential for plant growth.

Use of stabilised sewage sludge on land

The use of stabilised sewage sludge on agricultural land has a long tradition and is subject to strict legal requirements for quality control, monitoring and documentation (see section 1). Especially for small treatment plants in rural areas this method represents an easy and economically favourable solution for P-recycling. For national agriculture use of sludge in agriculture is of of low economic relevance (Kroiss et al., 2007). For farmers able to substitute mineral phosphorus fertiliser free of charge by sewage sludge this is economically interesting

(Kroiss, 2005). For the treatment plants it has the important consequence that a sludge storage capacity for up to 6 months has to be provided, as during wintertime fertilising is not allowed. For large treatment plants the main problem of this disposal route is the restricted reliability (legislation, public perception) as well as increasing costs for storage and transport.

Sludge can be composted if additional carbonaceous material (e.g. wood chips) is added. The compost can be applied in agriculture and for landscaping as it is possible for sludge depending on national regulations. If sludge or compost made of sludge is used for landscaping in most of the cases the area specific phosphorus dosing is much too high as compared to the uptake if relevant area specific mass of organic material is applied. This is detrimental for P-resource protection and may contribute to eutrophication by erosion products. In EU15 currently 40 % of sewage sludge produced (4 Mio t/a) are directly applied in agriculture. 17 % are used for recultivation. In North America 61 % (4.6 Mio t/a) were applied on land.

Problematic of harmful substances

In principle the application of sewage sludge can cause an increase of heavy metals in soils if removal by harvesting and washout is lower than supply. There is continuous loss of HM via surface runoff, intermediate runoff and the ground water which is very difficult to quantify due to the limited analytical and sampling accuracy. Numerous studies show, that the accumulation of heavy metals is very low as the dilution factor of sludge in the top soil is in the order of 1:5000 up to 1:10.000 if sludge is applied according to modern legal requirements. Only monitoring with sophisticated sampling procedures over several decennia can prove an accumulation. Heavy metal loading of soils has therefore to be monitored in order to avoid potential risks which are different for several metals (VDLUFA, 2001).

heavy metal	soil protection		plant nutrition, quality of food plants	risk
	increase of soil content	mobility		
Cd	possible	high	endangered	high
Pb, Cr, Ni, Hg	possible	minimal	not endangered	medium
Cu, Zn	possible, welcome by fertiliser need	Cu low, Zn high	encouraged by fertiliser needs, otherwise no risk	low

Table 9. Assessing heavy metals concerning their possible risk

Plants have "root barriers" which inhibit or even stop the uptake of certain heavy metals (Pb, Cr, Ni, Cu, Hg) and many organic micro-pollutants. With the exception to Cd and Zn, plants are protected concerning the uptake of high concentration of these substances. Zn is also an important trace element for plant growth and human nutrition, Cd concentration in much sludge from Central European and also US treatment plants has dropped below the soil standards.

Soils contain the most versatile natural microbial communities with high performance potential in mineralizing organic substances, even so called persistent harmful substances as PCB and PCDD as could be verified by research Also the adsorption potential as very high

due to the extremely large surface area. As a consequence the controlled application of sewage sludge on land does not result in acute risks, long term risks by accumulation can be avoided by adequate monitoring. Sludge is not the only pathway for micro-pollutants to the soils (air pollution, precipitation).

2.4.2 Incineration and P-recovery

A process enabling P recovery of phosphorus is the incineration of sewage sludge in mono-incineration plants. All organic compounds will be destroyed, while phosphorus and the heavy metals are transferred to the ash. The direct application of this ash to agricultural fields is still a matter of discussion. The availability of P in the ash is restricted. The main goals of new P-recovery technologies are on the one hand the elimination of pollutants and on the other hand making phosphorus available to plants. Currently there are only few technologies available which meet both requirements, but they are still not ready for market introduction. The following technologies for P-recovery from ash are reported in literature: ASH DEC, PASCH, Mephrec and ATZ Eisenbadreaktor (Mocker and Faulstich, 2005). An immediately applicable option could be to store the P-rich ash in a monofill for future recovery The use of mono-incineration ash for construction material or its dumping in landfills together with other waste should be avoided as phosphorus recovery will be disabled.

2.4.3 Incineration without P-recovery

Because of the relatively high calorific value (11 - 17 MJ/kg) of dried sewage sludge, comparable to brown coal and therefore used in the cement industry, in coal power plants but also in ordinary municipal waste incineration plants. Dried sewage sludges are used in the cement industry, in coal power plants but also in ordinary municipal waste incineration plants. In these processes all organic compounds will be destroyed completely, but the valuable nutrients as P cannot be recovered. End products ash bottom as and fly ash with low content of pollutants can be used as a construction material or get landfilled. Pollutant rich filter cake need to be disposed of in underground disposal facilities.

2.4.4 Landfilling

In Europe and North America about 2.5 Mio tons of sewage sludge are currently dumped in landfills. This causes gaseous emissions as CH_4 and CO_2 from these landfills, which are climate relevant. Phosphorus in this dumped sewage sludge is lost irretrievable. European landfill legislation therefore requests a continuous reduction of organic material to be put to landfill, with the goal to completely stop it in the near future. Several central European countries have already banned landfill disposal of organic matter in the past (Germany, Austria).

2.4.5 Possibilities of P-recovery from sewage sludge

Due to the pollutants contained in sewage sludge a great number of research and development projects have been started to recover phosphorus fertiliser with low pollution from the sludge, in order to meet the same quality standards as for market fertilisers. Most of the processes described below have not proved economic viability up to now, some of them are still lacking full scale experience.

Processes with precipitation

There are three main processes to recover phosphorus fertiliser with low pollution levels and high plant availability from sewage sludge. Enhanced biological P-elimination without

or low use of precipitants during the waste water treatment process is advantageous for working-recovery by precipitation from the sludge. In sewage sludge phosphorus is bound to several organic and inorganic solids. By changing the pH using acids, phosphorus can be brought into solution. Particulate matter will be separated and the pH is increased to about 8.5 by adding alkalinity. If e.g. MgCl is used as precipitant for MAP a fertiliser rich in phosphorus with high plant-availability and low heavy metal content will be produced. (Airprex, Seaborne, Stuttgarter Verfahren)

Wet oxidation process

During the wet oxidation process the organic fraction of sewage sludge is oxidized with pure oxygen at super-critical conditions (pressure > 221 bar, T > 374 °C). Phosphorus concentrates in a highly reactive form and will be extracted by precipitation with calcium hydroxide. (Aqua Reci)

Thermal hydrolysis with following precipitation

Sewage sludge will be heated under pressure up to 140 C and treated with sulphuric acid to reach a pH of 1 - 3. Part of the inorganic material dissolves and is separated from the particulate matter. By increasing the pH in the liquid phase phosphorus is precipitated by adding iron salts. The plant availability of P is comparable to simultaneous precipitation. (KREPRO)

2.4.6 Discussion

The direct application of sewage sludge on land is a well-established method of nutrient and organic substance recovery. The sludge treatment processes applied (storage, dewatering, drying) have to be adapted to the specific local situation including the legal requirements for, monitoring and reporting and the whole logistics. Sludge composting is also a well-established sludge disposal method. If sludge compost is used according to the requirements for organic material (land reclamation or soil conditioning in agriculture normally the P-addition is much higher than plant uptake which is detrimental for P-recovery and eutrophication abatement. The relevance of the potentially harmful substances in the sewage sludge applied on land for long term soil protection and related health effects are still a matter of research and discussion. It finally can only be solved by a political agreement on an acceptable risk at acceptable costs. The processes to recover phosphorus from sewage sludge with a quality as market fertilisers with new technologies, as described in section 1.4.1, use large quantities of chemicals (acids, bases) and energy. The remaining waste fraction after phosphorus extraction still contains potentially harmful compounds and will have to be disposed or reused. Currently these technologies are not competitive economically. Incineration is applied to recover the energy contained in the organic fraction of the sludge. During incineration micro-pollutants are destroyed and phosphorus is concentrated in the ash if mono-incineration of sludge is applied. Co-incineration of sludge with coal (power plants) or solid waste therefore should not be used in the future, the same is with sludge incineration in cement factories. Whether the ash of mono-incineration plants can directly be applied on land (P-contents similar to market fertiliser) is still a matter of discussion because of the heavy metal content and the reduced P-availability.

Sludge from nutrient removal plants with bio P and/or aluminium P-precipitation can be used as raw material for phosphate fertiliser industry (Schipper et al., 2004)

3. Phosphorus in waste management

Vegetable and animals wastes contain significant quantities of phosphorus. Major sources for such wastes are agriculture, the food processing industry and private households.

3.1 Private households
The average P-content in mixed household waste is reported with 0.9 g P/kg fresh mass (FM) in Schachermayer et al. (1995) and 1.4 g P/kg FM in Skutan & Brunner (2006). This translates into a P-load of 190.000 to 300.000 tons/a for the EU15. The proportion of organic waste at the whole municipal solid waste generation is up to 35 %. In EU15 this corresponds to 75 Mio tons every year and a P-load of about 150.000 (Figure 19). Thereof only about 30 % or 22 Mio tons are collected separately. This separately collected organic waste fraction consists of kitchen- and garden waste from households and park- and garden waste from public area. The current waste treatment options are shown in Figure 19.
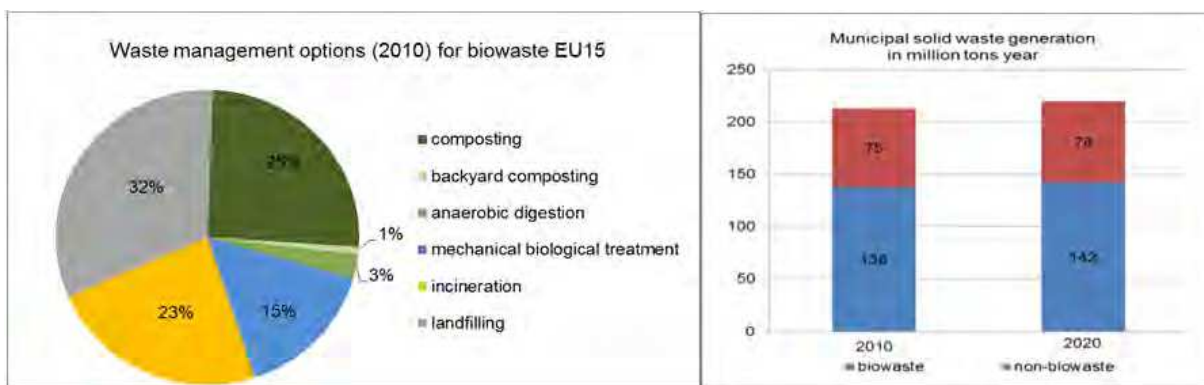

Fig. 19. a) MSW generation in households; b) Waste treatment of biowaste (Arcadis Eunomia, 2010)

Taking the loss of composting into account, 11 Mio tons of compost can be generated and therefore 50.000 tons of phosphorus can be recovered every year at current collection rates. The potential amount is ca. three times higher under real conditions. If this potential can be exploited, up to 150.000 tons P could be recovered from biowaste annually. In Europe approximately 50 % of the produced composts are applied on agricultural fields. The remaining quantities are used in landscaping, gardens or in humification processes. Another appropriate treatment for organic waste, especially pasty wastes is anaerobic fermentation. The resulting biogas slurry can be used as an organic fertiliser.

3.2 Food industry (vegetable and animal waste)
The amount of organic waste generated by manufactures of food products, beverages and tobacco products is about 150 kg per habitant and year in Europe (EU15) (Oreopoulou, 2007; EU STAT, 2011). This corresponds to a total of 59 Mio tons. Because of the heterogeneity of these wastes the P-recovery potential is difficult to determine. Under the assumption of an average phosphorus concentration of 0.5 %, the recovery potential of vegetable and animal waste is about 290.000 t/a. Due to the high P-concentration, especially in bones and teeth, animal wastes contain most of the phosphorus load from the food industry. Waste from slaughtering and meat processing are treated in animal cadaver utilization plans. Therefore

annually approximately 9 kg (Nottrodt, 2001; ASH DEC, 2008) of carcass meal emerge per inhabitant in Europe. Related to all inhabitants in the EU15 3.5 Mio tons of carcass meal arise every year. Calculated with a P-concentration of about 5 to 6 % the recovery potential is approx. 200.000 tons of phosphorus. This P-load corresponds to about 70 %of the total wastes from food industry.

3.3 Ash from energy wood

According to the statistics of EU STAT, 60 Mio tons (dry matter) of energy woods like firewood, wood chips and wood residues (including pellets) are used as alternative energy source. With an assumed ash content of 1.5 % and a P-concentration in ash of 1.2 % a potential P-load of 10.000 tons/a can be calculated.

3.4 Steal production

In steel production P is viewed as harmful to the production of high-quality steel. P occurs in coal, iron ore, and limestone, which are the main raw materials for iron making. During the steelmaking process P is transferred from the molten pig iron to the slag. Yoon and Shim (2004) report P concentrations in dephosphorization slag of 1 - 3 % (P_2O_5). Jeong et al. (2009) demonstrate the potential of such slag for P recovery by a P balance for South Korea where they show that steelmaking slag contains about 10 % of the domestic P consumption. They argue that technologies to recover this waste flow could substantially reduce the dependence on imports of phosphate rock.

3.5 Recovery processes for organic waste
3.5.1 Composting

The main treatment option of separately collect organic waste in households is composting. During this aerobic treatment process, the organic fraction gets stabilized through microbial decay and volume and mass are reduced while the concentration of nutrients increases. Composting requires three key activities: aeration (by regularly turning the compost pile), moisture, and a proper carbon to nitrogen (C:N) ratio. A ratio between 25:1 and 35:1 is generally considered as optimal.

3.5.2 Biogas plants

Biogas plants are a well-known technology to transform organic wastes into a useful fertiliser, to gain electricity and thermal energy from them and to increase their nutritive characteristics. Through biologic decomposition under anaerobic conditions methane bacteria produce biogas. The methane is used for combustion either in a gas motor or combined heat and power plant to produce electricity and heat (e.g. for district heating). The resulting biogas slurry can be used as an organic fertiliser.

3.5.3 Thermal treatment

Utilization of carcass meal as animal feed has been banned as a consequence to the BSE crisis and therefore most of the carcass meal is utilized as a substitute fuel in the industry (mainly in cement kilns and coal-fired power plants). This treatment does not allow a recovery of phosphorus since it is either diluted in the product (cement) or in the coal ash. A possibility could be the co-incineration with sewage sludge in mono-incineration plants and recovering phosphorus from ash (Driver, 1998).

3.5.4 Conclusion

The present amount of organic waste from households and food production waste will not change significantly. But there is additional P-recovery potential concerning the separately collected organic waste. By tapping these potential the amount of P could theoretically rise from 50.000 to approx. 150.000 tons of P. In the sector of food production the recovery (anaerobic and aerobic treatment, fodder) is nearly 100 % and therefore there is no additional potential. As demonstrated in section 3.2, phosphorus is highly concentrated in animal wastes, but the present treatment (mainly incineration without P-recovery) does not allow using the possible P-quantities of over 200.000 t. Mono-incineration would allow the future recovery of the containing phosphorus if the ashes are stored in monofills. The potential phosphorus in ashes from energy wood is not practical for the production of a secondary P fertiliser because of the low phosphorus amount and the decentralized occurrence of these ashes. However, these ashes can be applied directly to the soil if the contents of heavy metals are moderate.

4. Scenario evaluation for European P-management

Figure 20a shows a simplified P-balance for the EU15. The dominating process is "agriculture" consuming 1.9 Mio t of P per year. Less than 0.4 Mio t/a of it reach the consumer ("Household"), showing that the P-chain is characterized by low efficiency and large losses such as accumulation of P in soils and landfills, losses to the hydrosphere by erosion, leaching, and waste water discharges. Figure 20b shows a partly optimized system, where the following adjustments or assumptions are made:
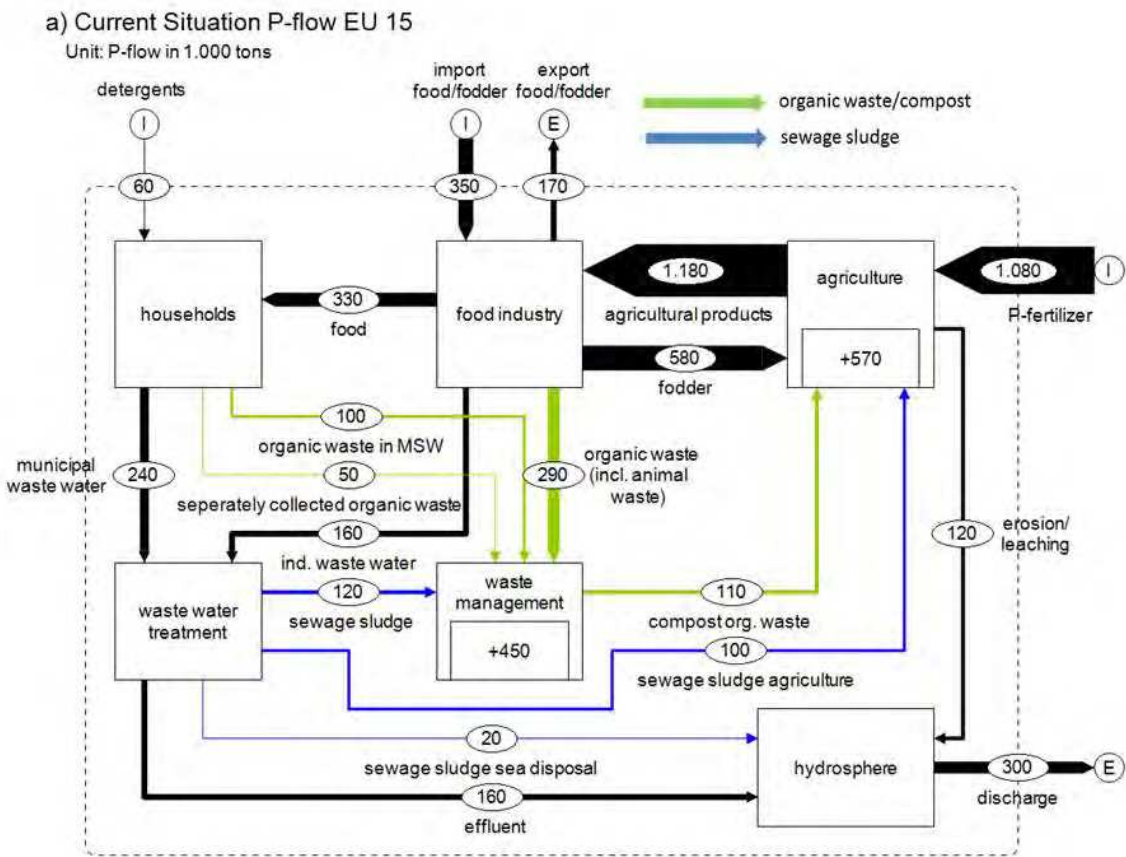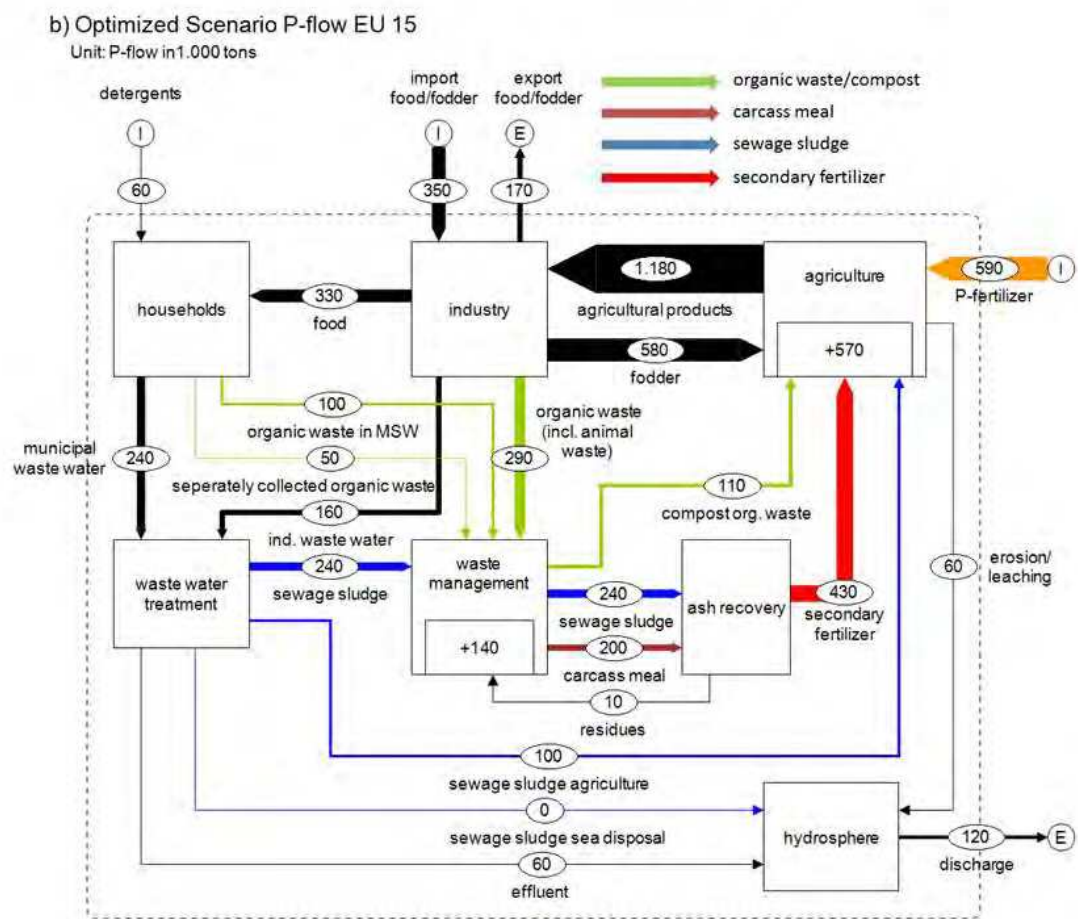
Fig. 20. Simplified phosphorus balance for the EU15: a) current situation (average year in the period 2005-2008); b) optimized scenario

- 50 % erosion reduction by implementing an efficient erosion abatement strategy for Europe
- mono-incineration of contaminated sewage sludge combined with carcass meal and production of a P-fertiliser from the ash
- no ocean dumping of sludge (already forbidden)
- 85 % P removal at all waste water treatment plants
- the amount for sewage sludge recycled in agriculture is maintained

The result as shown in Figure 20b is that losses to landfills and the hydrosphere are reduced significantly (-69 % and -60 %, respectively) and the import of P to the EU15 decreases by 45 %. Such scenarios show that there is considerable potential to optimize P management whereby optimization is a mixture of the implementation of new technologies and management practices in agriculture and waste management.

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