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Management of Phosphorus Resources – Historical Perspective, Principal Problems and Sustainable Solutions

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1. Introduction

Phosphorus, a common element ranking 11th in order of abundance in the Earth's crust, is essential for life and part of all biological systems. It is a major component of the vertebrate skeleton, an important element of gene pools, a component of cell membranes and an essential element for energy transfer. Consequently, phosphorus is a major plant nutrient. Today, about 80% of the phosphate rock mined is converted into mineral fertilisers in order to sustain world food production (Heffer et al., 2006).

Mineable phosphate rock is a non-renewable resource. However, a main proportion of the phosphorus fertiliser present in food ends up in urban wastes such as sewage sludge and slaughterhouse waste. Urbanisation and population growth impose specific challenges for phosphorus recirculation. At the global scale, more than 50% of the human population (3.3 billion) lives in urban locations and urbanisation is increasing (United Nations, 2010). In future, it will be of the utmost importance to recycle and reuse the phosphorus present in waste in order to minimise losses and conserve existing resources. In fact, phosphorus recirculation in society already has a high priority in national environmental programmes. However, the re-use of municipal wastes in agriculture is currently impeded by problems such as: (i) the presence of unwanted metals, organic pollutants and pathogens, limiting recycling of municipal wastes (sewage sludge, slaughterhouse wastes and household compost) to agricultural land; (ii) logistical difficulties in re-distributing surplus municipal wastes such as sewage sludge from urban areas back to arable land; and (iii) a low fertiliser value.

Two contrasting situations for nutrient recirculation can be identified: huge urban centres with large-scale treatment of wastes requiring long-distance transportation of nutrients back to arable land; and rural settlements with small-scale, on-site waste collection/treatment and sufficient arable land nearby for soil application. This chapter mainly focuses on phosphorus recirculation from densely populated areas.

The chapter begins by reviewing earlier waste treatment in society, the production of phosphorus fertilisers and foreseeable problems. The conditions necessary to achieve recirculation of municipal wastes are then described and possible technical solutions that fulfil these conditions are presented.

2. Historical perspective

2.1 Lesson from waste treatment in the past – limited recycling of human waste to soil

It could be assumed that in the pre-industrialised age, complete nutrient cycling was achieved through spreading human, animal and plant residues onto agricultural land. However, recycling of human waste to land was limited in early societies.

Urban settlements require wastes to be handled in a planned manner, which was the case even in early history. The Indus and Harappa cultures, which settled along the Indus river (today Pakistan) around 3000 BC, seem to have used water to remove toilet wastes and conducted the wastewater into recipient water bodies (Glover & Ray, 1994). Houses with water toilets, bathrooms and outflows connected to brick-covered channels in streets have been found. The Minoan culture on Crete in 2000-1500 BC also used water toilets, which were connected to sewage channels. Stone-walled pits of about 5 m in diameter found at Knossos were probably used for solid waste treatment through deep litter decomposition (Joyner, 1995). In the Greek and Roman cultures, town planning, water supply, sewage discharge and waste treatment were highly developed services. Sewage water from Athens in 500 BC was applied to open fields in rural surroundings (White-Hunt, 1980a), while drains and sewers of Nippur and Rome, among the great structures of antiquity, were used to carry away storm runoff, toilet wastes and street washing water. From the Cloaca Maxima in Rome (the main sewage tunnel), effluents were transported through channels to far outside settlements for both discharge and infiltration (Dersin, 1997). Solid, settled waste material, 'black gold', was recovered from sewage systems and ponds and recycled to arable land.

Type of material	Mean water content (%)	Cadmium content	
		(mg kg ⁻¹ dry weight)	(mg kg ⁻¹ phosphorus)
Household compost	65	1.3	220
Human urine	99	0.02	1
Sewage sludge	75	1.05	35
Ash (sewage sludge)	<3	1.58	35
Harvested field crops:			
Wheat	16	0.04	12
Barley	16	0.02	6

Table 1. Some characteristics of municipal wastes compared with harvested field crops. Data compiled from: Kirchmann and Pettersson (1995), Kirchmann and Widen (1994), Cohen (2009), Eriksson (2009) and Svanberg (1971).

In contrast, historical documents from China, Korea and Japan show comprehensive and effective handling and treatment systems for organic human wastes not using water for sewage transport (King, 1911). Instead, careful collection and extensive transport of latrine, organic wastes, ash, etc. from some large cities back to agricultural land by human- or animal-drawn carts and manure boats is described. Extensive collection was followed by careful storage and treatment. Application of urine, pulverised human excreta, ash and

composts, often mixed with sod or mud, canal sediments, etc., to arable land ensured a high degree of nutrient recirculation and maintenance of soil fertility. It should be noted that the volume of waste transported back to agricultural land was larger than the volume of food consumed owing to the higher water content in different wastes compared with major food types (Table 1).

The Middle Ages were characterised by a decline in hygiene and sanitation standards in cities and towns in Europe. Failure to remove the wastes from houses and streets, overloaded ditches and sewer channels in and around cities caused heavy pollution of watercourses in many places, for example London (White-Hunt, 1980a; 1980b). Wastes could be stored in tanks in the bottom of buildings or discharged into narrow lanes between houses from toilets placed above (the narrow alleys present in romantic medieval town structures) and the removal intervals could be long. The absence of an effective sewage and waste handling system was a major hindrance in combating diseases in European cities of that era. Furthermore, even animal wastes were not necessarily applied to arable land, as a significant but unknown amount was leached to produce nitrate for use in gunpowder.

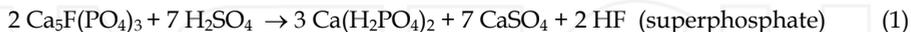
In summary, early cultures discharged or infiltrated wastes and wastewater from water-based sewage systems outside urbanised areas and thus the nutrients they contained were not recycled to arable land. Estimates show that at least 50% of total nutrients present in toilet wastes were lost, representing the proportion present in urine (see compilation by Kirchmann et al., 2005). The key lesson from this historical review is that recirculation of human wastes to soil was limited. As a result, the stock of nutrients in agricultural soils was gradually depleted and soil fertility decreased.

2.2 History of phosphorus fertiliser production - from bones to non-renewable resources

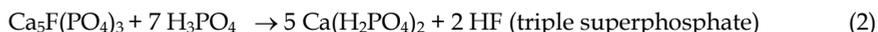
To slow down nutrient depletion in arable soils, especially of phosphorus, animal bones consisting of calcium phosphate were applied during earlier times. Several 17th Century publications in Europe mention the beneficial effect of bones. In 1769, the Swedish scientist J.G. Gahn discovered that calcium phosphate is the main component of bones, but the role of phosphorus as a major plant nutrient was still not known. Field trials demonstrated that bones should be crushed and applied in the form of powder, but the positive effect obtained was ascribed to organic components in bones. Attempts were made to improve the efficiency of bones by (i) composting them together with animal and plant wastes, (ii) boiling them in water; or (iii) treating them with steam under pressure. The widespread use of bones led to the idea of chemical treatment of bone material. H.W. Köhler of Bohemia was probably the first to suggest such a treatment and filed a patent for using acids (especially sulphuric acid) to process and produce commercial phosphate fertilisers (1831). In 1840, Justus von Liebig published work showing that plants take up nutrients in the form of inorganic components and carbon from air. Until then, academics from Aristotle (384-322 BC) to Thaer (1752-1828 AD) had considered organic matter in soil (humus) to be the source of plant dry matter. Liebig's findings contributed to the acceptance and development of phosphorus fertilisers. Together with the English businessman J. Muspratt, Liebig developed and patented a method to produce a combined phosphorus and potassium fertiliser. However, the fertiliser they produced was a complete failure, since the phosphate and potassium present were insoluble in water and therefore

unavailable to plants. When the initial failure of this fertiliser and the insignificant effect of bone powder as a fertiliser became understood, the importance of the water solubility of plant nutrients was fully recognised and the concept of producing water-soluble fertilisers was introduced (Finck, 1982).

Lack of bone material as a phosphorus source led to the import of guano from Peru around 1840. The discovery of low-grade mineral phosphates (apatite) in France and England eased the situation. The first 'artificial' fertiliser, superphosphate, was produced in England in 1843 from apatite and sulphuric acid (see reaction below).

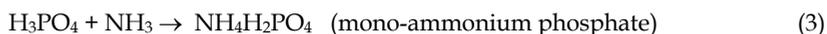


Superphosphate is a mixture of mono-calcium phosphate and gypsum, with a mean phosphorus content of 7-9.5%. In 1855, superphosphate was also produced in Germany and in 1860 the first plant was built in Sweden (Klippan). Due to increased use of artificial phosphorus fertilisers, cereal yields almost doubled between 1840 and 1880 from about 0.8 to 1.4 tons per hectare. Use of phosphoric instead of sulphuric acid for apatite dissolution resulted in triple superphosphates being commercialised in 1890. These also consisted of mono-calcium phosphate, but without gypsum (see reaction below) and had a phosphorus content of 17-23%.

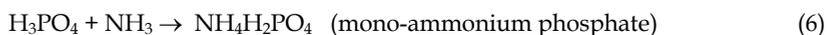
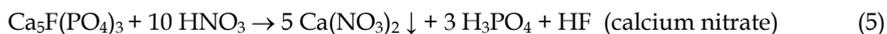


The development of the phosphate industry was secured by the discovery of large sedimentary phosphate deposits in South Carolina (USA). Mining began in 1867 and by 1889 the USA was supplying 90% of the apatite used worldwide for phosphate fertiliser production.

In 1917, a new phosphorus fertiliser was developed in the USA by reacting phosphoric acid with ammonia gas to form mono- and di-ammonium phosphate (see reactions below).



Mono-ammonium phosphate is the inorganic phosphate salt with the highest phosphorus concentration (up to 26%). The production of ammonia on a major industrial scale from nitrogen gas in air and hydrogen gas in coal through the Haber-Bosch process boosted the production of ammonium phosphate fertilisers. In 1926, IG Farbenindustrie in Germany announced the development of a series of multi-nutrient fertilisers based on crystalline ammonium phosphate. In the late 1920s, the nitro-phosphate process was developed in Norway. In this process, phosphate rock is treated with nitric acid and calcium nitrate and ammonium phosphate are produced (see reaction below).



Reviews carried out by Finck (1982), Kongshaug (1985), and Mårald (1998) show that phosphate rock, a limited mineable resource, has been the main source for phosphorus fertiliser production since 1867.

3. Relevant issues

3.1 Rock phosphate and the cadmium and uranium problem

About 80% of the phosphate rock currently mined is used to manufacture mineral fertilisers. Use for detergents, animal feeds and other applications (metal treatment, beverages, etc.) accounts for approx 12, 5 and 3 %, respectively (Heffer et al., 2006). The global production of rock phosphate amounted to 174 million tons in 2008 (IFA, 2010a). How long existing phosphorus reserves will last is difficult to forecast. Some estimates vary between 50 to 100 years, assuming peak phosphorus (Cordell et al., 2009; Cordell, 2010) and excluding reserve bases currently not economical to mine (Steen, 1998; Driver et al., 1999; Stewart et al., 2005; Buckingham & Jasinski, 2006). Other estimates are around 350 years, based on current production capacity and excluding increased demand for phosphorus (IFDC, 2010; USGS, 2011).

Depending on its origin, phosphate rock can have widely differing mineralogical, textural and chemical characteristics. Igneous deposits typically contain fluorapatites and hydroxyapatites, while sedimentary deposits typically consist of carbonate-fluorapatites collectively called francolite. Sedimentary deposits account for about 80% of global production of phosphate rock (Stewart et al., 2005). As high-quality deposits have already been exploited, the quality of the remaining sedimentary phosphorus reserves is declining and the cost of extraction and processing is increasing, mainly due to lower phosphorus content in the ore (Driver et al., 1999). Associated heavy metals such cadmium and uranium substituting for calcium in the apatite molecule are often present at high levels in phosphate rock, especially that of sedimentary origin. Rock phosphate may contain up to 640 mg cadmium per kilogram phosphorus (Alloway & Steinnes, 1999) and up to 1.3 g uranium per kilogram phosphorus (Guzman et al., 1995). Only a minor proportion of phosphorus reserves have low cadmium content (Fig. 1). Most (85-90%) of the cadmium and uranium in rock phosphate ends up in fertilisers (Becker, 1989).

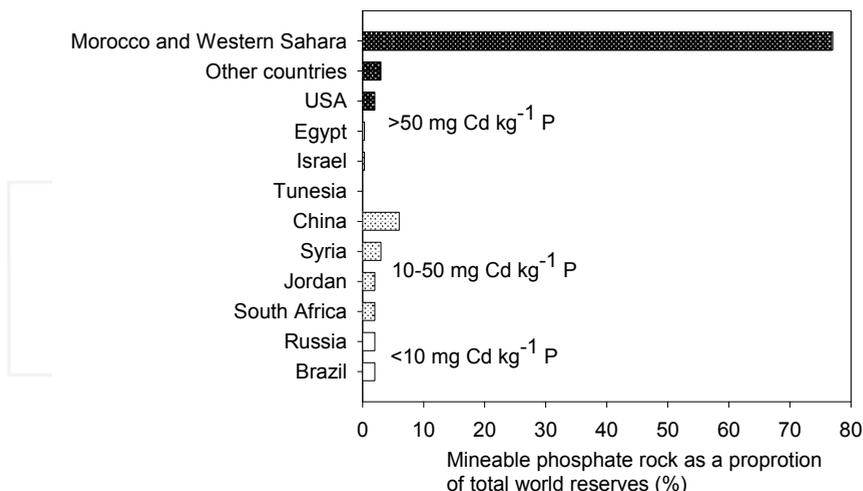


Fig. 1. Mineable phosphate rock and cadmium content. Estimates of mineable amounts taken from US Geological Survey (USGS, 2011) and cadmium contents from McLaughlin & Singh (1996).

Recent studies show that uranium originating from fertilisers accumulates in soils, leading to uranium losses to natural waters (Schnug & Haneklaus, 2008). The biochemical toxicity of uranium has been shown to be six orders of magnitude higher than the radiological toxicity (Schnug & Haneklaus, 2008). Uranium in soil enters the food chain mainly through consumption in drinking water.

A new standard for low cadmium content in phosphorus fertilisers is likely to become an issue, since the European Food Safety Authority recently reduced the recommended tolerable weekly intake of cadmium from 7 to 2.5 micrograms per kilogram body weight, based on new data regarding the toxicity of cadmium to humans (EFSA, 2009). Several countries already restrict cadmium levels in phosphate fertilisers and there is a need for exclusion of cadmium and uranium from phosphorus fertilisers for safe food production.

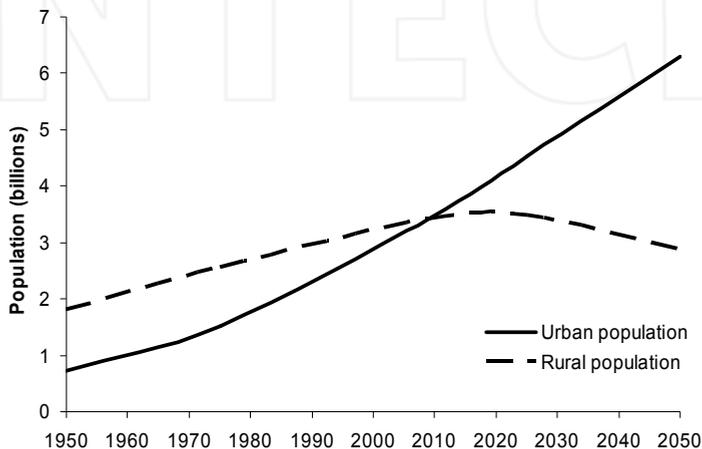


Fig. 2. Urban and rural population of the world, 1950-2050. Data from United Nations (2010).

3.2 Population growth and urbanisation

The global population is rapidly increasing. Between 1950 and 2009 the population increased from 2.5 billion to 6.8 billion and it is expected to reach 9.1 billion by 2050 (United Nations, 2009). In addition, the 20th Century witnessed rapid urbanisation in the world. The proportion of urban population increased from 13% in 1900 to 29% in 1950 and reached 50% in 2009 (United Nations, 2010). Population growth is expected to occur mainly in urban areas (Fig. 2), the population of which is projected to increase from 3.4 billion in 2009 to 6.3 billion in 2050. Cities in less developed regions will become centres of population growth. Table 2 shows the expected population growth for some large cities between 2010 and 2025. Statistics show that 1.4 billion people live in 600 cities, excluding suburban areas with a population larger than 0.75 million inhabitants (mean population of 2.3 million per city) (GeoHive, 2010).

Urbanisation and population growth impose specific challenges for phosphorus use: (i) long-distance recycling of nutrients from large cities back to arable land to avoid contamination of surrounding areas and to ensure long-term supply of P fertiliser; (ii) increase in crop production by at least 50% by 2030 to ensure sufficient food supply

(Bruinsma, 2003); and (iii) increased bio-fuel production to replace fossil fuels. As a result, agriculture will be intensified and the demand for phosphorus fertilisers will increase. The increase in phosphorus demand is estimated to be 2.8% per year (FAO, 2008).

3.3 Phosphorus in waste flows in society

All forms of agriculture remove plant nutrients from fields via the harvest of crops. The nutrients removed from fields flow through one or more of three cycles: the fodder cycle, the food cycle, and the industrial cycle (Fig. 3). The fodder cycle is the flow through housed animals, on or off the farm, which results in manures, slurries, urine, feed-lot wastes and deep-litter wastes. The food cycle concerns human consumption of food of plant or animal origin, and the resulting wastes. The industrial cycle concerns processing of animal and vegetable products into food and the resulting industrial residues.

The fodder cycle in the past was more or less closed, since manures were normally recycled to arable land except for the portion used for nitrate production for gunpowder. Today, however, transfer of fodder to a livestock farm can result in nutrient accumulation that far exceeds the absorption capacity of nearby farmland. Manure surpluses occur in many regions of Europe, Asia and the USA. For example, Haygarth et al. (1998) calculated that a typical intensive dairy farm of 57 ha in the UK with 129 lactating cows results in a net annual accumulation of approximately 26 kg phosphorus per hectare. The Netherlands has an estimated national surplus of about 8000 tons of phosphorus per year (Greaves et al., 1999). Incineration of manure to minimise the logistical difficulties of handling surplus manure and to recover energy is now practised in regions with a high animal density (Kuligowski & Poulsen, 2010).

Cities ranked according to expected size in 2025	Population (million)		
	2000	2010	2025
Tokyo, Japan	34.4	36.7	37.1
Delhi, India	15.7	22.2	28.6
Mumbai (Bombay), India	16.1	20.0	25.8
São Paulo, Brazil	17.1	20.3	21.7
Dhaka, Bangladesh	10.3	14.6	20.9
Ciudad de México, Mexico	18.0	19.5	20.7
New York-Newark, USA	17.8	19.4	20.6
Kolkata (Calcutta), India	13.1	15.6	20.1
Shanghai, China	13.2	16.6	20.0
Karachi, Pakistan	10.0	13.1	18.7
Lagos, Nigeria	7.2	10.6	15.8
Beijing, China	9.8	12.4	15.0
Manila, Philippines	10.0	11.6	14.9
Buenos Aires, Argentina	11.8	13.1	13.7
Los Angeles, USA	11.8	12.8	13.7
Al-Qahirah (Cairo), Egypt	10.2	11.0	13.5
Rio de Janeiro, Brazil	10.8	11.9	12.7
Istanbul, Turkey	8.7	10.5	12.1

Table 2. Population growth for some large cities 2000-2010 and prediction for 2025. Data from GeoHive (2010).

The food cycle suffers from severe problems regarding return of nutrients from cities back to arable land. Urban growth has resulted in centres of consumption, and hence accumulation of human wastes, that are far away from areas of agricultural production. Nutrients removed from the fields enter cities in the form of food of plant or animal origin, resulting in the production of municipal wastes such as toilet waste in the form of sewage sludge, and organic household waste in the form of compost or biogas residues. These organic wastes typically have high water and low nutrient contents. For example, dewatered sewage sludge contains 70-80% water and the phosphorus content is only about 3% of dry matter. Waste accumulation around cities leads to logistical difficulties in re-distributing human waste to arable land. The volume of urban waste is three- to five-fold larger than the volume of most harvested crops (Kirchmann et al., 2005). Lack of available arable land for organic waste application within reasonable distance from cities requires strategies for reducing the volume of urban wastes. In many cities sewage sludge is incinerated, whereby the volume of dewatered sewage sludge can be reduced by approx. 90%.

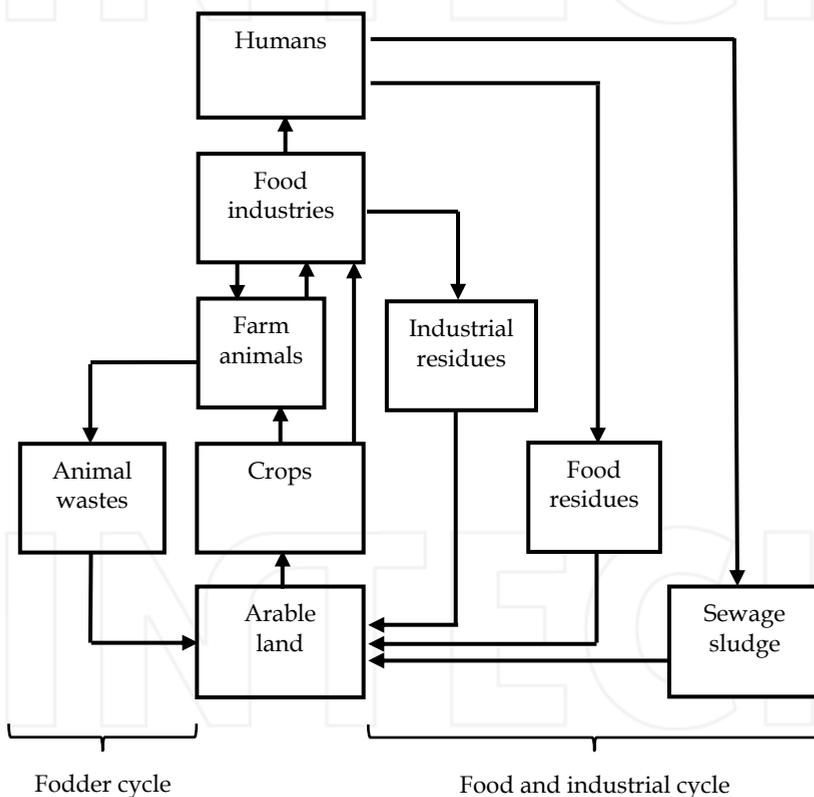


Fig. 3. Plant nutrient cycling in society can be divided into fodder, food and industrial cycles.

Fertilisation with sewage sludge has dramatically declined in many countries due to the logistical difficulties in handling surplus sewage sludge and the unwillingness of farmers to

apply sewage sludge on arable land because of the presence of heavy metals and organic contaminants. In some European countries, use of sewage sludge on arable land is completely prohibited (e.g. Switzerland). In addition, landfilling of organic material has been prohibited in EU countries since 2005. As a consequence, sewage sludge is increasingly being incinerated. As the ash is rich in heavy metals and its value as a phosphorus fertiliser is low, it is mainly landfilled.

The industrial cycle also suffers from problems regarding phosphorus recycling. The outbreak of Bovine Spongiform Encephalopathy (BSE) disease led to a ban on the reuse of meat and bone meal (MBM) in animal feed. Furthermore, many EU countries prohibit soil application of MBM. Again, incineration or gasification to destroy potential BSE infective material remains an option, normally followed by landfilling.

The amount of phosphorus in sewage sludge and MBM within the EU is estimated to be 250,000 and 133,000 tons per year, respectively (Werner, 2003). Approximately 25% of the sewage sludge and 44% of the MBM produced in the EU were incinerated in 2003 (Werner, 2003). A calculation for Sweden shows that phosphorus in sewage sludge and slaughterhouse wastes comprises 63% of the phosphorus applied through inorganic fertilisers (Table 3). In the USA, there are approximately 170 sewage sludge combustion plants incinerating approx. 20% of the sewage sludge and producing between 0.45 and 0.9 million tons of sludge ash per year (US Department of Transportation, 2005). In Japan and the Netherlands, all sewage sludge is incinerated. Donatello et al. (2010) estimated that about 1.2 million tons of sewage sludge ash are produced every year in North America and the EU and a further 0.5 million tons in Japan. Since ash is landfilled as a rule, an undesirable flow of phosphorus has arisen from fields, through cities, to landfill.

4. Possibilities for phosphorus recycling from toilet wastes

There are four main options available for recycling phosphorus from toilet wastes: a) spreading sewage sludge on arable land; b) separating human urine from faeces in special toilets and using the urine as a fertiliser; c) recovering phosphorus from sewage water in wastewater treatment plants; and d) recovering phosphorus from the ash of incinerated sewage sludge. Each option has advantages and disadvantages, as briefly discussed below, and the best choice depends on the conditions present.

Type of material	kg P ha ⁻¹ yr ⁻¹
Crops	15
Animal wastes	11
Inorganic fertilisers	6
Sewage sludge	2.6
Slaughterhouse wastes	1.2
Food residues	0.4

Table 3. Estimated amounts of relevant phosphorus (P) flows in Swedish society. Data from Kirchmann et al. (2005) and Swedish EPA (2002).

4.1 Spreading sewage sludge on arable land

The main advantage of spreading sewage sludge on arable land is that the majority of the phosphorus in toilet wastes can be returned to arable land. More than 90% of the

phosphorus entering a modern sewage treatment plant is normally incorporated into sludge (Palmgren, 2005). Additional advantages are that about 20% of the nitrogen content in sewage water is recycled and organic matter is added to the soil. The main disadvantage of phosphorus recycling via sewage sludge is the logistical problem of handling the large amounts of sludge produced in cities with limited arable land available within a reasonable distance. Another disadvantage is that sewage sludge may contain high concentrations of pollutants (metals, organic compounds, pathogenic organisms, pharmaceutical residues, viruses, etc.). An additional disadvantage is that the phosphorus in sewage sludge is mainly bound to iron or aluminium, which are used for phosphorus precipitation in wastewater treatment plants. Iron/aluminium phosphates have very low solubility and the plant availability of the phosphorus in sewage sludge is usually low.

4.2 Urine separation

About 75% of the nitrogen and 50% of the phosphorus and potassium in sewage water originate from urine (Lentner et al., 1981; Kirchmann & Pettersson, 1995; Viessman & Hammer, 1993; Bitton, 1994; Droste, 1997). Urine is a suitable fertiliser but urine separation is not a suitable option for phosphorus recycling from urban areas. The main reason is that urine is a very dilute solution, with a salt content of less than 1% and a phosphorus concentration of about 0.05% (0.36-0.67 grams phosphorus per litre), (Kvarnström et al., 2006). For a large city this would require storage and transport of very large volumes. For example, separating the urine from the London urban zone (approx. 11.9 millions inhabitants) would mean storage and transportation of approx. 6.5 million cubic metres of urine per year. This would require the equivalent of 1,300 Olympic swimming pools for urine storage, while spreading would involve 165,000 40-ton tanker loads per ca 3 month. In addition, separate collection of urine causes precipitation of phosphate salts (struvite, calcium phosphate, etc.) in pipes due to increased pH level (> 9) which leads to blockages (the pH in urine increases due to enzymatic splitting of urea to ammonia and bicarbonate). A recent study showed that around 45% of the phosphorus in urine precipitates in storage tanks (Wohlsager et al., 2010). It is therefore difficult to transport urine in pipes over longer distances. Richert Stintzing et al. (2007) reported that the maximum distance for transporting urine in pipes should not exceed 10 metres in order to minimise scaling problems. Other disadvantages of urine separation are the requirement for a separate pipe system and special toilets, losses of nitrogen due to ammonia volatilisation, possible contamination with pharmaceutical residues and the continuing need for wastewater treatment of faecal water, greywater (laundry, dishwashing and bathing) and industrial wastewater. Thus, half the phosphorus in wastewater will still end up in sewage sludge. The conclusion is that urine separation is a suitable recycling strategy for rural settlements and small villages lacking sewage treatment infrastructure (e.g. in developing countries) but having agricultural land adjacent to housing.

4.3 Phosphorus recovery from wastewater

Phosphorus recovery from wastewater is mainly based on precipitation of phosphorus from side-streams within sewage treatment plants. This produces calcium phosphate without organic matter or other impurities (van Dijk & Braakensiek, 1984; Eggers et al., 1991; Seckler et al., 1996a,b,c; Angel, 1999; Giesen, 1999) or struvite (magnesium ammonium phosphate) (Ueno & Fujii, 2001; Parsons et al., 2001; Britton et al., 2009). Calcium phosphate, which is

equivalent to rock phosphate, can be processed industrially (Schipper et al., 2001). Struvite cannot be processed industrially but can be used as a slow-release fertiliser (Johnston & Richards, 2003a). The main disadvantage of recovering phosphorus directly from sewage water is that only the phosphorus present in the liquid phase can be recovered, which reduces the efficiency of phosphorus recovery considerably. Anaerobic digested sludge usually contains 40-80% of the phosphorus present in wastewater and therefore only 20-60% of total phosphorus in sewage water can be recovered as inorganic salts from side-streams in treatment plants (Murakami et al., 1987; Wild et al., 1997; Sen & Randall, 1988; Gaastra et al., 1998; Strickland, 1999; Brdjanovic et al., 2000; Piekema & Giesen, 2001; Balmer et al., 2002; Hao & van Loosdrecht, 2003). Phosphorus can precipitate *in situ* during anaerobic digestion as struvite, calcium phosphate and/or iron/aluminium phosphate and is incorporated into sewage sludge and thereby withdrawn from the liquid phase. Another disadvantage of phosphorus recovery from wastewater is that the cost of the chemicals required for phosphorus precipitation as struvite or calcium phosphate currently exceeds the value of the phosphorus products recovered (Dockhorn, 2009).

4.4 Phosphorus recovery from sewage sludge ash

Sewage sludge contains more than 95% of the phosphorus entering a modern wastewater treatment plant. For example, the Käppala sewage treatment plant in Stockholm, Sweden, has a phosphorus removal efficiency of 97% (Palmgren, 2005). Incineration of sewage sludge at 800-900°C does not cause significant phosphorus losses through volatilisation and the phosphorus remains in the ash. Thus, the potential for phosphorus recovery from sludge ash is high. The main disadvantage of this option is the need for investment in sludge incineration. However, a considerable amount of sewage sludge is already being incinerated and sludge incineration is expanding due to the difficulties in handling large volumes of sewage sludge. The phosphorus concentration in ash of incinerated sewage sludge usually varies between 7 and 13% by weight (Cohen, 2009; Schaum et al., 2004) and is only slightly lower than the phosphorus concentration in beneficiated phosphate rock (12-16% by weight), indicating that ash of sewage sludge is a concentrated phosphorus source.

Several processes have been suggested for recovering phosphorus from sewage sludge ash. In some approaches, phosphorus is leached from the ash using an acid, followed by precipitation as iron phosphate (Takahashi et al., 2001) or aluminium phosphate (Schaum et al., 2004). The drawback of phosphorus recovery techniques based on chemical precipitation is that the products recovered, such as iron phosphate and aluminium phosphate, have a very low solubility and thus cannot release phosphorus at rates sufficient for crop demand. Their fertiliser value is therefore low. Furthermore, the separated precipitates cannot be processed by the phosphate industry, since iron and aluminium cause undesirable reactions. In other approaches, phosphorus is leached from the ash using an alkali, followed by precipitation as calcium phosphate (Stendahl & Jäferström, 2003, 2004; Nishimura, 2003) or sodium phosphate (Ek, 2005). Ash dissolution with an alkali is inefficient as only a minor proportion of the phosphorus (< 50%) can be leached, whereas dissolution with an acid achieves almost complete phosphorus leaching (Cohen, 2009). Another process for phosphorus recovery involving dissolution of ash from sewage sludge in acid using ion exchange and recovering the phosphorus in the form of phosphoric acid has been suggested by Jensen (2000). Hong et al. (2005) describe how phosphoric acid can be extracted with organic solvents after dissolution of incinerated sewage sludge ash with sulphuric or

hydrochloric acid. Another process is based on heating the ash up to 1,400°C to vaporise elemental phosphorus, which is condensed in water and oxidised to phosphoric acid (Japanese patent 9145038, 1997). Heating sludge ash to evaporate the phosphorus requires large amounts of energy and the efficiency of phosphorus recovery is moderate due to the formation of iron phosphate slag (Schipper et al., 2001). A process for thermochemical removal of heavy metals from sludge ash and use of the residue as a fertiliser has been developed by the company AshDec (Herman, 2009; Adam et al., 2009; Mattenberger et al., 2008, 2010). A new process for production of ammonium phosphates, called CleanMAP™ Technology, has been developed by the company EasyMining Sweden AB (EasyMining, 2011). The technology enables production of pure mono-ammonium (MAP) or di-ammonium phosphate (DAP), irrespective of the quality of the phosphorus raw material, and is based on selective liquid-liquid extraction coupled with precipitation. Cadmium, uranium and other metals are separated out and not incorporated into the fertiliser. Furthermore, the costs are lower than those of state-of-the-art technology for phosphorus fertiliser production and no energy is required for water evaporation. Energy savings of around 5 tons steam per ton phosphorus are achieved compared with state-of-the-art fertiliser production. The technology can be used for phosphorus extraction from phosphate rock and other raw materials such as ash (of incinerated sewage sludge, slaughterhouse wastes or incinerated manure). Processing the ash of incinerated sewage sludge includes the following steps: (i) ash is dissolved in sulphuric acid and insoluble material is separated out and washed; (ii) phosphate ions are recovered from the leach solution as mono-ammonium phosphate using the CleanMAP™ Technology; (iii) iron and aluminium ions mainly originating from phosphorus removal during wastewater treatment are recovered in hydroxide or sulphate forms to be reused for phosphorus precipitation in wastewater treatment plants; and (iv) remaining dissolved heavy metals are removed from solution as sulphides upon precipitation with sodium sulphide. Outgoing water from the process has neutral pH and a low phosphorus and metal content. In summary, the advantages of this process are that the chemical used for phosphorus separation (ammonia) becomes part of the product, the product is concentrated and water-soluble, and metals are separated out during the process and the fertiliser is of high quality.

5. Soluble phosphorus fertilisers – essential for efficient use in agriculture

Rock phosphate is the raw material from which all types of phosphate fertilisers are produced. Most rock phosphates are not suitable for direct application to soil, since they are insoluble in soil and water. Phosphate rock is therefore processed by the fertiliser industry into soluble fertiliser with high plant availability (see section 2). The four most common phosphorus fertilisers are mono-ammonium phosphate (MAP), di-ammonium phosphate (DAP), single superphosphate (SSP = mono-calcium phosphate + gypsum), and triple superphosphate (TSP = mono-calcium phosphate), all with high water solubility. Ammonium phosphates dominate worldwide (Fig. 4), and the phosphorus in NPK compound fertilisers is usually based on one of these compounds.

It is commonly believed that the use efficiency of phosphorus fertiliser by crops is low, ranging from 10 to 25% based on calculations of the difference between crops fertilised with phosphorus and unfertilised controls (Crowther et al., 1951; Mattingly & Widdowson, 1958, 1959; Johnston & Richards, 2003b). However, through calculations based on the balance between inputs and outputs of phosphorus, Syers et al. (2008) showed that a use efficiency

of 95% could be obtained at optimal phosphorus levels by replacing the amount removed with harvest with soluble phosphorus fertiliser. A substantial proportion of the phosphorus added with fertilisers to soil was found to be utilised by crops during following years, which means that some fertiliser phosphorus accumulates in the soil in reversible residual forms. Thus, the objective should be to maintain the amount of readily plant-available soil phosphorus at the optimum level. It is therefore important that phosphorus fertilisers are highly soluble in water.

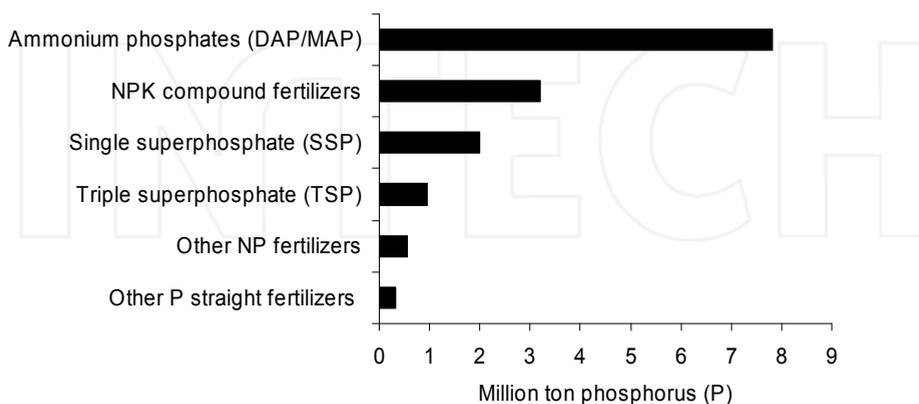


Fig. 4. World consumption of phosphorus fertilisers in 2008. Data from IFA (2010).

6. Conditions necessary to achieve efficient nutrient cycling

An environmental target in modern societies is to recycle nutrients back to agricultural land in a sustainable way. Therefore, municipal wastes must be ‘safe and clean’. In order to achieve this target, a number of actions have been taken. For example in EU countries, landfilling of organic material has been prohibited. The use of certain metals (e.g. cadmium, mercury) has been prohibited or is highly restricted to reduce contamination of wastes. Industries connected to sewage treatment plants must keep discharge of pollutants at a minimum to avoid contamination of sewage sludge. Source-separation of household wastes has been introduced to produce composts without contaminants. These efforts have improved the quality of municipal wastes. For example, the cadmium level in sewage sludge in Sweden has declined from rather high concentrations to only 20-40 milligrams per kilogram phosphorus (Eriksson, 2009).

However, it is questionable whether these commendable improvements will result in long-term use of municipal wastes on arable land, considering that a number of conditions must be fulfilled for sustainable recycling. Table 4 summarises the most important conditions that must be fulfilled to achieve sustainable recycling of municipal wastes back to soil, including: (i) ‘safe and clean’ wastes that have a negligible effect on the soil and environment (refers to their possible content of metals, organic contaminants and pathogens); (ii) high plant availability of nutrients in wastes to give a significant fertiliser effect (i.e. if nutrients in wastes are bound in less soluble or insoluble form, recycling will not replace inorganic fertilisers); and (iii) redistribution of nutrients to arable land through wastes must be related to nutrient removal (i.e. the ‘law of nutrient replacement’ should be followed).

Nutrients removed from soil through harvest and losses should be replenished with equivalent amounts. Application of excessive amounts to arable land is unacceptable and long-distance transportation would be required to achieve equitable redistribution while avoiding accumulation of nutrients in arable land surrounding cities. It seems that all these conditions can only be achieved if handling of municipal organic wastes in society is greatly improved.

Condition for nutrient cycling

No adverse effect on food quality and the environment

Low levels of unwanted metals
 Low levels of organic pollutants
 Low levels of pharmaceuticals
 Low levels of pathogens

Efficient nutrient supply

High plant availability
 Low nutrient losses

Equitable redistribution and spreading on arable land

Long-term transportation
 Energy-saving compared with mineral fertiliser use

Table 4. Defining conditions for recirculation of nutrients in wastes back to agricultural land to achieve sustainable management.

7. Closing the phosphorus cycle in society through incineration of phosphorus-containing wastes and fertiliser production from ash

As pointed out above, the demographic trend for increasing urbanisation makes towns and cities hot-spots for accumulation of nutrients and metals, which can cause biogeochemical imbalances (Grimm et al., 2008). The accumulation of wastes in mega-cities is managed through dumping, partial recycling (e.g. Færge et al., 2001) and incineration (Donatello et al., 2010). Re-applying nutrients to arable land only as recycled organic wastes is not a viable option any longer (Fig. 3). The trend for incinerating more sewage sludge, not only in mega-cities but also in cities and towns, means that spreading of sewage sludge will decrease in future. We consider ash to be the main waste product from increasing urbanisation and processing of ash for nutrient extraction to be an important step to close nutrient cycling in society (Fig. 5). The approach of not recycling urban organic wastes as such but producing

inorganic fertilisers from nutrients present in wastes has been proposed earlier (Kirchmann et al., 2005).

Incineration of manure to recover energy is also increasing, as other treatment options are often more expensive when large volumes have to be handled. Phosphorus and potassium can both be extracted from ash of incinerated manure. For example, ash of poultry litter can contain up to 10% phosphorus and 8% potassium (Blake & Hess, 2011). A considerable amount of the potassium in ash of poultry litter originates from bedding materials such as straw. The company Kommunekemi AS has developed a process for production of pure potassium fertilisers (potassium chloride or sulphate) from straw ash contaminated with cadmium (Ottosson et al., 2009). Potassium and phosphorus are major plant nutrients that are obtained through mining of non-renewable minerals. In the past, potassium was in fact obtained from ash. The term ‘potash’, which commonly refers to potassium-containing minerals, originates from the old method of leaching wood ash and evaporating the solution in large iron pots to obtain potassium carbonate (Prud’homme, 2011).

The potassium content of sewage sludge is very low (0.1% of dry matter in activated sludge) (Binnie et al., 1995), since potassium is generally water-soluble and not incorporated into the solid phase. Therefore, recovery of potassium from sludge ash is not relevant. However, about 20% of the nitrogen in sewage water is incorporated into sewage sludge (Palmgren, 2005). This cannot be recycled if sewage sludge is incinerated, since during sludge incineration the nitrogen in organic matter is oxidised into nitrogen gas. However, nitrogen is not a limited resource like phosphorus or potassium, since it is recovered from air (air contains approx. 78% nitrogen) and thus the nitrogen lost during incineration of sewage sludge has little relevance for agriculture. For example, the total sewage sludge produced in Sweden every year contains around 5000 tons of nitrogen, which is equivalent to around 2 kilograms per hectare arable land. The nitrogen demand of crops usually varies between 80 and 150 kg per hectare and year. Furthermore, during sludge incineration organic matter is oxidised into carbon dioxide but as sludge is based on renewable biomass, it is a carbon-neutral fuel. The role of sewage sludge as a source of organic matter for agriculture is minor. For example, the organic matter content of sewage sludge is about 60% of dry matter

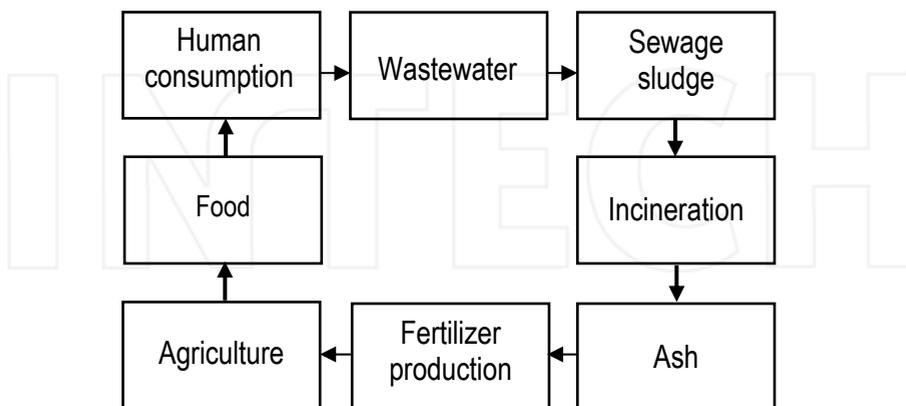


Fig. 5. Incineration of sewage sludge followed by nutrient extraction and fertiliser production from ash as a way to close the food cycle in society.

(Palmgren, 2005), which for Sweden corresponds to a supply of 48 kilograms per hectare arable land and year through sewage sludge. The average supply of organic matter through crop residues is about 2000 kilograms per hectare and year. The conclusion is that incineration of sewage sludge does not represent a great loss of valuable resources. Recovery of only phosphorus and precipitation chemicals seems to be an acceptable strategy.

8. Conclusions

Recycling of the phosphorus present in wastes back to arable land is a key issue in achieving sustainable phosphorus management. According to the conditions and difficulties described above, it appears that recirculation of extracted phosphorus from municipal wastes rather than whole waste redistribution on arable land is a logical way forward.

One approach would be to incinerate phosphorus-rich wastes, followed by further treatment of the ash for phosphorus extraction. The extracted phosphorus should be concentrated to enable redistribution to all arable land, allowing long-distance transportation, and non-contaminated to ensure safe food production. In addition, the recycled fertiliser should be water-soluble, containing plant-available nutrients and having the same fertiliser value as mineral fertiliser. Extraction of phosphorus fertiliser from ash has the potential to partly replace rock phosphate-based fertilisers. The trend for increasing incineration of municipal wastes is in line with this approach.

In future, wastes will be re-used, replacing valuable raw materials. We believe that continued technological development of waste treatment will lead to sustainable nutrient recycling in society, characterised by efficient processes and high quality products.

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