Phosphorus fertilisers from by-products and wastes

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by

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Summary

This paper addresses the question ‘Can fertilisers from processed by-products and wastes become a competitive alternative for conventional mineral phosphorus fertilisers?’ In answering this question, we take a global perspective. Firstly, we briefly summarize the global phosphorus (P) stocks and flows. We then describe the main by-products and wastes available in the world that may be used as P fertiliser. Next, we discuss the possible processes and treatments used before by-products and wastes are used as fertilisers, and consider the P availability of these fertilisers to crops. We argue that fertilisers from (processed) by-products and wastes may become a competitive alternative for ordinary mineral P fertilisers only regionally. We proceed by addressing the question ‘How to use ordinary P fertilisers from rock phosphate and P fertilisers from by-products and wastes in an optimal way, from the viewpoints of food security, resources use efficiency, equity, environmental sustainability and feasibility?’

Animal manure is by far the largest by-product and source of P. Estimates suggest that the total amount of P in manure produced per year (20-30 Mt P) is rather similar to the annual amount of ordinary P fertiliser consumed per year (15-20 Mt). However, only a fraction of the manure is collected and applied to crop land, while the remainder is dropped in pastures or wasted. Sewage sludge (3-5 Mt) is a much smaller source. Slags, ashes, chars and bone meal are other relatively small and uncertain sources. The availability of P from by-products and wastes is highly variable, but our compilation of literature results indicate that the availability is as large as that of ordinary P fertiliser.

The major advantage of increasing the use of P fertilisers from by-products and wastes is the contribution to increasing resource use efficiency, to decreasing surface water eutrophication and associated biodiversity loss, and to decreasing the rate of P rock depletion. The major disadvantage of using P fertilisers from by-products and wastes is their variable nutrient composition and P availability, potential presence of contaminants, unknown status and low acceptance by farmers, and the lack of a proper marketing and distribution infrastructure.

In the end, society will need the P fertilisers from by-products and wastes, because of the likely future depletion of P rock deposits. Strategies should be developed for optimal, long-term use of the various possible P sources. It is argued that an international agreement and institution might help here.

Key words: Ash, animal manure, biochar, phosphorus cycling, phosphorus recovery, resource use efficiency, sewage sludge, soil phosphorus, waste, waste treatment,
1. Introduction

Life depends on phosphorus (P). Phosphate esters and anhydrides dominate the living environment; the genetic materials DNA and RNA and most coenzymes are esters of phosphoric acids. The principal reservoirs of biochemical energy are phosphates (Westheimer, 1987). Not surprisingly, the availability of P (and nitrogen, N) controls many aspects of global biogeochemistry; it often limits the rate of net primary production on land and in sea (Schlesinger, 1991). The availability of P in nature is largely controlled by the mineralisation and recycling of P from dead organic matter, rock weathering, deposition of dust and biogeochemical reactions of P with soil minerals, especially iron and aluminium oxides and hydroxides. The latter reactions lower the solubility of P in (soil) water, leaving only small quantities for biota. Although the biota has mechanisms to increase the weathering rate and the availability of P (e.g., Marschner, 2012), primary production in many natural environments and traditional farming systems is strongly limited by P.

Continuous crop production requires application of P from external sources in order to replenish the P taken up by crops and to avoid a decreasing, and finally too low soil availability of P. Before the introduction of mineral fertilisers around 1850, application of P and other nutrients occurred via locally available sources, such as animal manures from livestock grazing on communal land, bone meal, composts, and wastes (Stewart et al., 2005). A shortage of bone meal led to searching of mineral rock deposits, which were first found in Spain and Great Britain, and later in the USA, (former) USSR and Morocco (Cathcart, 1980). The manufacture and use of mineral fertilisers from the mid-19th century and especially from the mid-20th century have greatly increased the availability of P and other nutrient elements in soils and thereby primary production. Global food production has increased by roughly one order of magnitude during last two centuries, through a combination of the increased availability of high-yielding crop varieties, fertilisers, irrigation and pesticides, increased acreage of crop land, and improved farm management. As a drawback, the necessity of reusing N, P and other nutrient elements from human and animal wastes became less, leading to inefficient use and also to considerable losses of these elements to the wider environment (Schröder et al., 2011).
There is a longstanding debate about the depletion of mineable rock P, which was fuelled by the spikes in fertiliser P prices in 2008 and 2009 and the awareness of the geopolitical dependency on only a few countries with significant primary P resources. Reports suggest that economically mineable P rock is depleted within 60 to 400 years (Steen, 1998; Stewart at al., 2005; Hilton et al., 2010; Van Kauwenbergh 2011; Scholz et al., 2013). These reports, together with reports about the depletion of mineable copper, zinc, potassium and various rare earth metals provoked various policy initiatives, including also the ‘Flagship initiative for a resource efficient Europe’ by the European Commission (COM, 2011). They also provoked the search for by-products and wastes as sources of P and other nutrient elements in food production. This paper addresses the question whether ‘fertilisers from processed wastes can become a competitive alternative for conventional mineral P fertilisers?’ Before answering that question, we briefly describe the global P cycle and the relative contributions of by-products and wastes to the global P cycling. We then summarize the processes and treatments used before by-products and wastes are used as fertilisers, and briefly consider the P availability of these fertilisers to crops. We close by arguing that fertilisers from (processed) by-products and wastes have to be used especially for maintenance fertilization and high-grade P fertilisers for ‘fertilization of crops’.

2. Global flows of phosphorus

Figure 1 shows a simplified version of the global P cycle. Most of the P is stored in marine sediments and rocks, in the order of billions of Mt (1 Mt = 1 million tons = 1 Tg). Only a fraction of these stocks is economically minable, about 0.1 million Mt (e.g. Stewart et al., 2005). Also, large amounts of P are stored in the top 50 cm of agricultural soils (0.05 million Mt), in the top soil of soils under forests and grasslands (0.15 million Mt) and in ocean waters (0.1 million Mt). Relatively small amounts are stored in biomass, about 500 Mt in vegetation, 50 Mt in animals, and only 3 Mt in humans. In addition, increasing amounts are stored in infrastructural areas, including landfills. Much smaller amounts are in the atmosphere (~0.03 Mt), and therefore not shown in Figure 1.

Large annual fluxes between natural pools occur in the oceans between the dissolved P pool and the biomass pool (~ 1000 Mt) and in the terrestrial biosphere between soils and
aboveground biomass (~100 Mt). The annual uptake of P in harvested crops and forages is much less, in the range of 30 Mt per year. Losses of P from soils through erosion, burial of detritus P in marine sediments and the ‘appearance’ of fresh rock P though tectonic uplift are in the same order of magnitude, i.e., between 15 and 35 Mt per year. Fertiliser P use (~15 Mt during the 2000-2010) is also in that order of magnitude. About 5-8 Mt P enters households in plant and animal derived food, and about 3 to 6 Mt P in food is ingested. In addition, some 2-3 Mt P enters households via detergents and other products. The unused P in households and industry is returned to crop land, is discharged to surface waters or ends up in the ‘infrastructural pool’. Atmospheric deposition has been estimated at 3-4 Mt P per year. This flux originates mainly from wind-eroded particles (Smil, 2000); it is not shown in Figure 1.

The kinetics of the P cycling between pools differs greatly. The surface layers of oceans waters and the solution pool of rooted top soils have relatively low P concentrations (low stocks); these pools are depleted by phytoplankton and plant roots and replenished again by mineralisation and desorption processes a few times per year (e.g., Pierzynski et al., 2005). The biogeochemical cycling of P in terrestrial biomass P, including crop residues, manures and wastes in soil has turnover times of 1-10 years. Depletion of mineable rock P, increased soil erosion rates, and increased discharges and runoff transport to oceans, where the P eventually sinks into sediments, occurs at civilization times scales, i.e., $10^3$ years (Smil, 2000). On the time scale of hundreds of millions of years, these sediments are uplifted and subject to rock weathering, completing the global cycle (Schlesinger, 1991).
Figure 1. The global phosphorus cycle. Boxes represent pools and arrows represent annual fluxes. Numbers in pools are P stocks in Mt, numbers near arrows are P fluxes in Mt per year (1 Mt = 1 million tons = $10^{12}$ g = 1 Tg). After Schlesinger (1991) and Smil (2000).

The global P cycle is not well examined and many of the pools and fluxes shown in Figure 1 have large uncertainty (Smil, 2000). This holds especially also for the quantifications of regional distributions of pools and fluxes, for which data availability is limited. Estimates of stocks and fluxes of P in the biosphere are quite often estimated from assumed C/P and N/P ratios, as the cycles of carbon (C) and nitrogen (N) are much more examined, though not necessarily better quantified. Also, the P cycle is less dynamic and complex compared to the C and N cycles.

Humans have greatly affected the biogeochemistry of the terrestrial biosphere and the surface layers of the hydrosphere during the last two centuries. The amounts of P in harvested crops have increased more than 10 times, erosion rates have been tripled, and discharges of P to surface waters have increased greatly. These changes have been
brought about mainly through an increased area of cropped land, increased number of domestic animals, and increased fertiliser use. The increase in P fertiliser use between 1961 and 2009 is depicted in Figure 2. Significant use started in the early 1950s, especially in Europe and North America, and levelled off from the 1990s, due to a combination of saturated markets in Europe and North America and political changes (collapse of the Soviet Union). Most of the fertiliser P use is now in Asia (~60%). The availability of relatively cheap fertilisers has both boosted crop production and animal production, but has also contributed to the neglect of the plant-nutritive value of by-products and wastes (e.g., Schröder et al., 2011).

Figure 2. Annual consumption of ordinary phosphorus fertilisers during the period 1961–2009 (Source: FAOSTAT).
3. Role of by-products and wastes in global phosphorus cycling

A wide range of possible by-products and wastes are available as P sources for direct recycling or for processing P fertiliser (e.g., Power and Dick, 2000; Table 1). Many of these have high organic matter content, suggesting that P is partly organically bound and partly in inorganic forms: manure, sludge, compost, seaweed. The other half is largely inorganic; here P is associated with various cations (calcium, Mg, K, Al, Fe, Zn, etc) and oxi-hydroxides: ashes, bone meal, stone meal, soils, sediments. Most of these sources also contain various other nutrient elements, including micro-nutrient. Various sources have relatively high levels of potentially toxic elements, and are therefore not permitted to be used in agriculture in countries of the European Union and North America (e.g., Davis, 2008; Hilton et al., 2010).

Table 1. By-products and wastes as sources of phosphorus, in Mt per year. Estimates based on literature and own calculations.

<table>
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<tr>
<th>Sources</th>
<th>Amounts, Mt P per year</th>
<th>Ref.</th>
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<tbody>
<tr>
<td>Animal manures</td>
<td>20 - 30</td>
<td>1</td>
</tr>
<tr>
<td>Sewage sludge</td>
<td>3 - 5</td>
<td>2,3</td>
</tr>
<tr>
<td>Phosphogypsum</td>
<td>0.3 – 2</td>
<td>1,4,5</td>
</tr>
<tr>
<td>Composts from crop residues, processing industry</td>
<td>0.1 - 1</td>
<td>2</td>
</tr>
<tr>
<td>Ashes from coal-driven power plants</td>
<td>1 – 10</td>
<td>1</td>
</tr>
<tr>
<td>Ashes from biomass and waste incineration</td>
<td>0.1 – 2</td>
<td>1</td>
</tr>
<tr>
<td>Ashes from the steel industry (basic slag)</td>
<td>0.5 – 1</td>
<td>1</td>
</tr>
<tr>
<td>Animal bones from slaughter houses</td>
<td>0.1 – 1</td>
<td>1</td>
</tr>
<tr>
<td>Fish</td>
<td>0.3 - 0.6</td>
<td>1</td>
</tr>
<tr>
<td>Mining P-rich soils</td>
<td>&lt; 0.1</td>
<td>1</td>
</tr>
<tr>
<td>Dredged sediments</td>
<td>&lt; 0.1</td>
<td>1</td>
</tr>
<tr>
<td>Stone meal, crushed olivine, amphibolites, low-grade P rocks</td>
<td>1-10</td>
<td>1</td>
</tr>
</tbody>
</table>


3.1. Animal manures

Estimates of the global amounts of P in excreted animal manures are in the range of 20 to 30 Mt in 2010. Sheildrick et al (2003) estimated the total amount at 21 Mt for the mid-1990s and Smil (2000) estimated at least 16 to 20 for the mid-1990s. In 2010, production is very likely much larger, because animal production is increasing rapidly, especially in south-
east Asia and Latin-America. For example, amounts of P in animal excrements more than doubled in China between 1980 and 2005 (Ma et al., 2012).

Between 50-90% of the global yields of major cereals like wheat, maize and soybean are now used to feed animals. Animals retain only 10 to 40% of the P in feed, depending on animal species and productivity, and excrete the remainder. The P in manures can be used as effectively as that in P fertilisers, when properly collected and applied in the right amount and place (Smith and Van Dijk, 1987; Greaves et al., 1999; Schröder et al., 2011). However, less than half of the manure produced in the world is collected in stables, and not all collected manure is returned to land. It has been estimated that 45 % of P in animal manure is discharged to surface waters in China (Ma, et al., 2012).

Traditionally, domestic animals were kept on pastoral systems or in mixed systems where the feed was produced on the farm, and where all manures produced were returned to land. Modern livestock production systems are specialized and tend to agglomerate near markets, i.e., in urban areas. These systems most often miss the land-base for proper manure disposal, and there is often a strong positive relationship between animal density and surpluses of both N and P (De Clerck et al., 2001; Csatho and Radimszky, 2009), and soil P status (Maguire et al., 2005). Figure 3 shows a positive correlation between the amount of P in animal manure produced and soil P surplus, calculated as P applied minus withdrawal by crops, for the OECD countries (data for 2004). This indicates that in countries with high livestock density, a large part of P applied to soil via manure is given as a surplus, leading to accumulation of P in the soil, thereby increasing the risk of P losses to surface waters (Sharpley and Syers, 1979), and groundwater (Leinweber et al., 1997; Koopmans et al., 2007).
Environmental regulations by governments increasingly restrict the amount of manure applied to land. This forces livestock farmers to transport the manures to other areas, or to process the manures and then to export the processed manures, or to relocate livestock farms (Menzi et al., 2010). The processing of manure is discussed further in paragraph 4.

3.2. Sewage sludge
Based on mean estimates of human excretion (1.2 g P per capita per day) and household use of detergents (0.8 g P per capita per day), Smil (2000) calculated total human output of 0.75 kg P per capita per year. At the current human world population of 7 billion, this translates to a total of 5 Mt P per year in human wastes. In principle, all P in these waste can be reused as soil amendment, but the reality is that only some 10% is re-used.

Until recently, collection and reuse of human excreta in agriculture was common in most small villages and small cities, for hygienic reasons and for nutrient recycling purposes. The collected human excrements are often termed ‘night soil’ and subjected to some treatment (e.g., composting) before reuse on land (e.g., Yang, 2006). In rural areas, households usually dispose of the night soil on own farm land. However, in most larger cities excreta were discharged directly into canals and rivers or dumped in landfills, and this practice has...
increased over time during last centuries due to urbanization. The smell and health problems related to these practices induced the development of communal sewage collection systems and treatment plants, especially in Europe and North America, but increasingly also in big cities of other continents. These sewage treatment plants make it possible in principle to recycle most of the nutrients from human excrements via the produced sewage sludge. Yet, it is estimated that at present only a small percentage of the P in human excreta is recycled within agriculture or aquaculture.

Application of sewage sludge on agricultural land in Europe and North America is hampered by regulations, which set limits to the content of pollutants such as heavy metals in sludge. Heavy metals mostly originate from small industries that use the same sewerage systems as humans. Although the content of heavy metals has gone down through treatment of these point sources, nutrients from sewage sludge are still not much re-used in agriculture, also because of the presence of other pollutants (e.g., pathogens, antibiotics, hormones). In organic farming, the use of sludge is banned by the USDA and the European Commission (Schröder et al., 2011;http://www.ota.com/organic/foodsafety/manure.html). As a consequence, sewage sludge is now often dumped in landfills or incinerated and the ashes dumped in landfills. This practice is not considered sustainable and worldwide many projects focus now on the recovery and recycling of P from sewage water, through selective precipitation as calcium phosphates or struvite (MgNH4PO4.6H2O).

3.3. Ashes and biochar
Estimates suggest that some 10 million Mt of biomass is burned annually (Levine, 1991). Humans are responsible for about 90% of the biomass burning, which includes wood, leaves, trees, grass, manure and trash as sources. The burning is done for various reasons, such as clearing land, heating and cooking, electricity generation and as method to dispose of wastes. Ashes of biomass make up some 4% of the original weight of woody biomass, but the ash weight is much higher in case of incomplete burning or in the case of manure as source. Ashes contain commonly between 0.1 and 1.5% P, which are recycled in-situ in the case of forest and grassland fires. Estimates of the total amount of P in burned biomass range from 0.1 to 2 Mt per year. In case of manure and biomass incineration in power plants, ashes are not always recycled, because of logistical problems or because of too high pollutant contents (Cd, As, Zn, Pb and also organic pollutants). The power plant Moerdijk in
The Netherlands incinerates 0.5 Mt poultry manure per year and produces 0.06 Mt ash, which contains on average 25% CaO, 5-6% P, 8-10% K, 3-4% Mg, 2% S and micro nutrients (Unpublished results). Currently, there is no proper destiny for these ashes, because of legal barriers, but the relatively high content of nutrient elements makes these ashes valuable as soil amendment. Legal barriers also exist for ashes from power plants that use coal and organic wastes as fuel, mainly because of high pollutant contents. Evidently, high pollutant content is a main barrier for recycling ashes back to agricultural land.

In 2007, there were over 50,000 active coal plants worldwide and this number is expected to grow. The total amount of coal burned for energy generation is about 7000 Mt per year (EIA, 2012). The ash content of burnt coal ranges between 3 to 10%, depending on composition of the coal. Phosphorus is an unwanted element in coal, especially when used for steelmaking. The average P content of coal is 0.05%, but in some coals as low as 0.01% and in others as high as 1%. The P content of ash varies between 0.1-1%. We estimate that the global amount of P in ashes of coal ranges between 1-10 Mt. Almost all of these ashes are disposed of in landfills, because of the relatively high content of pollutants.

There is an increasing research interest worldwide in the pyrolysis of biomass and organic wastes, mainly for the following reasons (e.g., Lehman and Joseph, 2009):

• pyrolysis can be an effective and efficient way to utilize the energy from the biomass and organic wastes;
• it produces a biochar that may have soil quality amending properties; and
• pyrolysis of organic materials and biochar in soil may contribute to the mitigation of greenhouse gas emissions CO₂ and N₂O.

The total production of biochar is still very limited, and not all of the aforementioned claims may hold to such extent that pyrolysis will replace incineration fully. Figure 4 shows that P is slightly less extractable from soil amended with biochar and ash compared to soil amended with TSP. Pyrolysis temperature did not have much influence on the P availability of biochar. Ash and biochar P were equally extractable. Gell et al. (2011) examined phytotoxicity effects in seedlings of lettuce, raddish and wheat in soils amended with different biochar. They found that one biochar had phytotoxic effects, likely due to high EC or water-soluble phytotoxic organic compounds. However, biochar consistently reduced phytotoxicity in soil amended with residues from ethanol production (Gell et al., 2011).
Figure 4. Extractable phosphorus from soil amended with ash, biochar (pyrolysed at 400 and 700°C) and TSP, on the basis of equal amounts of P applied. Ash and biochar were derived from the solid fraction of pig manure. Phosphorus was extracted with the PAL-method (Unpublished results, P.A.I. Ehlert).

3.4. Other by-products and wastes

There are a number of other by-products and wastes that can be used as P fertiliser. One of these is phosphogypsum, which is formed during the production of phosphoric acid from phosphate rock, according to the simplified reaction:

$$\text{Ca}_3(\text{PO}_4)_2 + 3 \text{H}_2\text{SO}_4 \rightarrow 2 \text{H}_3\text{PO}_4 + 3\text{CaSO}_4$$

Due to incomplete recovery of the $\text{H}_3\text{PO}_4$, some P remains in the gypsum and is therefore termed phosphogypsum. Miller et al. (2000) estimated that the P content of phosphogypsum ranges between 0.8 – 1.6 % dry weight, but also much lower values of 0.2 % have reported (Ekholm et al., 2012). In the period 1982 to 2006 about 45 Mt Phosphogypsum was produced per year in the USA, where one-third of the world production of phosphoric acid takes place (Hilton, 2006). Thus, approximately 135 Mt phosphogypsum would be produced in the world annually. The total amount of P in phosphogypsum produced per year thus ranges between 0.3 – 2.2 Mt P per year. Most of the phosphogypsum is stock-piled, dumped in landfill or used in building materials,
suggesting that this P is not used effectively nowadays. Experiments have shown that phosphogypsum can be used in certain conditions to improve soil quality and to reduce erosion (Hilton, 2006; Ekholm et al., 2012). A disadvantage of phosphogypsum is its relatively high pollutant content.

Another by-product is slag from smelting ore, which separates the desired metal from the unwanted fraction. Slag is usually a mixture of mainly metal oxides and silicon dioxide. Iron ores contain a relatively high P content, depending on the origin of the ore. Basic slag is a by-product of steelmaking based on the Bessemer process or the Linz-Donawitz process. It consists of slag with a large percentage of limestone, which absorbed P from the iron ore being smelted. It contains about 12% $\text{P}_2\text{O}_5$. Because of the relatively high P content, and because of its liming effect, it has been and is still being used as slow-release fertiliser. However, steelmaking processes have changed and basic slag has become a rather rare fertiliser. During the last decades, the steel market has circumvented the use of iron ores with more than 0.1 % P (for high-grade steel, the critical level is 0.01% P), because P increases the brittleness of steel (Gorden, 1996). This will change in future, because high-grade and low-P iron ores become depleted. Current slags from steelmaking still contain P, but much less than basic slag. If we assume that current ores contain 0.05% P, and that slags make up 50% of the iron ores, the current production of 2400-3000 Mt iron ores per year will yield 1200-1500 Mt slag, which contains 0.5-1.0 Mt P. Most ground slag is used in concrete in combination with Portland cement, or is used as base materials for road construction.

Stone meal or lava meal are almost unlimited, low-grade, slow-release sources of P. They are used in organic farming as a multiple source of nutrient elements. The P content is relatively low. Also because of their acid-neutralizing capacity, these finely ground rocks are seen as maintenance fertiliser.

Another source of P discussed here is the harvesting of fish. Fishing can be seen as a method that brings back P into the food cycle that previously had been lost to the sea via waste water discharge or erosion. While the amount of harvested wild fish has more or less stabilized since 1995 at 90 Mt, the amount of farmed fish (aquaculture) has increased sharply, from 12 Mt in 1990 to 67 Mt in 2012 (Roney, 2012). It has been estimated that
about 67% of the farmed fish was fertilized by wastewater in 2005 (Cordell et al., 2009). Using an average P content of fish of 2.5 g per kg (see http://apjcn.nhri.org.tw/server/info/books-phds/books/foodfacts/html/data/data5f.html), this yields a flow of 0.23 Mt P per year for wild fish. For fish farms, we estimate a P flow of 0.17 Mt. Hence, the total catch amounts to 0.4 Mt P per year, which is 10-20% of the annual discharge of P from households into surface waters (Figure 1).

4. Processing of by-products and wastes

The processing and treatment of by-products and wastes has a long history, and is done for various reasons (e.g., Scharrer and Linser, 1968; Yang et al., 2006). The processing and treatment with the aim to recover P from by-products and wastes is of more recent date. In the period 1960-1980, only 19 publications were found in the ISI web of knowledge database with the keywords phosph* and recycling, and only 2 with the keywords phosph* and struvite. In the period 1980 to 2010, these numbers increased exponentially to more than 6000 and 800, respectively (Figure 5). Regular updates on the recovery of wastes are provided by Scope Newsletters at http://www.ceep-phosphates.org/). The interest in biochar is of very recent nature; only 9 papers addressed the combination of phosph* and biochar until 2010.

Figure 5. Cumulative number of publications in the ISI web of knowledge database that carry a combination of the key words ‘phosph* and recycling’,‘phosph* and struvite’ and simply ‘biochar’, respectively. (database consulted 20 November 2012)
The separation/extraction of P from by-products and wastes can be done at various stages of the P life cycle (e.g., Hilton et al., 2010). Most of current efforts focus on the recovery of P from end-stream wastes, but P can be extracted also from for example animal feed ingredients as a means to lower the P content of animal feed to the level of animal requirements. Thereby, the P content of animal excrements also decreases. Source-separated collection of human urine, a sterile liquid that contains 60-70% of all P in human excreta at concentrations of 200-700 mg per litre, yields a relatively ‘easy’ source for recycling P in a relatively clean form (Cordell et al., 2011; Zeeman, 2012). In most current animal houses, animal excrements are collected as mixtures (slurries, dung), but in many tie stables, faeces and urine of cattle were collected separately, with the greater part (>90%) of the P in the solid dung and little in the liquid urine. Such source-separated collection would facilitate the recovery of P from animal and human excrements, similar as the separated collection of paper, glass, batteries, metals, etc. in most western countries. The current practice though for the recovery of P from P-rich wastes is still a sort of collecting first all sorts of wastes together and then try to separate the P-rich fractions from a highly variable mixture of wastes, which is complicated and thereby also costly.

Here, we briefly discuss the main processes and treatment steps for the production of marketable P-rich products. We choose sewage sludge, pig slurry and wastewater from food producing industries as examples. These are main by-products and wastes and greatly differ in nutrient content (Table 2). Pig slurry was chosen, because it is increasingly produced on livestock holdings with limited or no land for manure disposal, and therefore has to be transported to other areas, with or without prior treatment so as to lower transport costs. We present and discuss a general scheme for pig slurry treatment, but emphasize that such a scheme is also applicable to sewage waste. Most of the experience with pig slurry treatment reported here comes from the Netherlands (e.g., Schoumans et al., 2012). We expect that the experiences would be applicable also to other areas with large agglomerations of pig production, such as Catalonia in Spain, Po-delta in northern Italy, Brittany in France, and around many big cities in emerging countries such as China and Brazil.
Table 2. Composition of fattening pig slurry, liquid fraction of pig slurry, sewage sludge and waste water in kg/m³. After Römkens and Rietra (2008) and Schoumans et al (2010).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Fresh pig slurry</th>
<th>Liquid fraction</th>
<th>Solid fraction (wet)</th>
<th>Waste water</th>
<th>Sewage sludge (wet)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry matter</td>
<td>10 - 130</td>
<td>10 - 50</td>
<td>225 - 350</td>
<td>5 - 40</td>
<td>50 - 250</td>
</tr>
<tr>
<td>Organic material</td>
<td>5 - 100</td>
<td>5 - 30</td>
<td>200 - 275</td>
<td>1 - 20</td>
<td>25 - 100</td>
</tr>
<tr>
<td>N-total</td>
<td>1.0 - 10</td>
<td>1.0 - 8</td>
<td>20 - 35</td>
<td>0.5 - 2</td>
<td>-</td>
</tr>
<tr>
<td>Ammonia-N</td>
<td>0.7 - 6</td>
<td>1.0 - 6</td>
<td>10 - 20</td>
<td>0 - 1.5</td>
<td>-</td>
</tr>
<tr>
<td>P</td>
<td>0.5 - 5</td>
<td>0.2 – 1.0</td>
<td>5 - 15</td>
<td>0.1 – 0.5</td>
<td>5 – 10</td>
</tr>
<tr>
<td>K</td>
<td>1.0 - 8</td>
<td>1.0 – 8.0</td>
<td>2 – 4</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

4.1. Recovery of phosphorus from pig slurries

Pig slurry contains about 8 to 10% solids, but much less in warm climates where water is used to cool the pigs in summer or in stable where lots of drinking water are spilled. Phosphorus is partly organically-bound, partly in inorganic form, and mainly bound to the colloidal and suspended particles.

Basically all treatment steps start with the mechanical separation of the pig slurry into a relatively P-rich solid fraction and a liquid fraction, with low P but relatively high N and K contents (Figure 6; Burton and Turner, 2003; Schoumans et al., 2012). Different separation techniques are available; these differ in efficiency to separate the solids and colloid fraction from the liquids. The higher the efficiency, the higher the costs, commonly in the range of 2 to 4 euro per m³ (Schoumans et al., 2012). The liquid fraction contains little P and should be disposed of locally as a NK fertiliser. Alternatively, the liquid fraction is further treated into mineral concentrates and dischargeable water (Velthof et al., 2012). The treatment of the liquid fraction is not further discussed here.
A possible second step is the drying of the solid fraction, which has an initial dry matter content of 15 to 25%. Drying is usually combined with a pelleting process to facilitate the handling and marketing. Drying is energy-intensive and thereby relatively expensive. Three drying techniques are common: convection dryers, conduction dryers and radiation dryers. Conduction dryers offer the best opportunities when combined with initial anaerobic digestion for biogas production. The pelleted material can be exported as an organic matter and P-rich soil amendment. However, the acceptance of pelleted pig manure in practice is less than for example for poultry manure or ordinary P fertilisers.

A possible third step is the incineration of the (partly) dried solid fraction in a power plant to generate electricity, thereby further decreasing the volume and weight of the ‘wastes’. The cost of incineration roughly balances the income generated with the production of electricity. The ashes can be used as P-rich soil amendment, with a whole range of secondary nutrient elements and micro nutrients (see also paragraph 5).
When the content of heavy metals (e.g. copper and zinc) are too high, a thermo-chemical treatment step can be included to evaporate the heavy metals as chlorides and to collect the P from the manure as high-grade elemental P (P4). This treatment at >1000 °C is energy-intensive and thereby costly. However, the fertiliser industry is interested in using P-rich ashes as a resource for producing high-grade P fertilisers.

Another pathway for the beneficiation of ashes is through wet extraction processes. Chemical extraction of P from ashes has been tested at laboratory scale, and a few chemical extraction processes are currently available for application in practice. This treatment pathway could produce high-grade phosphates. Alternatively, the ashes are mixed with rock phosphate and partly acidulated. The fertiliser industry is also here interested to further explore the opportunities. The final product would contain also essential micro-nutrients.

Instead of incineration, the dried solid fraction may be pyrolysed or gasified in a low oxygen environment, to produce energy rich oils and gases, and biochars or ashes. Pyrolysis involves the heating of organic matter fractions to a temperature of 300 - 550 °C in the absence of oxygen, to produce pyrolysis oil, gas (syngas) and charcoal. Roughly 40 to 70% of the carbon originally present in the manure cake ends up in the char, depending on the composition of the manure, temperature and pyrolysis process. The pyrolysis oils and gases can be used for the production of electric energy. The biochars can be used as soil amendment.

Gasification involves the breakdown of organic matter in combustible gases and ash at temperatures of 800-1000 °C in an atmosphere with a reduced amount of oxygen. The process results in a so called syngas (combination of mainly methane, carbon dioxide and water vapour) that can be used as a fuel for electricity generation. More syngas is produced through gasification than through pyrolysis. Conversely, the amount of carbon in gasification ashes (<5% of the initial amount in manure cake) is much less than the amount in biochar from pyrolysis. All P is retained in gasification ashes and these can be used as a source for the production of P fertiliser or elemental P.
Further, experiments have started to oxidize the organic matter in manures through ‘supercritical wet oxidation’. The result is a P-containing ash. Alternatively, it is also possible to convert manure by ‘supercritical wet gasification’. In this case, a syngas is produced that can be used as a fuel for the production of electricity or heat, and a P-containing ash. The supercritical oxidation and the supercritical gasification are fast; they are carried out at a temperature of 600 - 700 °C and a pressure of more than 200 bar. The P can be extracted from the ash and used for fertiliser production. For manure this process is still in the development phase.

4.2. Recovery of phosphorus from sewage sludge.
A large body of experience has been built up as regards the recovery of P from sewage sludge. Following initial steps, such as removal of large particles, decomposition of biodegradable organic matter, and the removal of nitrogen through nitrification-denitrification, the sewage suspension is flocculated and most of the P is concentrated in the sewage sludge. Two common methods have been implemented. One method is to concentrate P containing compounds in the sewage sludge by chemical precipitation with calcium hydroxide, iron salts or aluminium salts. The other methods is enhanced biological concentration of P containing compounds in the sewage sludge. Both methods yield a P-rich sewage sludge, but the subsequent recovery of P from the sewage sludge greatly depends on the flocculation/precipitation pathways.

Three pathways can be distinguished for the recovery of P from sludge:

a. Anaerobic treatment of the sewage sludge so as to release the P from the sludge. After separation of the sludge particles, the dissolved P can be recovered as calcium phosphate or as struvite by precipitation or crystallization processes.

b. In case of the biological P removal pathway described above, it is also possible to produce a phosphate-rich supernatant liquor in a side stream of the wastewater treatment process. Through precipitation or crystallization, a calcium phosphate pellet is produced that can be used directly as fertiliser or soil amendment or as resource for the P fertiliser industry.

c. Incineration, gasification, supercritical wet gasification, and supercritical wet oxidation of sewage sludge can be applied to reduce volume and weight of the sludge and to recover the P as a P-rich ash. This ash can be used as fertiliser or can be used as raw
material by the fertiliser industry or can be used by the elemental P-producing industry (see also paragraph 4.1).

4.3. Wastewater from the food industry
Wastewater from the food processing industry contains variable amounts of P, which can be recovered as struvite or as calcium phosphates. An example is the wastewater derived from the potato industry that processes starch derivates. The wastewater is digested anaerobically, to lower the organic carbon content and to generate energy, and then treated to recover P as struvite. It has been shown that a P removal efficiency of 85 % can be achieved (Moerman et al, 2009).

5. Availability of phosphorus from by-products and wastes
There is a long history of determining the availability of P in fertilisers, by-products and waste to crops, but the term ‘availability’ remains rather ambiguous, as availability is defined in various ways and often relative to reference fertilisers and for a restricted length of time. Yet, there is widespread adoption and support of this way of defining availability, although conventional views are changing currently (e.g., Hilton et al., 2010).

Much can be learned from the long history of testing P fertilisers (e.g., Sauchelli, 1965; Johnston, 2008). Raw materials with low P availability were modified in their chemical characteristics to increase the P availability so as to meet crops demands. There has been a strong emphasis on the short-term availability and the water-soluble P fraction in fertilisers. The availability of P is generally a result of five important manageable and interacting factors: (i) chemical form of the fertiliser, (ii) particle size of the fertiliser, (iii) amount applied, (iv) application method, and (v) time of application. Of course, soil and crop types, soil P status (SPT), weather conditions and crop management are also extremely important.
### Table 3. Chemical inorganic phosphorus minerals in by-products and wastes.

<table>
<thead>
<tr>
<th>Byproduct</th>
<th>Chemical form of P minerals</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dairy cattle slurry</td>
<td>Struvite (MgNH₄PO₄·6H₂O)</td>
<td>Fordham &amp; Schwertmann (1977a, 1977b); Rückert, 2003</td>
</tr>
<tr>
<td></td>
<td>Trimagnesiumphosphate (Mg₃(PO₄)₂·8H₂O)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Octacalciumphosphate (Ca₄H(PO₄)₂·3H₂O)</td>
<td></td>
</tr>
<tr>
<td>Digestate of dairy cattle slurry</td>
<td>Struvite (MgNH₄PO₄·6H₂O)</td>
<td>Brüss, 2003;</td>
</tr>
<tr>
<td></td>
<td>Hydroxylapatite (Ca₁₀(PO₄)₆(OH)₂)</td>
<td>Güngör et al., 2007</td>
</tr>
<tr>
<td></td>
<td>Newberyite (MgHPO₄·3H₂O)</td>
<td></td>
</tr>
<tr>
<td>Pigs slurry</td>
<td>Struvite (MgNH₄PO₄·6H₂O)</td>
<td>Bril &amp; Salomons, 1990; Burns et al., 2001</td>
</tr>
<tr>
<td>Broiler slurry</td>
<td>Struvite (MgNH₄PO₄·6H₂O)</td>
<td>Bril &amp; Salomons, 1990; Güngör et al., 2007</td>
</tr>
<tr>
<td>Sheep dung, solid</td>
<td>Dicalciumphosphate (CaHPO₄·2H₂O)</td>
<td>Barrow, 1975; Güngör et al., 2007</td>
</tr>
<tr>
<td>Compost (MSW, separated)</td>
<td>Apatites</td>
<td>Frossard et al., 2002</td>
</tr>
<tr>
<td></td>
<td>Octacalciumphosphate (Ca₁₂₄(PO₄)₆·3H₂O)</td>
<td></td>
</tr>
</tbody>
</table>

A wide range of inorganic P containing mineral forms are found in by-products and wastes (Table 3). Most dominant are calcium phosphates. In addition, phosphates are bound to various iron and aluminum oxihydroxides, which are mostly amorphous, and to surfaces of clay particles and organic matter. In addition, P is locked up in organic molecules such as nucleic acids, inositol hexaphosphate (phytate) and phospholipids (Peperzak et al., 1959; Westheimer, 1987; Barnett, 1994; He et al., 2004; 2009). All these different forms lead to differences in solubility, reactivity and availability characteristics in soil. Effects of granule size and placement of fertilisers in the soil on the effectiveness of the fertilisers have been discussed extensively (e.g., Davies, 1984; Bolland et al., 1988); the smaller the granule size and the closer placed to the plant roots, the higher the accessibility and uptake rate.

### 5.1. Assessing the availability of phosphorus in byproducts and wastes

The first test for evaluating P fertilisers with neutral ammonium citrate was proposed in 1871 by the Association of Official Agricultural Chemist at its first meeting in 1884 (Sauchelli, 1965). Since then additional methods have been introduced, also in a way to regulate the free trade of mineral fertilisers. These methods differ in strength of extraction or dissolution. Table 4 provides an overview of current methods used within EU-27. For ‘insoluble’ fertilisers there is the additional legal requirement of a maximal particle size (fineness).

<table>
<thead>
<tr>
<th>Number</th>
<th>Methods</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1.1</td>
<td>Extraction of phosphorus soluble in mineral acids</td>
</tr>
<tr>
<td>3.1.2</td>
<td>Extraction of the phosphorus soluble in 2 % formic acid</td>
</tr>
<tr>
<td>3.1.3</td>
<td>Extraction of phosphorus soluble in 2 % citric acid</td>
</tr>
<tr>
<td>3.1.4</td>
<td>Extraction of phosphorus which is soluble in neutral ammonium citrate</td>
</tr>
<tr>
<td>3.1.5.1</td>
<td>Extraction of soluble phosphorus according to Petermann at 65 °C</td>
</tr>
<tr>
<td>3.1.5.2</td>
<td>Extraction of soluble phosphorus according to Petermann at ambient temperature</td>
</tr>
<tr>
<td>3.1.5.3</td>
<td>Extraction of phosphorus soluble in joulie’s alkaline ammonium citrate</td>
</tr>
<tr>
<td>3.1.6</td>
<td>Extraction of water soluble phosphorus</td>
</tr>
<tr>
<td>3.2</td>
<td>Determination of extracted P (gravimetric using quinoline phosphomolybdate)</td>
</tr>
<tr>
<td>7.2</td>
<td>Determination of the fineness of grinding of soft natural phosphates</td>
</tr>
</tbody>
</table>

These methods provide a first assessment of the availability of the P in fertilisers, by-products and wastes. The proof of the pudding follows from tests in the field. Here, the extent to which an applied nutrient is effectively utilized by the crop is expressed in an availability index. These indices are often expressed in various ways, for example on yield (fresh, dry), growth rate (fresh, dry), P uptake, P uptake rate, changes in soil P status, etc. Here, we present a few common effectiveness indices, which are all so-called ‘difference methods’.

The index ‘P fertilisation effectiveness expressed in crop yield (FEY)’ indicates the fraction of P in by-product or wastes that has the same effect as a reference P fertiliser on crop yield, under optimal management conditions. The index is derived from the crop yield responses to the tested product and a 'reference' fertiliser, such as TSP. At a given P dose FEY is calculated as:

\[
\text{FEY}_{\text{byproduct}} = \frac{\text{Yield}_{\text{byproduct}} - \text{Yield}_{\text{no P-fertilisation}}}{\text{Yield}_{\text{reference}} - \text{Yield}_{\text{no P-fertilisation}}} \times 100\% \tag{1}
\]

Similarly, the ‘P fertilisation effectiveness expressed in crop uptake (FEU)’ index expresses the fraction of P in by-product or wastes that has the same effect as a reference P fertiliser on P uptake in the crop, again under optimal conditions. Hence, at given P application:
The Apparent P Recovery in crops (APR) indicates the amount of P taken up by the crop in fertilized plots corrected for the P uptake from plots where the P fertilization was withheld. Hence,

\[
\text{APR} = \frac{\text{P-uptake}_{\text{byproduct}} - \text{P-uptake}_{\text{no P-fertilisation}}}{\text{P-uptake}_{\text{reference}} - \text{P-uptake}_{\text{no P-fertilisation}}} \times 100\% \quad (3)
\]

These indices can be obtained only from field or greenhouse trails and are therefore rather expensive. Alternatives have been developed based on measuring solely the response of the soil P status to P fertilization. The P recovery efficiency in soil (RES) is defined relative to a reference fertiliser again, and follows from:

\[
\text{RES} = \frac{\text{STP}_{\text{byproduct}} - \text{STP}_{\text{no P-fertilisation}}}{\text{STP}_{\text{reference}} - \text{STP}_{\text{no P-fertilisation}}} \times 100\% \quad (4)
\]

Where STP is a suitable soil P test method (for example Olsen-P or P-Al).

Several additional agronomic indices have been proposed and developed to measure the effectiveness of P fertilisers, by-products and wastes, because of the limitations of the aforementioned 4 methods. The main criticism is that none of these methods sufficiently address the residual effect of the applied P, as the trials are usually limited to one or few growing seasons. A balance method over a four or five years’ period would better account for the residual effects (Johnston and Syers, 2006; Syers et al., 2008; Hilton et al., 2010). The P availability indices derived from the balance method are roughly twice the indices values of the difference methods presented here (Johnston and Syers, 2006).
5.2. Overview of results from literature

Annexes 1 and 2 provide literature overviews of the P fertilisation effectiveness in crop yield (FEY), the ‘P fertilisation effectiveness in P uptake (FEU) and of the apparent P recovery (APR) measured over a relatively short period (<1 year) and a relatively long period (>1 year, respectively). Tables 5 and 6 summarises the data for respectively efficacy on short term and long term. The effectiveness of the P in by-products and wastes is expressed in per cent of that in ordinary P fertiliser, which was often TSP.

Table 5. Phosphorus fertilisation effectiveness (FEY or FEU) of by-products and wastes, in per cent of that of mineral P fertiliser on a short term (< 1 year) and on a long-term; average, minimum and maximum values derived from published data compiled in Annexes 1 and 2.

<table>
<thead>
<tr>
<th>By-product</th>
<th>Average</th>
<th>Minimum</th>
<th>Maximum</th>
<th>Number of observations</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Short term (&lt; 1 year)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Compost</td>
<td>69</td>
<td>37</td>
<td>165</td>
<td>11</td>
</tr>
<tr>
<td>Manure, chicken, composted</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>1</td>
</tr>
<tr>
<td>Manure, chicken, solid</td>
<td>199</td>
<td>112</td>
<td>250</td>
<td>3</td>
</tr>
<tr>
<td>Manure, dairy, slurry</td>
<td>59</td>
<td>30</td>
<td>92</td>
<td>3</td>
</tr>
<tr>
<td>Manure, dairy, solid</td>
<td>121</td>
<td>30</td>
<td>378</td>
<td>13</td>
</tr>
<tr>
<td>Sewage sludge</td>
<td>138</td>
<td>75</td>
<td>214</td>
<td>6</td>
</tr>
<tr>
<td>Struvite from waste water</td>
<td>117</td>
<td>106</td>
<td>126</td>
<td>6</td>
</tr>
<tr>
<td>Struvite from veal manure</td>
<td>126</td>
<td>126</td>
<td>126</td>
<td>1</td>
</tr>
<tr>
<td>Struvite, synthetic</td>
<td>143</td>
<td>140</td>
<td>146</td>
<td>2</td>
</tr>
<tr>
<td>DCP from waste water</td>
<td>127</td>
<td>127</td>
<td>127</td>
<td>1</td>
</tr>
<tr>
<td><strong>Overall short term</strong></td>
<td>112</td>
<td>30</td>
<td>378</td>
<td>47</td>
</tr>
<tr>
<td><strong>Long term</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Compost</td>
<td>74</td>
<td>52</td>
<td>100</td>
<td>3</td>
</tr>
<tr>
<td>Manure, dairy, slurry</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>1</td>
</tr>
<tr>
<td>Manure, dairy, solid</td>
<td>80</td>
<td>18</td>
<td>165</td>
<td>24</td>
</tr>
<tr>
<td><strong>Overall long term</strong></td>
<td>80</td>
<td>18</td>
<td>165</td>
<td>28</td>
</tr>
</tbody>
</table>

Not surprisingly, there is a large variation between studies and also between fertilisers, by-products and wastes. Surprisingly though, the effectiveness of the by-products and wastes is often as large as or larger than that of the reference P fertiliser, both in the short-term and long-term studies. Also, the arithmetic means of the effectiveness of all studies is close to 100%, both in the short-term and long-term studies. This suggests that the effectiveness of P in by-products and wastes is as good as that in ordinary P fertiliser.

The high effectiveness of P in some by-products and wastes may be also an artefact of applying other growth-limiting nutrients with the by-products and wastes. Differences
between FEY/FEU compared with lower APR point in this direction. A low effectiveness of P in some by-products and wastes may be related also to growth negative factors associated with the use of by-products and wastes, such as smothering of the crop, high salt content and presences of pollutants. The effectiveness of the P in by-products seem not higher in long-term compared to short-term trials, although the presented results in Tables 5 and 6 do not allow a direct comparison.

Table 6. Apparent phosphorus recovery in crops (APR) following the application of by-products and wastes to soil, in per cent of that of mineral P fertiliser; average, minimum and maximum values derived from published data compiled in Annexes 1 and 2.

<table>
<thead>
<tr>
<th>By-product</th>
<th>Average</th>
<th>Minimum</th>
<th>Maximum</th>
<th>Number of observations</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Short term</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ash from meat and bone meal</td>
<td>39</td>
<td>36</td>
<td>42</td>
<td>2</td>
</tr>
<tr>
<td>Bone meal steamed</td>
<td>29</td>
<td>23</td>
<td>35</td>
<td>2</td>
</tr>
<tr>
<td>Manure, dairy, slurry</td>
<td>64</td>
<td>64</td>
<td>64</td>
<td>1</td>
</tr>
<tr>
<td>Manure, dairy, solid</td>
<td>88</td>
<td>88</td>
<td>88</td>
<td>1</td>
</tr>
<tr>
<td>Meat and bone meal</td>
<td>39</td>
<td>36</td>
<td>42</td>
<td>2</td>
</tr>
<tr>
<td>Sewage sludge</td>
<td>46</td>
<td>41</td>
<td>51</td>
<td>2</td>
</tr>
<tr>
<td>Struvite from waste water</td>
<td>91</td>
<td>27</td>
<td>120</td>
<td>8</td>
</tr>
<tr>
<td>Struvite from veal manure</td>
<td>115</td>
<td>115</td>
<td>115</td>
<td>1</td>
</tr>
<tr>
<td>Struvite, synthetic</td>
<td>139</td>
<td>137</td>
<td>140</td>
<td>2</td>
</tr>
<tr>
<td>Thermochemically treated sewage sludge</td>
<td>53</td>
<td>48</td>
<td>58</td>
<td>2</td>
</tr>
<tr>
<td>Thermochemically treated sewage sludge ash</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>1</td>
</tr>
<tr>
<td>DCP from waste water</td>
<td>68</td>
<td>68</td>
<td>68</td>
<td>1</td>
</tr>
<tr>
<td>Biochar from thick cake of co-digested pigs manure, 400°C</td>
<td>69</td>
<td>59</td>
<td>79</td>
<td>4</td>
</tr>
<tr>
<td>Biochar from thick cake of co-digested pigs manure, 700°C</td>
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<td>Ash from thick cake of co-digested pigs manure, 700°C</td>
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<td>23</td>
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<td><strong>Long term</strong></td>
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<td><strong>Overall long term</strong></td>
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</table>
6. Discussion and conclusions

6.1 Are fertilisers from processed wastes competitive P fertilisers?

Our shortest answer to the question ‘Can fertilisers from processed wastes become a competitive alternative for conventional mineral P fertilisers?’ raised in the Introduction section is ‘yes, but only regionally’.

*One* reason for our nuanced answer is the large diversity in waste treatment and processing pathways, which yield as a consequence different processed fertilisers. As discussed in paragraph 5, some by-products and wastes, with or without further processing, have P fertilisation effectiveness values, as high as that of TSP, while others have relatively low P fertilisation effectiveness values. Hence, by-products and wastes are not uniform. A *second* reason for our nuanced answer is related to the uncertainty in the future availability and cost of high-quality apatite as source of ordinary P fertilisers, as well as the uncertainty in the cost of waste processing. There is a tendency that the cost of production of ordinary P fertilisers goes up, while a decrease in the cost of P fertilisers from processed wastes and by-products may be expected, as the technology for processing improves and up-scaling of treatment plants takes place. Hence, there is uncertainty about the future availability and price of both ordinary P fertilisers and by-products and wastes. A *third* reason is the uncertainty related to the possible implementation of governmental regulations. For example, the European Commission has communicated policy strategies with the ambitious targets of ‘end of waste’ and ‘resource use efficient Europe’ (COM, 2012). Also, the EU regulations related to the use of fertilisers, by-products and wastes in agriculture are currently under revision, with the aim of having more harmonized criteria and regulations across EU-27, as well as to contribute to the targets listed above. Regulations may also help to lower the concentrations of pollutants in wastes, and thereby change the legal status into a ‘resource’ or ‘product’. Hence, governmental policies may influence the relative competitiveness of ordinary P fertilisers and by-products and wastes.

*Fourth*, households and industries are charged (levied) for the wastes that they produce, which allows treatment plants to treat and process the wastes. This levying is an effective mechanism for getting things done, including the processing of P fertilisers from wastes. Biomass burning for electricity generation is currently often subsidised as a ‘green energy’.
Levies and subsidies make by-products and wastes more competitive relative to unsubsidised ordinary P fertiliser. *Fifth*, most by-products and wastes are too diverse, too bulky and too limited (see table 1) to serve global markets, and although processing may reduce the bulkiness and variability, there is no by-product or waste that has similar size as current ordinary P fertilisers. Hence, by-products and wastes will serve merely local and regional markets. *Summarizing*, by-products and waste may become locally and regionally a competitive alternative for ordinary P fertiliser, similar as animal manure currently is.

6.2. Effectiveness of by-products and wastes as P fertiliser

Numerous field trials and pot experiments have been carried out to quantify the P fertilisation effectiveness and the apparent recovery of P from by-products and wastes (Tables 5 and 6; annexes 1 to 3). Animal manures and processed products from animal manures have in general a high P fertilisation effectiveness and a high relative apparent P recovery, while bone meal and ash from incinerated bone meal have a low effectiveness. Sewage sludge also has a relatively high P fertilisation effectiveness. Ash and biochar have a medium relative apparent P recovery, in the short-term. However, the variability is large, which hampers generalisation. Ordinary P fertilisers tend to have a higher relative APR (Table 6), but also tend to have a lower P fertilisation effectiveness than by-products and wastes (Table 5). The variability in effectiveness and APR are in part related to the difficulty of measuring the crop response to P fertilisation (e.g., Johnston and Syers, 2006; Hilton et al., 2010); a response is only obtained when the soil P status is low. The huge variability in responses shown in Tables 5 and 6 is somewhat in contrast to the large number of official P extraction methods for fertilisers and by-products (Table 4), as this large number would suggest a high precision of the extraction procedures and hence a high precision of the measured P availability.

6.3. Benefits of using by-products and wastes

Evidently, the advantage of using by-products and wastes as sources of P fertilisers is the recycling of P and other nutrients from these by-products and wastes, thereby lowering the loading of surface waters with nutrients and/or reducing the costs associated with disposal in landfills. Another possible advantage is the presence of secondary nutrients and micro nutrients. With the continuing harvests of high crop yields, there is the increasing risk that
secondary nutrients and micro nutrients become depleted, especially when straight NP(K) fertilisers are being used only. Hence, fertilisers of processed wastes may contribute to replenishing the soil with these other nutrients, and thereby achieve a high P fertiliser value. Manure, ashes and biochar have also a liming effect, and thereby may improve soil biological activity and soil structure. Possible disadvantages are a variable composition, the likely presence of contaminants and the relatively low content of nutrients and as a consequence high transport and transaction costs.

6.4. Where and how to use by-products and wastes as sources of P fertiliser?
Though rock phosphates may remain the primary source for P fertilisers during the next decades, one may also argue that P-containing by-products and wastes will have to be increasingly recycled in the near future. The likelihood of a relative shortage of rock phosphates on the market is not beyond imagination, given the geopolitical dependency of these resources (Steward et al., 2005; Scholz et al., 2013). Price spikes for ordinary TSP, governmental regulations and financial support will certainly spur the development of processing of waste-derived P fertilisers. The technology for processing these products to P fertilisers is largely available but should be optimized further, also to bring more uniform products on the market for easy recognition.

Soils differ greatly in P sorption and buffering characteristics, in pH and the availability of other nutrient elements. Crops differ greatly in the response to soil P status and P application (e.g., Beegle, 2005; Johnson, 2005). Short-lived and shallow-rooted vegetables require higher soluble P levels in the top soil than perennial grasslands and cereals like wheat and barley. Hence, high-grade water soluble P fertilisers should then be used preferentially for vegetables and arable crops with relatively low root-length density. By-products and wastes, low-grade P fertilisers from processed wastes and low-grade rock phosphates should then be used for perennial crops and arable crops with relatively large root-length density. Carbonate-rich ashes and primary rock phosphates could be used for soils that are low in pH and P.

6.5 Towards a global phosphorus fertilisation strategy
Current P management is largely market driven and unregulated, although industrialised countries have in the past stimulated P fertiliser use through research, education and also
subsidies. Fertiliser P use has also been stimulated through subsidies (e.g., in China), and western countries have stimulated fertiliser use in Africa in the past through various aid programmes. In general though, P management is market driven and unregulated, and the question is whether P use in the world should remain unregulated and market-driven?

A related question is ‘how to use ordinary P fertilisers from rock phosphate and P fertilisers from by-products, wastes and ashes in an optimal way?’ Here, ‘optimal’ should be defined from the viewpoints of food security, resources use efficiency, equity, environmental sustainability and feasibility. These are big issues, which we can only address here in a very superficial, explorative way. Current estimates of mineable rock phosphate (15-112 x 10^3 Mt) are in the same range as the total global amount of P in soils of agricultural land (Figure 1). One hypothetical but naïve strategy would be to distribute the P fertiliser from all minable rock P equally to all agricultural soils in the world. This would increase the mean amount of total soil P by ~4000 kg per ha agricultural land and would raise soil P status to ‘more than sufficient’. Thereafter, P supply would depend primarily on processed by-products, ashes and wastes. Another hypothetical strategy would be to use about half of the current mineable rock P for raising the soil P status of agricultural land in countries with very low-P soils, such as in large parts of Africa and Latin America, and to use the remainder for the future, where needed. Industrialized countries with relatively high-P soils, as in most countries of the northern hemisphere would than use P fertilisers from processed wastes and by-products as ‘maintenance fertiliser’ and ordinary P fertilisers from rock phosphate only in ‘special cases’. A third strategy would be to use available P resources soil-type and crop-type specific, according fertilization recommendations (e.g., Csatho and Radimszky, 2009). This would be the most scientific approach, but the question still is how to implement such strategy in practice?

There is as yet no international agreement and institution that addresses global P management strategies. We argue that such a strategy may be needed. It should have five pillars (5 Rs), namely (i) Reduce P input where possible and necessary, i.e. in soils with high P status and crops with low P requirements, (ii) Reuse P from easily available by-products, wastes and ashes effectively and efficiently, i.e. notably animal manures, wastes and ashes with low content of pollutants, (iii) Recover and recycle P from waste streams and polluted sources, i.e. from sewage and industrial wastes and from ashes, (iv) Reduce P losses
through erosion, leaching and deep ploughing from P-rich (top)soils, and (v) Redefine systems where possible and needed, i.e., if the aforementioned pillars are not effective, parts of the production-consumption food chain may have to be reconsidered. The latter may relate for example to the agglomeration of intensive livestock production units near cities, where opportunities for manure disposal are limited. If direct reuse and recovery and recycling of P and other nutrients from manure through processing and transport are not feasible, production systems may have to be re-designed and re-located (Menzi et al., 2010).

6.6 Conclusions

Summarizing, fertilisers from processed wastes may become a competitive alternative for conventional mineral P fertilisers, but only regionally. Reuse of P from animal manures and crop residues occurs, but not always in effective ways due to various constraints. Large-scale and effective re-use of P from all by-products and wastes may happen only with appropriate incentives and regulations, because of the current barriers and constraints. The major advantage of increasing the use of by-products and wastes is their contribution to increasing resource use efficiency, to decreasing surface water eutrophication and biodiversity loss, and to decreasing the rate of P rock depletion. The major disadvantage of using by-products and wastes is their variable composition, relatively low content and likely presence of contaminants, and the lack of a marketing and distribution infrastructure. The availability of the P in by-products and wastes seems much less of an issue (paragraph 5). In the end, society will need the P fertilisers from by-products and wastes, because of the likely future depletion of P rock deposits. It would be wise then to think about and develop strategies for optimal long-term use of the various possible P sources. It is argued that an international agreement might help.
7. References


Annex 1. Literature overview of the effectiveness of phosphorus in by-products and wastes, expressed as the P fertilisation effectiveness in crop yield (FEY), the P fertilisation effectiveness in P uptake (FEU), and as the apparent P recovery in crops (APR), measured over a relatively short period (< 1 year). All indices (FEY, FEU and APR) are expressed in per cent relative to a reference fertiliser. Note that literature references are in annex 3.

<table>
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<tr>
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Annex 2. Literature overview of the effectiveness of phosphorus in by-products and wastes, expressed as the P fertilisation effectiveness in crop yield (FEY), the P fertilisation effectiveness in P uptake (FEU), and as the apparent P recovery in crops (APR), measured over a relatively long period (> 1 year). All indices (FEY, FEU and APR) are expressed in per cent relative to a reference fertiliser. Note that literature references are in annex 3.

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<td>Source</td>
<td>Yield/P-uptake</td>
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<td>Loam</td>
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<td>Monocalcium phosphate</td>
<td>120</td>
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<td>Loam</td>
<td>Johnston &amp; Richards, 2003</td>
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(1) P-AL, P-citr., P-DL, P-Olsen, and Bray-Kurtz No. 1 are STP, chemical method of soil testing used for phosphate fertilisation recommendation.
(2) Substrate and Neubauer method.
Annex 3. Literature references for annexes 1 and 2


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To provide an international forum for discussion and dissemination of knowledge of scientific, technical, environmental, economic and safety aspects of the production, marketing, use and application of fertilisers.

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