European Sustainable Phosphorus Platform

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ESPP Briefing Note:
Phosphorus as a Critical Raw Material – ESPP

15th January 2015

Introduction: phosphorus uses and flows

Phosphorus, the element, is essential for life, because it is a non-substitutable constituent of many fundamental biological molecules including bones (calcium phosphate – hydroxyapatite), cell membranes, DNA, cellular energy cycling and storage (ATP-ADP).

Uses: Phosphorus is also used in a wide range of human industrial activities, including fertilisers (85% - 90% of consumption of mined P resources), animal feed supplements (5 – 10%), drinking water treatment (prevention of lead solvency), human food additives, and a whole range of low volume, high specificity technical and industrial applications.

Mineral phosphorus flows: World production of phosphate rock is 224 million tonnes (data for 2013, USGS, 2014) that is approx. 30 million tonnes of phosphorus (P). The EU imports around 2.7 million tonnes P_2O_5 per year (not including Norway which has significant fertiliser industry), that is approx.1.2 million tonnes of phosphorus (P) of which approx. 25% as phosphoric acid, 25% as MAP/DAP, 30% as phosphate rock and the remainder as other products (mainly TSP, SSP, NPK fertilisers)

Other phosphorus flows: Phosphorus originating from mined phosphate rock represents only a (minority) part of total phosphorus flows, as phosphorus is cycled in organic forms (crops used as animal feed, wastes such as manures recycled as fertiliser …). In total, Europe uses annually around 1.45 million tonnes of phosphorus (P) in crop production (mainly in mineral fertilisers, but also inputs in imported seeds or agrochemicals) and a further 0.43 MtP in animal production (imported animal feed crops and products, mineral P feed additives, imported livestock). However, around 2.3 MtP is input into crop production by recycling of manures, food processing waste and other wastes (e.g. sewage biosolids) and 0.68 MtP is input into animal production from food processing (e.g. cake by-products from plant oil processing).

See diagram below. Source: Van Dijk K., Phosphorus use in the EU-27 in 2005, updated for European Sustainable Phosphorus Platform meeting 2/12/2014

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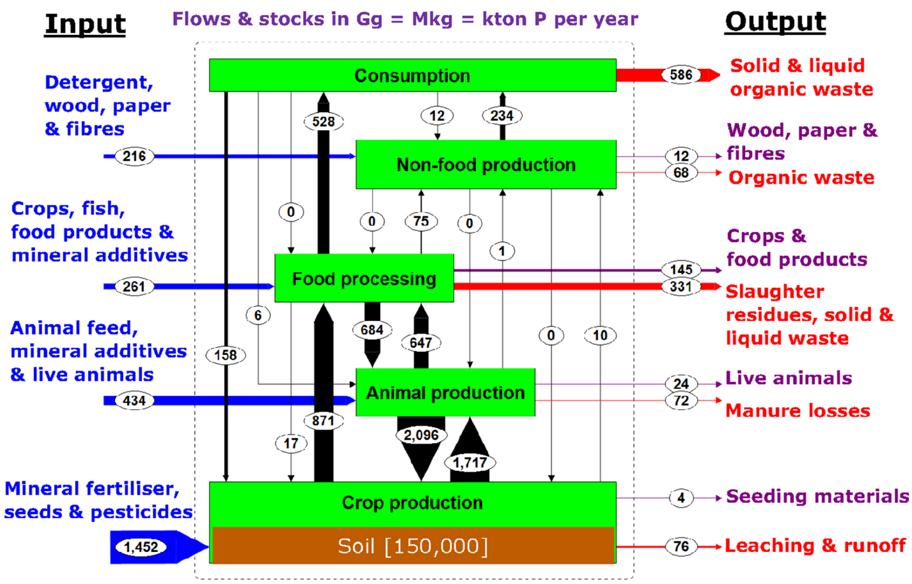

Which forms of phosphorus to consider

Around 70 – 80 % of mined phosphate rock is converted into phosphoric acid as the first step in processing[i]. Phosphoric acid is mainly used to produce fertilisers and animal feed phosphates, but these can also be produced by other routes directly from phosphate rock[ii]. Phosphoric acid, after purification, has a range of other important industrial uses. Phosphate rock can also be processed by a thermal (furnace) process to produce elemental phosphorus (P_4, White Phosphorus, see below), which can be used to produce very high-purity phosphoric acid, and importantly is the only route to produce many organic phosphorus compounds with specific industrial applications (low volumes compared to fertilisers and animal feeds, but high added value and industrial importance).

A criticality assessment of phosphorus could therefore consider some or all of the following different forms:

1. **Phosphorus (P) as an element**, irrespective in what form it is present (phosphate rock, fertiliser, manure …).
2. **Phosphate rock**
3. Phosphate rock with low cadmium levels (**igneous phosphate rock deposits**).
4. Non-purified **phosphoric acid** (MGA)
5. **Purified** phosphoric acid
6. **White phosphorus** (P_4)
7. Specific phosphorus containing **compounds** (e.g. MAP or DAP fertiliser, P_4 derivatives such as chlorides or sulphides …)

ESPP proposed approach

ESPP stakeholders emphasise that the supply, demand, processing and uses and recycling for these different forms of phosphorus are intricately linked. To give some simplistic examples: if world phosphate rock supply were constrained, then so would be merchant phosphoric acid supply and fertiliser compounds (MAP/DAP).

In the specific context of the EU Critical Raw Materials list, it may therefore be appropriate to keep 'phosphate rock' as the named Raw Material, because supply of mined phosphate rock is the base for phosphoric acid and fertiliser compound production. 'Phosphate rock' can thus be an "indicator" for overall phosphorus criticality (phosphorus in whatever form).

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However, the analysis should take into account both:
- **phosphate rock as a specific material**, which is critical for a significant part of the EU phosphate industry which uses this as raw material
- **but also**, **all forms of phosphorus** (P the element) in flow analysis (e.g. recycling of phosphorus in organic byproducts to soils to provide nutrients, such as manures, composts, digestates).

White phosphorus (P_4) and purified phosphoric acid raise specific questions (specific industrial uses in both cases; production plant capacity in the EU: zero for P_4, limited for purified acid), and should be assessed in themselves as independent and separate possible EU Critical Raw Materials.

Phosphorus P the element (in all forms)

Phosphorus[iii] is a "nuclear improbability" (nuclei with odd numbers of atoms are generally unstable), which results in "cosmic scarcity". On Earth, phosphorus is present at orders of magnitude lower than the other biogenic elements and so phosphorus is the "limiting element" for most ecosystems, in particular for crop productivity and food production.

Standard fertilisers are "NPK" = nitrogen, phosphorus, potassium. All these elements are essential for plant growth and crop productivity. However, nitrogen can be provided by planting crops which can fix nitrogen from the air ("green mulches"). Mineral nitrogen fertiliser is produced from atmospheric nitrogen using energy. Potassium is required at lower levels than phosphorus and potassium mineral reserves are significantly larger and more widespread[iv] and potassium is >1% of salt ions in seawater.

Significant quantities of phosphorus are already recycled today, mainly in organic forms (manures, crop by-products, sewage sludges after appropriate processing, composts, digestates, biochars), and also increasingly through recycling processes producing mineral fertiliser products (e.g. struvite). Nonetheless, without input of mineral phosphate fertiliser (produced from mined phosphate rock), it is estimated that European agriculture could support very approximately a population of only around 150 million[v], that is ¼ - $^1/_3$ of current population.

The following aspects should therefore be considered in assessing the criticality of "P" for Europe:

- **Non-substitutable** : phosphorus is essential for food production, cannot be replaced for food production
- **Quantitative requirements**: what levels of food production could be maintained in Europe without imported phosphorus (as imported mineral products or in imported animal fodder). This assessment should look at both crop production (fertiliser P requirements) and animal production (P in imported fodder, feed supplements) and should consider both business-as-usual scenario (current diet, current levels of recycling) and other scenarios
- **Global and EU phosphate rock reserves and resources**
- Global **demand for phosphate fertilisers** (the main consumer of phosphate rock), including drivers such as population, biofuels, agricultural intensification (with loss of farmland, climate change)
- **Geographical concentration and vulnerability of global reserves**
- **Concentration and vulnerability of global trade** in phosphorus (as rock, MGA, fertilisers) and of processing capacity (conversion of rock to MGA or fertilisers)
- Interactions between the global P market and **global food security** (price, supply)
- European **demand for phosphate fertilisers**, taking into account soil P status (legacy P) and European objectives for food security
- **Imports into Europe of phosphorus in non-mineral forms** (e.g. organic animal feeds such as soya cake, forage)
- **Overall Europe phosphorus flows, including organic forms, manures, biowastes**
- Potential for **recycling and reuse**
- Potential for reducing consumption by improved **use efficiency and reduced losses**
- **Risks to recycling and reuse** (e.g. social concerns and scientific issues with contaminants in biowastes)

Phosphate rock:

Europe is almost completely dependent on imports for supply of phosphate rock (92% import[vi]).

In Europe a number of fertilizer companies and producers of industrial phosphorus chemicals have limited (i.e. own mine cannot meet the demand) or no direct access to phosphate rock, they depend on imports (in some cases partly from their mother company, in other cases by purchasing on the world market).

Phosphate rock supplies could be critical because of political or commercial decisions: some countries or vertically integrated mining companies may decide to no longer export phosphate rock but only to export processed rock (phosphoric acid or phosphorus chemicals), in order to increase domestic employment and added-value. This is already largely the case for the USA and China (zero or negligible rock exports) and has also been intermittently implemented recently as policy by Russia. Phosphate rock supplies could also be critical because of potential social instability in some mining regions (Middle East, Mediterranean).

Phosphate rock supply shortages may have a strong impact on business and employment of most European NPK fertiliser producers and on some P-fertilizer producers which are not fully vertically integrated.

White phosphorus (P_4)

The situation for white phosphorus is comparable to that of magnesium metal in the EU Critical Raw Materials list: it should be considered independently of availability of phosphate rock, on the basis of supply from thermal plants necessary to produce white phosphorus. White phosphorus is a necessary and non substitutable raw material (either directly, or via intermediates such as $PCl_{4)}$ for a number of phosphorus compounds, necessary for a range of industrial chemicals and applications.

The EU had until 2012 a producer of P_4 – Thermphos, The Netherlands. This company went bankrupt and its production site closed, as a consequence of a number of factors, leaving Europe without a P_4 production plant.

P_4 user industries and applications

- Pharmaceuticals:
  - directly (phosphorus containing molecules), e.g. bone-active agents (bisphosphonates), treatment of arthritis, organophosphorus inhibitors for bacterial diseases
  - indirectly, e.g. acid chlorides in synthesis of several families of pharmaceutical.
- Medical diet supplements and similar (e.g. osteoporis treatment, bowel purges …)
- Vitamin production: triphenyl phosphine, synthesis of Vitamin A
- Toothpastes (fluorophosphates)
- Electronics grade phosphoric acid (currently not produced from MGA phosphoric acid)
- Doped semiconductors, LEDs
- Agrochemicals: pesticides and herbicides (e.g. glyphosate)
- Fumigation chemicals
- Lithium ion batteries (cathode materials, electrolytes)
- Lubricants/lubricant additives
- Drilling additives (e.g. for shale gas and mining)
- Water cooling and air conditioning circuits (phosphonates), corrosion inhibitors
- Fire safety (substitution of halogenated flame retardants, protection of steel and wood structures in buildings from heat, fire safety in applications where low smoke emission is essential such as aircraft and transport fittings, public buildings). Some P-based fire safety chemicals are produced from phosphoric acid, but others are produced from P_4
- Plastic additives (production of performance polymers for consumer and engineering applications, electronics …)
- Catalysts and ligands in the chemicals and petrochemical/refining industries …
- Electroless nickel plating (hypophosphites), e.g. used in IT hard disk drives
- Pyrotechnics (e.g. in transport safety applications), matches
- …

Some of the above are today still at the R&D or development phase. The absence of P_4 supply in the EU may be susceptible to inhibit development of relevant future industries in the EU.

The following aspects should therefore be considered in assessing the criticality of white phosphorus for Europe:

- Importance of these sectors and applications in Europe, both directly (phosphorus user) and in downstream industries
- Substitutability: of white phosphorus in the process (could the same product be made from phosphoric acid, possibly at cost penalty), of the product in downstream uses
- Vulnerability to white phosphorus supply insecurity

Supply of white phosphorus to Europe

- at present: Kazakhstan, Vietnam
- China has implemented export barriers on P_4
- possible future scenarios, e.g. dependency on China electricity supply to Vietnam
- transport issues: distance, transport obstacles (Ukraine)
- geopolitical concentration and stability
- reliability of supply
- opportunity, obstacles and feasibility of creating a new white phosphorus furnace in Europe: possible technologies, energy costs, environmental issues/emissions, possible use of secondary raw materials (biosolids incineration ashes alongside or instead of phosphate rock)
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Low cadmium phosphate rock:

There is ongoing discussion regarding the significance of cadmium and other metal impurities in fertilisers. Igneous phosphate rocks have very low levels of these (compared to sedimentary phosphate rocks) but are limited in quantity and distribution (mainly today Finland, South Africa, Russia, Brazil). Today around 13% of mined phosphate rock is igneous, 87% sedimentary[vii]. Such rock has a price premium because of its lower contaminant levels and so lower costs for uses where contaminant removal (phosphoric acid purification) is required.

However, stakeholders within ESPP consider that (a) cadmium limits as currently proposed in EU Fertiliser Regulation update discussions be achieved without leading significantly increased use of igneous rock for fertiliser production and (b) technologies exist and could be implemented to remove cadmium in some fertiliser production, phosphoric acid purification or rock treatment processes. Cadmium removal as is already done for many industrial applications which require purified phosphoric acid, but there are significant financial and environmental costs (energy consumption, generation of waste streams).

MGA – merchant grade phosphoric acid:

Merchant grade phosphoric acid is essentially a transport/intermediate, a convenient form for international trade of ‘phosphorus’.

Although fertilisers and other phosphorus products can also be produced by other routes, most are today produced from MGA (both in Europe and worldwide). Changing to other routes for fertiliser production would involve huge industrial investments, requiring unrealistic budgets and decade delays. The non-availability of MGA to import into Europe would bring much of Europe’s fertiliser and other phosphorus using industries to standstill. The non-availability of MGA on the world market would similarly affect world fertiliser production, so preventing Europe from importing fertilisers.

One specific factor which should be considered for MGA is the availability of sulphuric acid, often produced by burning sulphur (which also produces significant energy, which can be harvested for electricity generation or process heating). MGA phosphoric acid is produced by adding sulphuric acid to phosphate rock. Today, sulphur is readily available, largely as a byproduct of sulphur-removal from transport and heating fuels in oil refining. However, the long-term availability is not certain and should be considered in the future.

However, it could be considered that MGA phosphoric acid supply availability is largely related to phosphate rock supply and is thus mostly an image for general availability of phosphorus (P in any form) and therefore that MGA may not be an appropriate "entry" for assessing the criticality of phosphorus.

Purified phosphoric acid

Purified phosphoric acid and its derivatives are essential in a range of important industrial processes and products, including industrial cleaning processes, metal treatment, production of micro-chips and semiconductors, food processing additives, steel production, glasses and ceramics.

To our knowledge, the EU currently has only three phosphoric acid purification plants in operation (Belgium 2, Finland 1) with other EU user industries being dependent on imported purified phosphoric acid.

Specific chemicals

ESPP stakeholders do not identify particular process bottlenecks or vulnerabilities for other specific fertiliser compounds (eg. MAP, DAP), other than general world energy supply issues (which impact ammonia supplies, necessary for MAP and DAP production). Also, technologies are well known and capacity is available in Europe for production of e.g. fertilisers from MGA.

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[i] Most phosphate rock is converted to phosphoric acid mainly by the « wet acid » route (using sulphuric acid), and for a small part by the thermal route (via P_4 in phosphorus furnaces, the P_4 then is reacted with w ater to give very high purity phosphoric acid).

[ii] Probably 10-15% of phosphate rock is used to directly produce SSP (single super phosphate) and 2-5% to produce NPK fertilisers, by the nitric acid route or by other processes, e.g. EcoPhos process www.ecophos.com

[iii] Cummins C., "Phosphorus: from the stars to land & sea", Daedelus, J Am Ac Arts & Sciences, 143 (4), 2014

[iv] Scholz R. et al. "Approaching a dynamic view on the availability of mineral resources: What we may learn from the case of phosphorus?", Global Environmental Change, 23, pages 11-27, 2013

[v] Derived from Richards I. et al. "The phosphate life-cycle: rethinking the options for a finite resource", IFS (International Fertiliser Society) Proceedings n° 668, 15th April 2010, ISBN 978-0-85310-305-9,

[vi] Trade database of IFA (IFAPIT 2014)

[vii] industry expert estimate, 2014