Jenkins, T.A. and Jenkins, V. (2012). The future of phosphorus in agriculture and the environment. The 1st International Congress of Ecologists, University of Business Studies, Banja Luka, Bosnia and Herzegovina. pp. 1481-1497.

THE FUTURE OF PHOSPHORUS IN AGRICULTURE AND THE ENVIRONMENT

Jenkins, T.A.¹, Jenkins, V.¹

¹Centre for Sustainable Agricultural Technologies, P.O. Box 29683, Fendalton, Christchurch 8540, New Zealand, csat@csat.co.nz

ABSTRACT

Phosphorus is an essential element for life and is one of the most commonly applied fertilizer minerals. Most phosphorus fertilizer is first mined as phosphate rock and then treated with acid to increase phosphate availability.

The efficient use of phosphorus is a necessity in a world with finite phosphorus reserves but it is still common in agricultural systems for phosphorus to be applied at levels far exceeding produce exports. Recent interest in the sustainability of phosphorus resources and the potential for "peak phosphorus" highlights the issue of food security. There is also an issue of the environmental impacts on water resources of phosphorus lost from agricultural systems.

This paper uses a biogeochemical perspective to discuss the sustainability of supply and environmental issues surrounding phosphorus fertiliser use. Relevant methods for improving the sustainability of phosphorus approaches in agriculture are critically analysed.

Keywords: Peak Phosphorus, fertilizer efficiency, environment

THE BIOGEOCHEMICAL PHOSPHORUS CYCLE

Phosphorus is an abundant mineral accounting for around 0.12% by weight of the Earth's lithosphere (which includes the crust and the upper surface of the mantle). The distribution of phosphorus is, however, uneven. Topsoils typically have a natural Total P level less than the overall crust with 0.07% P being a typical level and New Zealand unfertilized soils varying from 0.02 to 0.2%P (NZIC, 2008). Fertilized New Zealand topsoils can range from 0.02 to around 0.3%P (pers. obs.). Heavily weathered soils as in much of Australia can often be less than 0.02%P (see ANRA, 2002).

Phosphorus is a highly reactive element and is not found in its free elemental form in nature. Most geological, soil and biological forms of phosphorus involve the oxide form phosphate (PO_4^{3-}) reacted with a range of other elements and compounds. The natural phosphorus cycle involves phosphate rock weathering to slowly release phosphate to soil or water where it is accessed as an essential element by microorganisms and plants (and indirectly by animals) and then returned to the soil or water where it can be reaccessed, or becomes incorporated into non-labile mineral forms in soil. Phosphate can eventually be leached, enter waterways and subsequently be washed into sea sediment where it can over time contribute to the formation of new phosphate rock.

A striking feature of the phosphorus cycle is the length of time from weathering phosphate becoming phosphate rock again which is over a scale of around 1 million or more years. This contrasts with much faster nutrient cycles for non mineral elements such as nitrogen, carbon, hydrogen and oxygen.

The industrialization of agriculture has included a major shortcut to several parts of the cycle. Phosphate rock has been extracted for the manufacture of fast available phosphate fertilizers which are applied to soils to increase crop growth rates. The addition of large amounts of available phosphate to soils has also increased the rate of entry of phosphate to waterways with negative environmental consequences.

Free phosphate ions in solution readily combine with a range of cations. Under high pH conditions, reaction is mainly with calcium to form di-calcium phosphate which is sparing soluble in water but soluble in weak acids including those produced by plant roots and some microorganisms. Tri-calcium phosphate can also possibly form which is practically insoluble in water and only slowly weathers with weak acids. Under low pH conditions, phosphate readily reacts with aluminium or iron to form sparingly soluble compounds. Reaction with aluminium and iron ions is generally thought to be a minor issue in soil solution compared to adsorption of phosphate onto soil minerals containing aluminium and iron (NZIC, 2008); at first adsorption is a reversible process but overtime the phosphate can absorb or penetrate into the soil minerals (clays) and become occluded (by coatings of aluminium or iron oxides) and unavailable for biological uptake.

The reactions that phosphorus has with free cations and soil minerals mean that movement of phosphorus in soil is often slow and availability to biology is often limited. This contributes to the long timeframe of the phosphorus cycle.

PHOSPHATE ROCK TYPES

The majority of world phosphorus reserves are true phosphate rock which is predominantly seabed (sedimentary) formed over a period of millions of years from phosphate gradually entering the sea from land areas. The main mineral form is francolite $(Ca_{10-x-y}Na_xMg_y(PO_4)_{6-z}(CO_3)_zF_{0.4z}F_2)$. Most sedimentary phosphate rocks naturally release phosphate only at a very slow rate their reactivity in soil being higher if there is increased carbonate substitution for phosphate in the chemical structure. Reactivity is also influenced by physical structure within the rock, compression and particle size.

Guano is often considered as a phosphate rock by industry and represents around 2-3 % of annual consumption of phosphate (Abouzeid, 2008). In some dry island environments it has been possible for guano to accumulate over time resulting in mineable reserves. Young Chilean guano rich in available nitrogen was once an important fertiliser internationally before the advent of chemical nitrogen fertilizer production. As guano deposits age, nitrogen and potassium are leached and phosphorus concentrations increase. The phosphorus slowly leaches into and reacts with calcium carbonate (limestone) substrate. The resultant mineral is phosphate, calcium and carbonate rich (carbonate-hydroxy-apatite $Ca_{10}(PO_4, CO_3)_6(OH)_2$) and can often be millions of years old.

Igneous and metamorphic rocks together with some weathered phosphate deposits (can be largely fluorapatite $Ca_{10}(PO_4)_6F_2$, hydroxylapatite $Ca_{10}(PO_4)_6(OH)_2$ or chlorapatite $Ca_{10}(PO_4)_6(Cl)_2$) make up around 15 % of current global phosphate consumption (Abouzeid, 2008).

PHOSPHORUS AND LIFE

Phosphorus is an essential element for life. Phosphate is part of the structure of the genetic material DNA and RNA, and is also a component of ATP and NADPH involved in energy transport, regulatory phosphorylation and oxidation/reduction processes. Phosphate is also contained in phospholipids which are a component of cell membranes involved in nutrient transport.

Many animals have additional functions for phosphate which include skeletal formation (mainly in the combination of calcium, phosphate and hydroxide ions as hydroxylapatite). Tooth enamel is constructed of a combination of hydroxylapatite and fluoroapatite, the latter involving substitution of the hydroxyl groups with fluoride ions resulting in a harder substance

The requirement for phosphorus cannot be replaced with other elements and this highlights the importance of being prudent with world phosphorus reserves. A report of a bacterium that could apparently be forced to utilise arsenic rather than phosphorus Wolfe-Simon *et al.* (2011) has been criticized (Hayden, 2011) and it remains unclear if even in this extreme example, there was any functional replacement of phosphate in biomolecules.

Due to the high reactivity of phosphate and its compounds, low availability of phosphorus to plants is often a limiting factor in many soil types and aquatic systems. This explains why phosphate fertiliser can increase crop yield even when Total P level in most soils is already one or more orders of magnitude above the level of phosphorus that would be removed by a successful crop. It also explains why the entry of new available phosphorus to an aquatic environment can cause eutrophication.

HUMAN USE OF PHOSPHORUS

Most (85 to 95%) mined phosphorus is utilised for agriculture with the vast majority of that being used as fertilizer. Phosphorus is also important in the production of animal feeds and non-agricultural uses such as detergents (partly as a water softening agent), matches, lithium ion batteries (a growing market with electric vehicles) and pesticides. In many nations there has been a ban on phosphates in detergents due to environmental concerns for waterways that could receive waste water.

Fertilizer use is not just the largest end use for mined phosphorus, but phosphorus fertiliser efficiency in terms of crop uptake is low. Phosphorus is often applied at a similar level to that of nitrogen (N) and potassium (K) despite being incorporated into plants at an order of magnitude less than those two other major elements. This imbalance is related at least in part to an inefficiency with which crops and pastures take up phosphorus; Zhu, Smith and Smith (2003) state that there is often as low as a 20% efficiency of plant uptake of applied fertiliser (similar levels are often reported but efficiency depends on conditions such as timing of application with crop growth).

A portion of the phosphorus applied as fertilizer also contributes to the nutrient load entering waterways causing water pollution issues. Thus in dealing with the sustainability of supply of phosphorus and the health of waterways, there needs to be particular emphasis on the efficiency of use of phosphorus fertilisers in agriculture.

The poor efficiency of plant uptake is related to the relatively immobile nature of phosphate ions in many soils. Bucher (2007) describes a localized phosphate depletion zone around plant roots. It takes time then for phosphate to enter that root zone or from the roots to expand into new areas where phosphate is available.

In the later section on nutrient budgeting, the options for improving P fertilizer efficiency are discussed.

PEAK PHOSPHORUS

There are limited accessible world resources of phosphorus and there may come a point in time where demand exceeds current capacity to supply, creating pressure on price and/or quality of phosphorus supply. Brinck (1978) stated that timely supply, price or quality could become an issue given growing

demand for phosphorus but still considered that such growth could be maintained indefinitely at a similar relative price, relying on consistent improvements in production technology over time. More recently, there have been a number of researchers warning of the limited nature of reserves and the potential for peak phosphorus (Cordell, Dragert and White, 2009, Vaccari, 2009)

Significant historic events include the depletion of guano phosphate reserves at both Nauru and Christmas Island by the late 1980's with significant production now ceased. These deposits had been identified previously as some of the most economically efficient reserves (Fantel, Peterson and Stowasser, 1985). Also the USSR (chiefly mining igneous apatite reserves) changed from being a net exporter to a net importer around 1980. US production of phosphate has declined in recent years and the USA ceased phosphate rock export declined in the 1990's and is no longer significant (IFDC, 2010). The important Florida reserves (already having been switched to production of refined phosphate products since a decline in rock purity prevented simpler uses as fertilizer) are predicted to be 60% depleted by 2030 (Jasinski, 2005). Significantly just one country, Morocco, is now calculated to represent over 80% of the world phosphate reserves (IFDC, 2010).

In response to the predictions of phosphate resources running out or at least peak phosphorus, the International Fertilizer Development Centre (IFDC, 2010) presented a preliminary reassessment of world reserves and resources of phosphate rock that represented a large increase on the previous estimate of the US Geological Survey (USGS, 1996-2010) primarily related to a much larger estimate of Morocco (including Western Sahara) reserves and resources. The IFDC emphasised that reserves are by definition limited to what commercial operations have projected as being required over a commercially relevant timescale and that there is a reserve base behind those figures and a larger resource figure. Based on their estimate for reserves the IFDC (2010) considered that these were sufficient for 300 to 400 years at current production levels with graphs showing that although consumption had generally increased over time in the last century, it was flatter since the late 1980's.

Cordell, White and Lindström (2011) criticized the IFDC (2010) report for not simply dividing the reserve by current production figures stating that demand is likely to continue to rise given continued population growth and that conditions (and implications of) peak phosphorus occur prior to reserves being fully depleted. They considered that a revised peak phosphorus prediction using the new IFDC reserve estimate still showed potential for peak phosphorus within the current century.

Given that there is a degree of uncertainty regarding the level of world phosphate rock reserves and how much of potential wider resources would be able to be economically accessed, it should be of concern to decision making authorities that the longevity of even these recent optimistic estimates of reserves and wider resources can be calculated in terms of hundreds of years at best rather than thousands of years or more. It must be borne in mind that phosphate cannot be replaced in agriculture and that world food production is vulnerable to shifts in fertilizer cost and access.

Prediction of phosphate consumption is problematic. The United Nations Development Organization (quoted in IFDC, 2010) predicted that by the year 2000, annual phosphate rock production would need to be 300 million tons (272 million tonnes which was around triple annual production at the time) to meet world demand. The IFDC (2010) reported that annual production of phosphate reached a high point at 1988 and again at 2008 at around 160 million tonnes per annum. Arguably a major reason for such a shortfall compared to the earlier prediction is the slow uptake of phosphate fertiliser use by developing countries (and to an extent developed countries) which could be attributed in part to the relatively high modern prices of phosphate fertilizers. Also significant could be reduced internal demand for phosphate in former Soviet countries since the change from the Soviet Union.

Although consumption has not grown over the last 20 years at the same rate as in previous decades, it would seem that an assumption of no future increase in demand by the IFDC (2010) forecast is overly conservative and may be based on too short a time span when compared to previous decades of high growth.

Regardless of the timing of peak phosphorus it can already be seen that there have been significant changes in the geographical sourcing of phosphorus, the quality of some of those sources and potential for political issues surrounding access to phosphate resources. The uneven distribution of phosphate resources worldwide may have significant economic and political impact in the future particularly for European and Australasian countries that are reliant on imported phosphate.

To further sustain the world wide resource of mineable phosphate rock, improvements should continue to be discovered and implemented in the processing of phosphate rock (much phosphate is lost in the various steps of fertiliser production).

Once phosphate is applied as fertiliser, much of it remains dissipate in the treated soil and some also becomes an environmental issue in waterways. It seems prudent to focus on sustainable use of phosphate to reduce individual country requirements for phosphate and to help conserve world wide resources of phosphate. At the same time this can help reduce the environmental impact of phosphate on waterways.

IMPURITIES IN PHOSPHATE ROCK

As world reserves are reduced the ability there will be an increased requirement for dealing with impurities. Even with current phosphate rocks utilised for fertilizer there are issues with the presence of aluminium and iron which can restrict processing or increase costs of fertilizer production. The Australian reserves in Queensland are currently largely restricted to export to South East Asia as unprocessed fertilizer on acid soils due to aluminium phosphate presence which is not suited to superphosphate and other processed fertilizer manufacture locally and does not release phosphate readily in neutral pH Australian soils.

Cadmium is a toxic heavy metal naturally present in soils and at more concentrated levels in phosphate rock where is partially substitutes for calcium in the apatite molecule. The addition of rock phosphates and superphosphates results in a gradual accumulation of cadmium in soil and an increased risk of cadmium contamination in plants and livestock. Many countries already have regulations or recommendations around maximum cadmium levels in phosphate fertiliser. The risk of cadmium accumulation in soil and produce is a further reason for improving the sustainability of use of phosphate fertilisers. A detailed treatment of the cadmium issue is presented by Chien *et al.* (2011).

Uranium is a further element present as a natural contaminant in phosphate rocks. While the levels of uranium are too low for current utilisation as an industry source of uranium they can be as high as 200 ppm and some attention needs to be placed on handling concentrated material that can result from phosphate product processing (Ragheb, 2010). Uranium tends to accumulate in the soil over time with phosphate fertiliser application but typical levels of increase are small (see Schipper *et al.*, 2011).

PHOSPHORUS AND WATERWAYS

Phosphates reaching rivers, lakes and even the seas can cause eutrophication. This is largely through the importance of phosphate as a nutrient for aquatic algal and plant growth. Aquatic alga and plant growth is often naturally limited by low levels of nutrient particularly carbon, nitrogen and very often phosphorus. Many waterways have reasonable levels of available carbon (e.g. as free carbonates or carbon dioxide) so that photosynthetic algae are not so limited by carbon source. Due to industrial air pollution, nitrogen is also often readily available in many northern hemisphere fresh waterways meaning that the organisms can respond dramatically to an increased amount of phosphate that entering a waterway. Even in low nitrogen aquatic environments, it is also possible for nitrogen fixing aquatic organisms (e.g. many cyanobacteria and also azolla species that have a nitrogen fixing actinobacteria symbiont) to respond to phosphate pollution.

As algae and aquatic plants "bloom" in response to phosphate pollution the increased biomass can senesce, settle and through the process of decomposition utilise oxygen from the water. Resultant anoxia can cause reductions in the health and levels of fish and other animal types. In coral reef areas, the decomposition of algae growth can also lead to decline in coral through the production of organic acids. Other negative consequences of eutrophication can be increases in some species such as jellyfish that impact on the balance of the aquatic community. Algal, cyanobacterial and diatom blooms can also produce levels of toxins harmful to aquatic organisms and animals utilising the affected water (including humans).

The use of phosphate fertilisers and in particular soluble phosphate fertilisers and animal manures is a major contributor to aquatic phosphate pollution (Foy, 2005; Chien *et al.*, 2011).

PHOSPHORUS NUTRIENT BUDGETS

Nutrient budgets involve an analysis of the exports such as livestock removed, milk, wool, excreta not returned, crop harvest, other crop parts removed (e.g. straw). This is compared with an analysis of imports of a nutrient usually from fertilizer, brought in feed or organic matter, brought in livestock, seed or brought in plant material (e.g. seed potatoes, seedlings) and even net inputs by wind and rain deposition (more relevant in low input systems).

For many horticultural operations, calculating crop export is a relatively simple exercise that mainly relies on assumptions or measurements around the nutrient concentration of the harvest material (and potentially other plant material removed) and a measurement of the amount produced.

For livestock operations, calculations can be more complicated if excreta is not fully returned to fields in which the pasture or fodder crops are grown. With good farm design though, most excreta can be returned thus limiting the amount of nutrient wasted in the system. It should be noted that most excreta P is in the dung and that very little in comparison is excreted in urine.

Livestock nutrient budgets frequently overestimate the amount of phosphorus contained in livestock themselves. Georgievskii, Annenkov and Samokhin (1982) calculated the grams of total P in sheep as 5.4 X weight (kg) + 9.6. Thus a 40 kg lamb is estimated to contain around 226 g P. The same reference provides estimates of 3.6 kg P for a 600 kg cow and 460 g for a 100 kg sow. Grace (1983) had a similar estimate for cow phosphorus level of 3.2 kg P. Cow's milk has an estimated 0.95 g P per L (Grace, 1983). Sheep wool has around 0.25% P by weight (Nash and Halliwell, 1999).

Highly intensive livestock operations can be significant sources of phosphate pollution to waterways (Smith and Alexander, 2000) since the dung contains phosphate from off-farm supplementary feed and even inorganic phosphate supplementation and can be applied to small areas close to the livestock operations (representing an oversupply of phosphate. Oversupply of phosphorus to the diet of US dairy cows was identified as an issue in the 1990's (Sink, Knowlton and Herbein, 2000) and this has been partly addressed according to Wu (2003). It is also well established that phosphorus losses to dung is

largely affected by dietary P levels (Morse *et al.*, 1992). Given both the importance of phosphorus resources and the major source that livestock excreta can be for water pollution, appropriate feeding of phosphorus is important. It remains important to manage the application of manure phosphate on agricultural land with attention to the nutrient budget with removal of biomass being an important feature of achieving the balance. In some cases export of manure material including as a formulated fertiliser is undertaken.

Particularly high proportions of phosphorus in grains and many forages (especially legumes) are bound in phytates (a storage form of phosphate). This is a significant issue fore the efficiency with which some livestock can access phosphorus since it is not accessible to endogenous enzymes of livestock. The microbial activity in the ruminant digestive systems is, however, efficient at accessing phosphorus from phytates (Knowlton *et al.*, 2001). For non-ruminants, phytase enzymes are increasingly being used to allow efficient use of phosphorus from the feed, thus reducing phosphorus input requirements and excreta P levels as well as reducing the potential lock up of zinc, iron, calcium and magnesium by dietary phytates. The issue of managing phosphate losses from intensive livestock management is dealt with in more detail by Knowlton *et al* (2004).

Sustainable reduction of exports can involve decisions around reducing stocking rates of livestock, minimising the amount of material that gets exported (e.g. only exporting grain rather than grain and straw or returning pruning material and waste from harvests) or minimising the amount of phosphorus added to avoid excess levels of phosphorus in produce.

Surface runoff (overland flow of water with sediment) can cause loss of phosphorus from the system. Even on areas with a slope, this can often be restricted to around 0.5 kg P ha⁻¹ but if a heavy rainfall event occurs within a month of applying phosphate fertiliser, much more significant losses can occur. Non-water soluble forms of phosphate fertiliser (e.g. reactive phosphate rock) do not contribute significantly to runoff losses even in these extreme events as heavy fertiliser particles tend not to move so far and most losses are with fine soil particles which can carry high levels of adsorbed phosphate from recently applied water soluble fertilizers (McDowell and Catto, 2005). Fertilizer choice can then be to avoid water soluble phosphate fertilizers at times of year prone to overland water flows or to switch at least partly to non-water soluble P fertilizer.

Leaching of phosphate is negligible in many soils much of the time due to the relatively immobile nature of phosphate ions in the presence of soil minerals and cations. There are notable exceptions including light sandy, pumice, podzol or peaty soils, and soils which are heavily already heavily loaded with phosphate ions on clay mineral surfaces (see Webb *et al*, 2010). There can also be significant leaching issues in heavier soils through preferential flow (macropores or cracks in the soil structure) and those with shallow drains (Powlson, 2008) or a free draining gravel base. An important feature that has increased the awareness of phosphate leaching issues has been the discovery that phosphate can often be leached in combination with soil colloids thus overcoming the low mobility of the phosphate ion itself (McDowell *et al.*, 2008). To reduce phosphate leaching, fertiliser choice is also important with slow release (e.g. non water soluble) phosphate representing less risk of leaching.

An issue often overlooked when considering phosphate leaching is the slow downward movement of phosphorus over time. While the downward movement may occur at slow rates this could mean that over a period of several decades, an eventual entry of phosphate into the water table even in soils that are not prone to significant leaching. Thus it is important for phosphorus budgets to be reasonably balanced avoiding excess levels of phosphorus accumulating in farmed soils. Downward movement

rates of phosphate fertiliser has been reported to be higher for watersoluble phosphate sources than for RPR (Loganathan and Hedley, 1997).

Soil loss through adsorption to soil minerals is often not a true loss as it is reversible. The net flow of adsorption and release of phosphate is also affected by fertiliser choices. Net adsorption is likely to be favoured by using high levels of phosphate fertiliser and with the use of fast release water soluble fertilisers. Loss through occlusion with iron oxide coatings on the minerals will likely be more significant if large amounts of available phosphate are applied regularly.

It is important in budgeting for phosphorus to assess the balance without taking into account perceived or known factors of fertilizer inefficiency or "soil loss". This way a picture is gained of just how efficient the system is in regard to produce. In many cases there will be potential yield gains from extra phosphorus fertiliser applied above the actual exports in produce but for sustainability of phosphorus use, attention should be paid to ways in which efficiency can be improved.

Rainfall and net dust deposition can deliver varying amounts of phosphorus with the figure often being around 0.2 kg P ha⁻¹ equivalent (0.35 kg P ha⁻¹ quoted by Harrison, 1978). This can be significant in some low input systems. If there is significant wind erosion from the property, there can instead be a large loss of P from the system.

Some budgets will consider the weathering of phosphate from natural rock and previously immobilized mineral resources in the soil, but the annual level is variable, uncertain to predict and an amount of phosphate will be immobilized in soil minerals in the same year. It is worth noting that the equilibrium between release from and immobilisation in soil minerals can be affected by fertiliser practice (with high rates of available phosphate applied increasing net immobilisation). As a topsoil increases in depth (as can occur with a system that improves soil organic matter status over time or with deep rooting plant species) there may also be greater access to phosphate resources from lower depths of the soil; this could represent a net importing of phosphate into the system over the period of time that the system is changing but is again uncertain.

There is clear evidence that as the absolute difference between phosphate imports and exports increases, there is not just reduced efficiency of phosphate use (including increased net "soil loss") but also greater levels of loss of phosphate to waterways. Imbalances are common in many livestock operations whether intensively housed or intensively pasture based (see Nash and Halliwell, 1999; Goh and Williams, 1999, Underwood and Suttle, 1999, Knowlton *et al* 2004,). Imbalances are also common in horticultural and arable operations worldwide though there is often a higher level of phosphate removal in harvest and the ratio of phosphate imports to exports will often be lower.

SILICON AND PHOSPHATE

Improved crop yield in response to silicon fertiliser has been reported in rice and sugarcane in particular and also in a range of crops including wheat, barley and cucumber (Ma, Miyake and Takahashi, 2001). Positive crop response to silicon fertilizer application may be the result of a range of factors including resilience to pests, diseases and climatic events, improved photosynthetic capacity and nutritional balance (Matichenkov and Bocharnikova, 2001). It has also been suggested that silicon may be useful in increasing phosphate ion availability by silicic acid binding preferentially to aluminium, iron and calcium ions. The chemical equations for the reactions for this have been set out by Matichenkov and Bocharnikova (2001) including the one for aluminium as follows.

 $2Al(H_2PO_4)_3 + 2Si(OH)_4 + 5H^+ = Al_2Si_2O_5 + 5H_3PO_4 + 5H_2O$

While these reactions with silicic acid have been known for some time (e.g. Lindsay, 1979), the relevance of them in explaining crop responses has not been conclusively shown. Jianfeng and Takahashi (1991) did not find any evidence for sodium silicate reducing P sorption to soil nor effect on release of P from soil minerals. The same authors did report improved growth of rice together with sodium silicate but attributed this to a pH effect and reduced uptake of manganese. They criticized previous research reporting an improvement of P availability with silicate addition for not taking pH effects into account.

There are still occasional reports of dramatically increased phosphorus availability with the use of a range of silicon fertilisers accompanied with dramatic yield improvements (e.g. Bocharnikova *et al.*, 2010) but most publications now attribute silicon fertilizer effects to aspects other than enhancing phosphate availability. Further research is required on the direct and indirect ways in which silicon fertilizers may reduce phosphorus fertilizer requirements.

THE IMPORTANCE OF NUTRIENT CYCLING

The rate with which organic phosphorus is remineralised and made available to soil organisms and plant roots is an important factor in phosphate efficiency of an ecosystem or agro-ecosystem (Harrison, 1978). This organic cycling is reliant on soil biology activity which can be stimulated by a range of means including liming, cultivation, temperature increase, adequate soil moisture level, addition of organic matter, nitrogen application and stimulation of plant growth. The sustainability of any of these approaches depends primarily on the maintenance or improvement of organic matter content in the soil and soil structure in general. Sustainability also depends on an adequate supply of phosphate over the years to make up for phosphorus removed from the area in harvesting and other true losses from the site. With improved rates of nutrient cycling it will be possible in many situations to reduce phosphate applications from current levels to levels that better reflect the system's phosphate budget deficit.

In many agricultural systems a key component of nutrient cycling rate will be the activity of earthworms. Earthworm levels are encouraged by appropriate liming, good soil structure, reduced cultivation and maintenance of soil organic matter levels and the presence of plant roots (avoiding bare soil where possible).

IMPROVING PLANT ROOT EFFICIENCY

In many agricultural systems, improved choice of plant species can bring greater phosphorus efficiency. In pastures, white clover (*Trifolium repens*) has a poor root system for phosphorus uptake efficiency. More phosphorus efficient root systems are present in alternative legume species such as the system can permit the use of *T. pratense* (red clover), *T. ambiguum* (Caucasian clover) and *Medicago sativa* (lucerne). In cropping situations it is sometimes possible to grow green manure cover crops in between cash crops. Some legume cover crop species such as *Lupinus* spp. have fibrous root systems that efficiently access phosphorus, acidify the rhizosphere (root zone) increasing mineral weathering of phosphate, and produce phosphatase enzymes that may assist further with accessing inorganic phosphate sources. When cover crops are reincorporated in to the soil, they allow a timely release of phosphate for cash crops that are often less efficient at phosphate uptake.

Good soil structure and soil biological activity are important for the general ability of crop roots to expand out and down more readily. This increases the volume of soil available for plant uptake.

MYCORRHIZAE

A key biological component to the efficient use of phosphate is the colonization of plant roots with mycorrhizal fungi (Miller and Jastrow, 1994). Most crop species (with the notable exception of

brassicas) can host arbuscular mycorrhizae (AM). AM fungi extend hyphae out beyond the plant roots to effectively increase the volume of soil from which the plant can access phosphate (Smith and Read, 1997). AM can produce their own phosphatase enzymes, stimulate phosphatase production by colonized plant roots, and they can promote plant root branching further improving phosphate uptake potential (Dighton, 1983). Koide and Kabir (2000) provide some evidence that AM fungi can also hydrolyse some organic phosphate sources which may further improve nutrient cycling. AM fungi bring additional benefits that may further improve phosphate efficiency, including the improvement of soil structure (Miller and Jastrow, 1994).

AM fungi are obligate symbionts with plants; in return for providing a nutritional benefit to plants (improved uptake of phosphorus and other minerals as well as nitrogen and water), they receive carbohydrate energy from colonized plants. Notably the relationship brings a net yield benefit to crop plants in many cases when phosphate availability is low. In cases of high phosphate availability such as the use of high levels of water soluble phosphates there can actually be a negative effect of colonization on crop yield (Janos, 2007) or a reduction in the actual level of colonization. Phosphate efficiency through AM fungi therefore is better achieved by avoiding large applications of water soluble forms of phosphate fertilizer. It is also important to avoid bare ground and non AM-fungi hosts (e.g. brassicas) for extended periods of time and to reduce the level of cultivation as tillage can disrupt AM hyphae.

RECYCLING OF WASTE MATERIAL

In highly populated countries there is significant scope for the recycling of sewage and other organic material. This is often complicated with the issue of heavy metals and other contaminants as well as pathogenic organisms in the material. Separation of the organic material from industrial sources of contamination needs to be addressed as it becomes practical and systems designed which allow the use of organic nutrients including phosphate without undue environmental or health effects.

CONCLUSION

Phosphorus is an abundant mineral in the earth's crust but it is distributed unevenly. Timing of peak phosphorus is uncertain but there are already indications of issues in local availability, price and quality. There are also significant issues around the effect of phosphate loss into waterways.

Agricultural fertilizer is the main use of mined phosphate and fertilizer use is often highly inefficient. Improved efficiency of fertiliser use through the appropriate choice of fertilizer type, timing, crop species, stimulation of nutrient cycling, encouragement of mycorrhizae and optimising farm design is imperative for sustainability of supply and reducing the entry of phosphate into waterways. Recycling of nutrients is also an important step in reducing mining requirements and avoiding point sources of phosphate pollution.

BIBLIOGRAPHY

- Abouzeid, A-Z.M. 2008. Physical and thermal treatment of phosphate ores An overview. International Journal of Mineral Processing 85: 59–84.
- ANRA (2002). Australian Natural Resources Atlas APPENDIX 2. Australian Soil Resources Information System, Canberra.

http://www.anra.gov.au/topics/soils/pubs/national/agriculture_asris_phos.html.

- Bocharnikova, E.A., Loginov, S.V., Matychenkov, V.V., Storozhenko, P.A. 2010. Silicon Fertilizer Efficiency. *Russian Agricultural Sciences* 36(6): 37-39.
- Brinck, J. W. (1978). World Resources of Phosphorus. In Ciba Foundation Symposium 57 -Phosphorus in the Environment: Its Chemistry and Biochemistry (eds R. Porter and D. W. Fitzsimons), Elsevier, Amsterdam. pp. 23-43.

- Bucher, M. 2007. Functional biology of plant phosphate uptake at root mycorrhiza interfaces. *New Phytologist* 173: 11-26.
- Chien, S., Prochnow, L., Tu, S., Snyder, C. 2011. Agronomic and environmental aspects of phosphate fertilizers varying in source and solubility: an update review. Nutrient Cycling in Agroecosystems 89(2):229-255.
- Cordell, D., J. Dragert and S. White. 2009. The Story of Phosphorus: Global Food Security and Food for Thought. *Global Environmental Change* 19: 262-305.
- Cordell, D., White, S. and Lindström, T., 2011. Peak phosphorus: the crunch time for humanity? The Sustainability Review 2(2). http://www.thesustainabilityreview.org/2011/04/peak-phosphorus-the-crunch-time-for-humanity.
- Dighton, J. 1983. Phosphatase production by mycorrhizal fungi. Plant and Soil 71: 455-462
- Fantel, RJ., GR. Peterson and W.F. Stowasser. 1985. The Worldwide Availability of Phosphate Rock. *Natural Resources* 9(1):5-24.
- Foy RH (2005) The return of the phosphorus paradigm: Agricultural phosphorus and eutrophification. In: Sims JT,
- Georgievskii, V.I., Annenkov, B.N. and Samokhin, V.T. 1982. Mineral Nutrition of Animals. Butterworths, London. 475 p.
- Goh K.M., Williams, P.H., 1999. Comparative nutrient budgets of temperate grazed pastoral systems. In: E.M.A. Smaling, O. Oenema and L.O. Fresco (Eds), Nutrient disequilibria in agroecosystems: concepts and case studies. CABI Publishing: Wallingford, UK. pp. 265–294.
- Grace, N. 1983. The Mineral Requirements of Grazing Ruminants. New Zealand Society of Animal Production, New Zealand.
- Harrison, J. W. (1978). Phosphorus cycles of forest and upland grassland ecosystems and some effects of land management practices. In Ciba Foundation Symposium 57 - Phosphorus in the Enviroment: Its Chemistry and Biochemistry (eds R. Porter and D. W. Fitzsimons), Elsevier, Amsterdam. pp. 175-192.
- Hayden, E.C. 2011. Study challenges existence of arsenic based life: Open science advocates fail to reproduce controversial findings. Nature (News). http://www.nature.com/news/study-challenges-existence-of-arsenic-based-life-1.9861. Accessed 29 Feb 2012
- IFDC (2010), *World Phosphate Reserves and Resources*, International Fertilizer Development Center, Washington D.C.
- Janos, D.P. 2007 Plant responsiveness to mycorrhizae differs from dependence on upon mycorrhizae. Mycorrhiza 17: 75-91.
- Jasinski, S. (2005). Phosphate Rock Reserves in the United States. Presented at the 2005 IFA Production and International Trade Conference, Sao Paolo, Brazil, September 11-14.
- Jianfeng, M.A., Takahashi, E. 1991. Effect of silicate on phosphate availability for rice in a P-deficient soil. Plant and Soil 133(2): 151-155.
- Knowlton, K.F. Herbein, J.H., Meister-Weisbarth, M.A. and Wark, W.A. 2001. Nitrogen and Phosphorus Partitioning in Lactating Holstein Cows Fed Different Sources of Dietary Protein and Phosphorus. J. Dairy Sci. 84:1210–1217
- Knowlton, K.F., Radcliffe, J.S., Novak, C.L., Emmerson, D.A. 2004. Animal management to reduce phosphorus losses to the environment. Journal of Animal Science 82(13) supplement E173-E195.
- Koide, R.T. and Kabir, Z. 2000. Extra radical hyphae of the mycorrhizal fungus *Glomus*. New Phytologist 148: 511-517.
- Lindsay, W.L. 1979. Chemical equilibria in soil. John Wiley and Sons, New York.
- Loganathan, P., Hedley, M.J. 1997. Downward movement of cadmium and phosphorus from phosphatic fertilisers in a pasture soil in New Zealand, Environmental Pollution 95(3): 319-324.

- Ma, J.F., Miyake, Y., Takahashi, E. 2001. Silicon as a beneficial element for crop plants. Chapter 2, pp. 17-39 In: L.E. Datnoff, G.H. Snyder and G.H. Korndörfer, Editor(s), *Studies in Plant Science Volume 8*. Elsevier, Amsterdam.
- Matichenkov, V.V., Bocharnikova, E.A. 2001. The relationship between silicon and soil physical and chemical properties. Chapter 13 pp 209-219 In: L.E. Datnoff, G.H. Snyder and G.H. Korndörfer, Editor(s), *Studies in Plant Science Volume 8*. Elsevier, Amsterdam.
- McClellan and Hignett, 1978. Some economic and technical factors affecting use of phosphate raw material. In Ciba Foundation Symposium 57 Phosphorus in the Environment: Its Chemistry and Biochemistry (eds R. Porter and D. W. Fitzsimons), Elsevier, Amsterdam. pp. 49-63.
- McDowell, R.W., and Catto, W. (2005) Alternative fertilisers and management to decrease incidental phosphorus loss. Environmental Chemistry Letters 2, 169-174.
- Miller, R.M\, Jastrow, J.D. 1994. Vesicular arbuscular mycorrhizae and biogeo-chemical cycling. In: Pfleger, F.L. and Linderman, R.G. (Eds). Mycorrhizae in Sustainable Agriculture. Crop Science Society and Soil Sciences Society of America, Madison, WI pp. 29-44.
- Morse, D. H., Head, H., Wilcox, C.J., Van Horn, H.H., Hissem, C.D., Harris, B. 1992. Effects of concentration of dietary phosphorus on amount and route of excretion. J. Dairy Science 75:3039–3049.
- Nash, D.M. and Halliwell, D.J. 1999. Understanding phosphorus transfer from land to water. Agricultural Science (12): 37-42.
- NZIC (2008) The fate of phosphate fertiliser in soils. New Zealand Institute of Chemistry. http://nzic.org.nz/ChemProcesses/soils/2D.pdf. Accessed 29 Feb 2012
- Ragheb, M. 2010. Uranium Resources in Phosphate Rock. Available from https://netfiles.uiuc.edu/mragheb/www/NPRE%20402%20ME%20405%20Nuclear%20Power %20Engineering/Uranium%20Resources%20in%20Phosphate%20Rocks.pdf.
- Schipper, L.A., Sparling, G.P., Fisk, L.M., Dodd, M.B., Power, I.L. & Littler, R.A. (2011). Rates of accumulation of cadmium and uranium in a New Zealand hill farm soil as a result of long-term use of phosphate fertilizer. Agriculture, Ecosystems & Environment, 144(1), 95-101.
- Sink, S. E., K. F. Knowlton, and J. H. Herbein. 2000. Economic and environmental implications of overfeeding phosphorus on Virginia dairy farms. Journal Animal Science 78 (Suppl. 2):4.
- Smith, R. A., and R. B. Alexander. 2000. Sources of nutrients in the nation's watersheds. Pages 13–21 in Managing Nutrients and Pathogens from Animal Agriculture. Natural Resource, Agriculture, and Engineering Service (NRAES), Ithaca, NY.
- Smith, S.E. and Read, D.J. 1997. Mycorrhizal Symbiosis. 2nd Ed. Academic Press, London
- USGS, 1996-2010. *Mineral Commodity Summaries, Phosphate Rock.*, U.S. Geological Survey, U.S. Department of the Interior, Washington, DC, U.S.A.
- Underwood, E. J., Suttle, N.F., 1999. The Mineral Nutrition of Livestock 3rd Ed. CABI Publishing, CAB International, Wallingford, Oxon, UK.
- Vaccari, D.A. 2009. Phosphorus: A Looming Crisis. Scientific American 300: 54-59.
- Webb, T., Hewitt, A., Lilburne, L., McLeod, M., Close, M. 2010. Mapping of vulnerability of nitrate and phosphorus leaching, microbial bypass flow, and soil runoff potential for two areas of Canterbury. Environment Canterbury Report No. R10/125. http://ecan.govt.nz/publications/Reports/mapping-vulnerability-nitrate-phosphorus-leaching-microbial-bypass-flow-soil-runoff-potential-000610.pdf.
- Wolfe-Simon, F., Switzer Blum, J., Kulp, T.R., Gordon, G.W., Hoeft, S.E., Pett-Ridge, J., Stolz, J.F., Webb, S.M., Weber, P.K., Davies, P.C.W., Anbar, A.D. and Oremland, R.S. (2011). A Bacterium That Can Grow by Using Arsenic Instead of Phosphorus. Science 332(6034): 1163-1166.
- Wu, Z. (2003) People still are feeding too much phosphorus. Hoards Dairyman 148: 210.

Zhu, Y.G, Smith, F.A., Smith S.E. 2003. Phosphorus efficiency and responses of barley (*Hordeum vulgare* L) to arbuscular mycorrhizal fungi grown in highly calcareous soil. *Mycorrhiza* 13: 93-100.