SIGNIFICANCE OF LOW CONTAMINANT LEVELS IN AN INDONESIAN GUANO PHOSPHATE FERTILISER

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Summary

Phosphorus is a major element required for pasture and crop production and phosphate fertiliser has been applied in New Zealand for over a century. Undesirable elements including cadmium (Cd), uranium (U) and fluorine (F), are associated with most phosphate sources and can either be directly toxic or have accumulated detrimentally in agricultural soils.

The Javanese guano phosphates described here were formed by relatively unique biogeochemical processes resulting in distinctly lower contaminant levels and suitability for direct fertiliser application. Levels of Cd are typically around 45 mg(kg P)$^{-1}$, U 60 mg kg^{-1} and F 0.065% compared to general sedimentary phosphate rock levels of Cd 27 to 641 mg(kg P)$^{-1}$, U 50 to 200 mg kg^{-1}, and F around 2.2 to 4.1%. This guano resource expands options for sustainably addressing phosphate requirements.

Background

Contaminants are a common feature of phosphate resources. Cadmium is a toxic heavy metal and there is some concern about residues in produce if soil levels become elevated (McLaughlin and Hamon, 2001). Uranium can also reach levels of concern in some phosphate resources potentially presenting a risk for people handling the material, livestock toxicity and residues in produce. A further element, fluorine, is a reasonably major component of many phosphate rocks at up to 4% by weight. The fluoride is potentially toxic to livestock if consumed directly from fertiliser contaminated pasture or potentially if soil levels become elevated (Cronin et al., 2000). All three contaminant elements are accumulating in some New Zealand agricultural soils due to phosphate fertiliser application.

The levels of cadmium, uranium and fluorides vary between different phosphorus reserves around the world and choice of source is one method of reducing the potential risk from the contaminants. Viafos guano phosphate is sourced from Central and Eastern Java including the Island of Madura. Samples of the guano were analysed for aspects of composition relevant to reactivity and contaminant level.

Formation of Phosphorus Resources

Guano Phosphate: Seabird guano deposits accumulate in some dry island environments and eventually form mineable reserves. As guano deposits age, nitrogen and potassium nutrients are leached out and phosphorus concentrations increase. Over millions of years, phosphate leaches into and reacts with a calcium carbonate substrate. The resultant biogenic mineral is phosphate, calcium and carbonate rich (carbonate-hydroxy-apatite $Ca_{10}(PO_4,CO_3)_6(OH)_2$). Guano make up 2 to 3 % of the world's phosphorus supply (Abouzeid, 2008).

Sedimentary Phosphate Rock: The majority of world phosphorus reserves are true phosphate rock (non-biogenic) and sedimentary formed. This is predominantly marine formed over a period of millions of years from phosphate gradually entering the sea from land areas. The main mineral form is francolite (Ca, Mg, Sr, Na)10(PO4, SO4, CO3)6F2–3.

Other Phosphate Rocks: Igneous (particularly in Russia and South Africa) and metamorphic (India) and 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).

Sources of Contaminants

Undesirable elements that can concentrate in phosphate rock and guano include fluoride, cadmium and uranium. In guano these elements may form part of the original deposits but it is common for the reserves to develop in tidal conditions or fully immersed in seawater such that seawater elements replace some of the apatite elements. Fluoride can replace hydroxyl ions while cadmium and uranium can replace some of the calcium ions or otherwise bind into the mineral. Sedimentary phosphate rocks typically have high levels of fluoride, cadmium and uranium due to interaction of the mineral with seawater elements.

Table 1. Composition of Javanese Guano Phosphate

Component	**Javanese Guano Phosphate (Viafos®)***	**Typical Sedimentary Rock Phosphate**	**Significance for Reactivity and Toxic Load**
Phosphorus (P)	11.0% $\pm$ 0.38 n=9	~ 12.7 to 14.2% (Zapata and Roy, 2004)	
Calcium (Ca)	27.7% $\pm$ 0.98 n=9	22.8 to 34% (Zapata and Roy, 2004)	
$CaO:P_2O_5$ Ratio	1.54 $\pm$ 0.049 n=9	1.33 to 1.67 (Zapata and Roy, 2004)	Higher Ca:P ratio linked with higher reactivity.
pH	7.74 $\pm$ 0.094 n=9	Around 7 (Stevens and Carron, 1948), higher with increasing reactivity	Higher levels of calcium carbonate result in increased liming effect and reactivity.
Fluoride (F)	0.071% $\pm$ 0.005 n=4	2.2 to 4.1% (Cronin et al, 2000)	Lower levels linked with higher reactivity. Lower level of toxic contaminant for livestock toxicity and accumulation in soil.
Uranium (U)	60 mg kg^{-1} $\pm$ 39.4 n=2	50 to 200 mg kg^{-1} and higher (Ragheb and Khasawneh, 2010; Schipper et al., 2011)	Lower level of toxic contaminant means less risk of accumulation.
Cadmium (Cd)	45 mg(kg $P)^{-1}$ $\pm$ 6.0 4.8 mg kg^{-1} $\pm$ 0.5 n=9	27 to 641 mg(kg $P)^{-1}$ (McLaughlin and Hamon, 2001)	Lower level of toxic contaminant means less risk of accumulation.

* Confidence interval for guano analyses is one standard error, n = sample number.

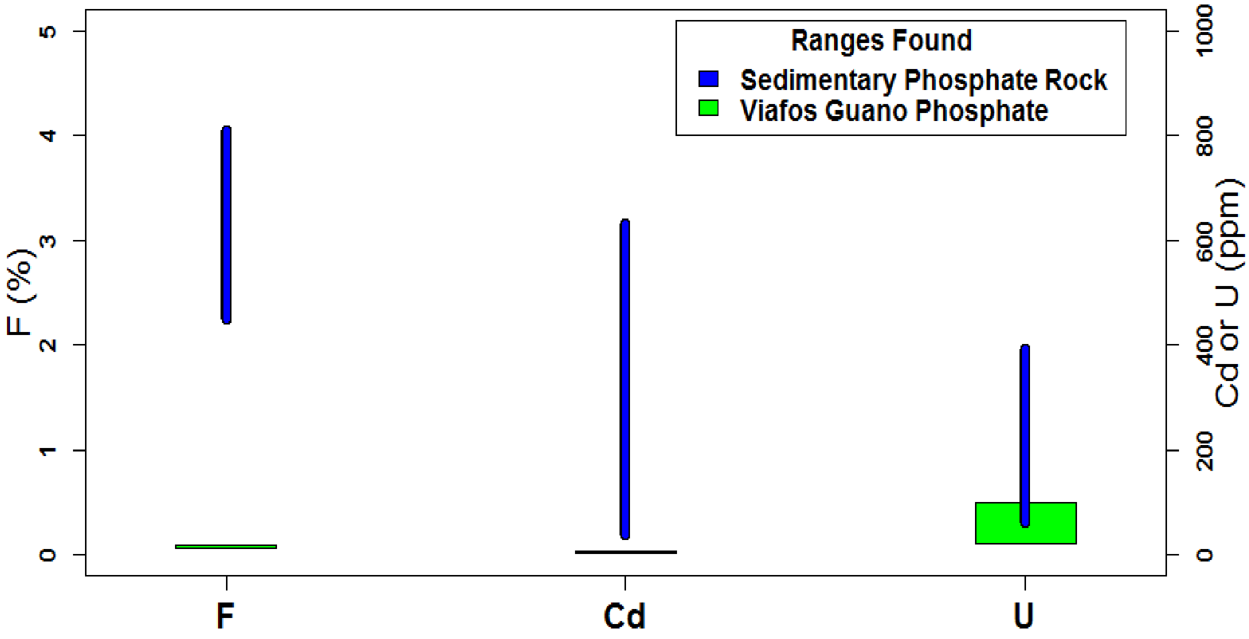

Figure 1. Contaminant levels in Viafos (Indonesian) Guano Phosphate compared to ranges reported in sedimentary phosphate rocks.

The Javanese guano samples had high calcium to phosphate ratios, high pH and low fluoride levels, all linked with higher phosphate rock reactivity (Zapata and Roy, 2004). Water soluble phosphorus tested at <0.01 % for one sample. Acid solubility of the guano was tested at around 170 micron mean particle size (as retailed) compared to Gafsa (highly reactive phosphate rock) ground to a similar size. Citric acid (2%) solubility for the Javanese guano sample was 39.2% of total P compared to the Gafsa RPR level of 31.3%. Formic acid (2%) solubility for Javanese and Gafsa phosphates were 56.8% and 32.8% respectively providing further evidence of high acid reactivity for use as a direct applied fertiliser.

The low levels of fluoride, uranium and cadmium represent likely absence or low level of contact with the marine environment during formation of the Javanese reserves unlike some other guano derived phosphate reserves e.g. Nauru and Christmas Island where marine contact is likely to be responsible for comparatively high levels of Cd, F and U.

Discussion and Conclusions

The Javanese phosphorus reserves here have formed in such a way that contaminant levels are low and reactivity or release of phosphorus is high, allowing use as a direct applied fertiliser while posing relatively low risk of Cd, U and F contaminant accumulation in soil. The Javanese guano contains no significant water soluble phosphate representing less risk of phosphate losses to waterways from runoff, preferential flow or leaching.

Analysis Methods

Total P, Ca, Cd, pH and Water Soluble P analysed by Eurofins NZ Laboratories Ltd with ICP-MS and a 1:5 water slurry for pH.
U analysed by Waikato University with X-Ray fluoresence.
F analysed by ICP-MS or APHA 4500 F C method (SGS NZ Ltd).
Citric and Formic Acid P solubilities analysed by Land Research Services Ltd according to the methods of McKay et al. (1984) and Blakemore et al. (1987).

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