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Soil chemistry: understanding phosphorus in the environment

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Soil chemistry: understanding phosphorus in the environment

Abstract

It is an essential ingredient in food production, but poor management means bad news downstream. Understanding the way phosphorus behaves in the environment calls for soil and plant biology, and some new soil chemistry.

Keywords

phosphorus, understanding, environment, chemistry, soil

Disciplines

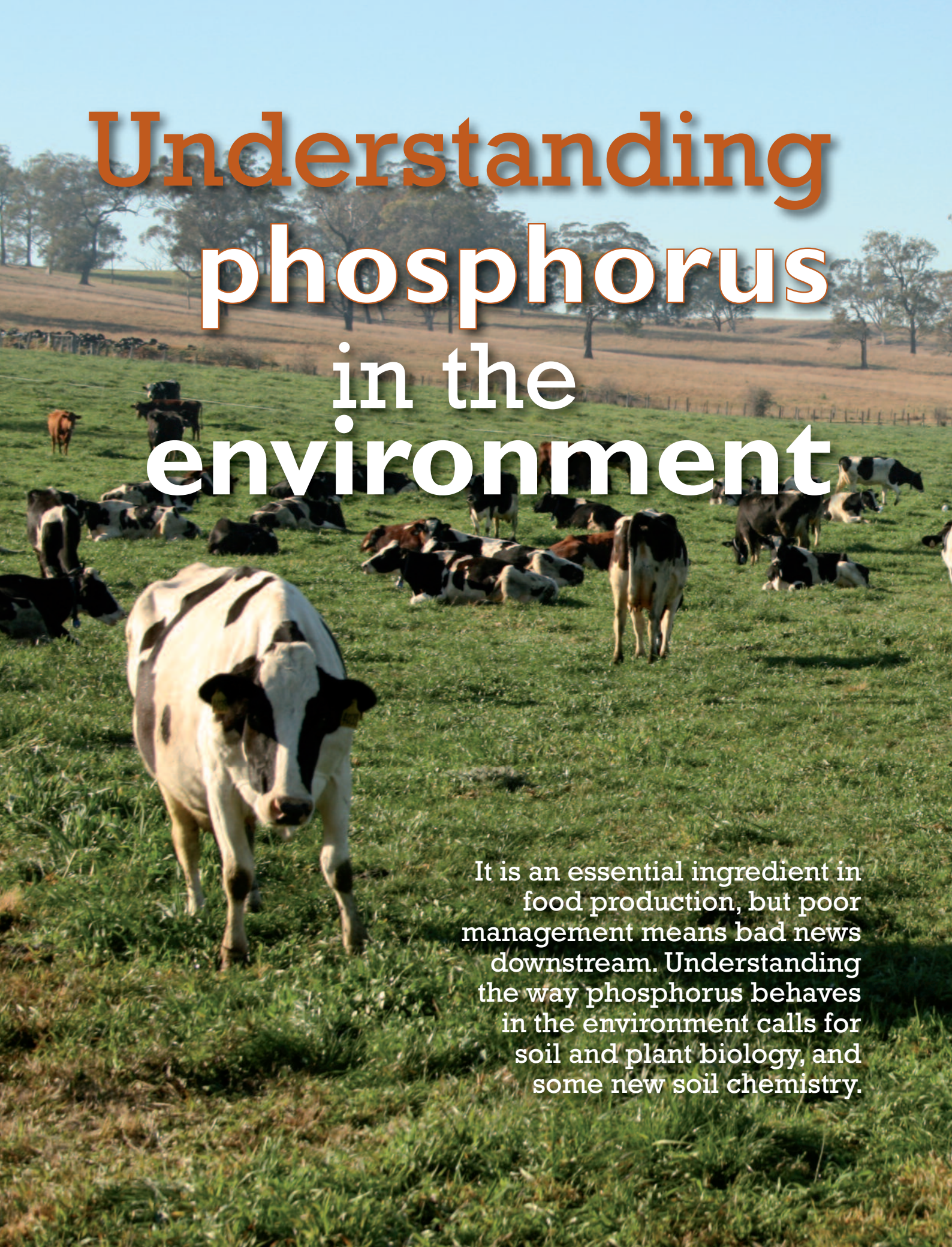
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A photograph of a herd of black and white cows grazing in a lush green field. In the foreground, a cow with a white body and large black patches is walking towards the camera. Other cows are scattered across the field, some standing and some lying down. The background shows a line of trees and a clear blue sky.

Understanding phosphorus in the environment

It is an essential ingredient in food production, but poor management means bad news downstream. Understanding the way phosphorus behaves in the environment calls for soil and plant biology, and some new soil chemistry.

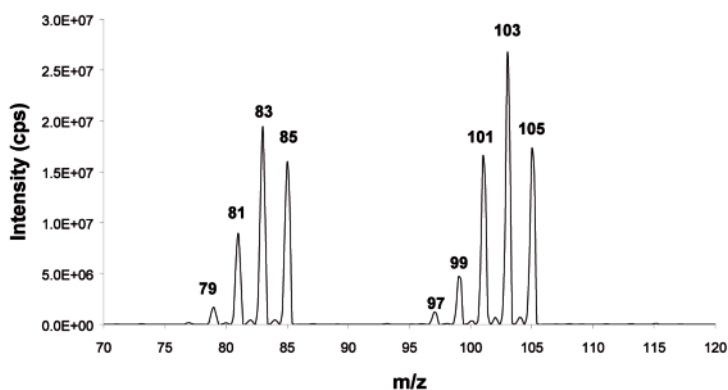


Managing soil phosphorus (P) is a global goal especially relevant to Australia, where P has been leaching from the soils for millennia. The productivity of the crop and pasture plants that underpin global food production

depends on inputs of P. These inputs to agriculture, mostly as fertilisers, seemed to be environmentally benign until the latter part of the 20th century because of the strong sorption of P by soils. But a pattern slowly emerged of decreased water quality downstream of agriculture

due to the proliferation of aquatic weeds and algal blooms. Investigation showed that it was caused by the movement of P in surface run-off to waterways (Dougherty et al. *Journal of Environmental Quality* 2008, **37**, 417–28; *Soil Research* 2011, **49**, 523–8).

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Typical ESI-MS spectrum of a solution of highly ^{18}O -enriched potassium dihydrogen orthophosphate prepared via the first reaction. The O isotope analogues of metaphosphate are observed at m/z 79–85, and of orthophosphate at m/z 97–105.

Aquatic issues aside, there are cogent reasons to better utilise P. First, world demand for food, and therefore P inputs to agriculture, is increasing steeply. Second, increased carbon dioxide concentrations in the atmosphere will potentially increase plant growth and sequester more carbon. However, to realise this potential, plants require greater concentrations of P in their leaves. These increased demands for P coincide with a decline in the readily recoverable mineral resources of P, which should therefore be husbanded.

As a research collaboration, we contribute to the international effort to improve P management by studying its behaviour in soil. The research we showcase is an example of skills pooling across institutions and geographic distance to meet complex challenges, and of the importance of young researchers in scientific research.

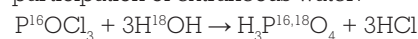
In soils, P occurs as organic compounds and orthophosphate in about equal proportions. Plants and soil biota synthesise organic P compounds, which find their way into the soil where they degrade and ultimately relinquish the P as orthophosphate. Orthophosphate, the form of soil P taken up by plants and released into surface run-off, is our main research focus.

In many soils, including those in Australia, orthophosphate is largely associated with the oxyhydroxides of iron(III) and aluminium (hereafter M^{3+}). A small, variable proportion of this orthophosphate occurs at the surface of these species due to competition with OH^- to bind to M^{3+} . This ligand-exchange reaction has long been posited to control the concentration of orthophosphate in the soil solution and consequently to control processes as important as the uptake of P by plants and its transfer to surface water. Testing these hypotheses is difficult because measuring the exchangeable fraction of orthophosphate is complex. This assay uses a 'dilution' technique involving the addition of orthophosphate labelled with a radioisotope of P, typically ^{32}P . (A radioisotope of P is the only option because the addition must be in the form of orthophosphate, but distinguishable from naturally occurring orthophosphate, and P has just one stable isotope, ^{31}P .) The requirement to use a radioisotope has placed a surprisingly severe constraint on testing the hypotheses – even in Australia, only one laboratory routinely performs the assay. Part of our effort is therefore directed towards developing a more accessible measure of exchangeable orthophosphate.

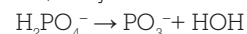
To measure exchangeable orthophosphate in soil, the required

distinction between natural and added orthophosphate might be achieved by labelling the constituent O atoms instead of the central P atom of the latter, provided that the PO_4 species remains intact. Such O-labelling is technically feasible because O has three stable isotopes and highly enriched sources are readily available. The rounded atomic masses of these O isotopes and their approximate natural abundances are 16 (99.76%), 17 (0.02%) and 18 (0.22%).

Foundation research was conducted by Rebeca Alvarez (PhD 2004, University of Technology Sydney). Rebeca distilled POCl_3 and reacted it with highly ^{18}O -enriched water under conditions that minimised the participation of extraneous water:



Don't try this at home! The reaction is strongly exothermic and autocatalytic (i.e. explosive). The product was isolated as KH_2PO_4 . Electrospray ionisation mass spectrometry (ESI-MS) had not been used to characterise $^{16,18}\text{O}$ isotope analogues of orthophosphate, but was considered as a candidate technique. After some annoying setbacks, Rebeca started to acquire spectra and the next development was that these spectra showed that a portion of the dominant ion, H_2PO_4^- , dehydrated in the ESI-MS:



Dehydration added complexity to the study because it was necessary not only to test the possibility of O-exchange between H_2PO_4^- and the 'carrier' water in the ESI-MS, but to extend the study to include PO_3^- . None of these O-exchange reactions occurred at a measureable rate: the ESI-MS data represents authentic O isotope signatures and a typical spectrum is shown. The $^{16/18}\text{O}$ proportions observed using ESI-MS were confirmed by NMR spectroscopy.

The ESI-MS spectrum for both meta- and ortho-phosphate shows a full complement of all possible O isotope analogues, from entirely ^{16}O to entirely ^{18}O . This observation was

unexpected and became the starting point for a subsequent study by Andrew Thomas. Andrew tamed the first reaction by using dry tetrahydrofuran as the solvent under a blanket of dry nitrogen gas. He used ESI-MS to show quantitatively that, during the first reaction, the O in the reactants was distributed randomly to all four positions on the P atom, i.e. that the P–O bond in POCl_3 is not conserved.

Rebeca's and Andrew's work makes it possible to safely produce gram quantities of ^{18}O -enriched KH_2PO_4 with a predictable $^{16}/^{18}\text{O}$ isotopic signature, and to rapidly measure that signature. These advances make it possible for the first time to measure the rate of O-exchange on the central P atom of PO_4 , when the PO_4 exchanges at the surface

of M^{3+} oxyhydroxides. Studying this reaction is perhaps just one step removed from testing the underpinning concept – that O labelling of orthophosphate may substitute for P labelling in the measurement of exchangeable orthophosphate.

We have also examined the occurrence of organic forms of soil P including myo-inositol hexakisphosphate (phytate). Phytate is synthesised by plants and soil biota, and prior to our work was widely held to be a major component of the organic P fraction in soils. The results of an NMR study of organic P extracted from soils by using alkaline EDTA challenged this accepted view (Smernik and Dougherty, *Soil Science Society of America Journal*, 2007, **71**,

1045–50). Subsequent research by Ashlea Doolette demonstrated that the commonly held view was based on incorrect assignment of the NMR peaks and on inappropriate data deconvolution (Doolette et al., *Organic Geochemistry*, 2011, **42**, 955–64). The data shows that much of the P thought to be phytate is instead a constituent of larger humic molecules.

Modern approaches to P chemistry in soils are yielding a new understanding of P behaviour and challenging pillars of the current theory. This new knowledge will underpin more effective management to maximise the benefits of P inputs and minimise the environmental risks. Research on soil P is providing training opportunities for students with a wide range of backgrounds and interests.



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