



## Introduction to the special issue: Developments in soil organic phosphorus cycling in natural and agricultural ecosystems



Phosphorus is essential for life, but its availability often limits productivity in both terrestrial and aquatic ecosystems (Elser et al., 2007). From tropical rain forests to the open oceans, organisms depend on organic phosphorus turnover for their phosphorus nutrition and have evolved complex adaptations that allow them to compete efficiently for this scarce resource (e.g. Lambers et al., 2006; Whitton et al., 2005). Yet organic phosphorus continues to be largely overlooked in biogeochemical, agricultural, and ecological research, and remains poorly understood in comparison to inorganic phosphorus. This limits our understanding of phosphorus cycling in ecosystems, inhibits the development of sustainable agricultural practices, and constrains our ability to predict the response of the earth's major biomes to global change.

In 2003, the first organic phosphorus workshop was held at Monté Verita in the mountains of southern Switzerland. The meeting brought together a multidisciplinary group of scientists seeking to unravel the complexity of organic phosphorus in the environment. The resulting book *Organic Phosphorus in the Environment* (Turner et al., 2005) overviewed the state of the field at that time in a series of review chapters on topics ranging from the detection of organic phosphorus compounds in environmental samples to the dynamics of organic phosphorus in terrestrial and aquatic environments.

Since the meeting in Monté Verita there have been a number of important conceptual and methodological developments that have significantly advanced our understanding of soil organic phosphorus dynamics. Many of these were presented at two recent meetings on organic phosphorus in the environment. *Organic Phosphorus 2013: Integration across Ecosystems* was held in February 2013 at the Smithsonian Tropical Research Institute, Republic of Panama (see <http://www.stri.si.edu/sites/organicphosphorus2013/index.html> for a list of presentations and extended abstracts). *The Ecological Significance of Soil Organic Phosphorus* was held in July 2014 at the World Soil Science Congress on Jeju Island, Korea.

This special issue is a product of these two meetings and brings together fifteen papers on the common theme of soil organic phosphorus cycling. The papers cover a variety of subject areas, including soil ecology, agriculture, microbial ecology, and ecosystem development, and involve a variety of analytical techniques, such as nuclear magnetic resonance (NMR) spectroscopy, enzyme hydrolysis, microbial sequencing, and stable and radioactive isotopes. Together, they provide a cross-disciplinary insight into recent developments in organic phosphorus cycling in agriculture and the environment.

### Overview of the special issue: developments in soil organic phosphorus

There has been increasing recognition of the finite nature of mineral phosphorus reserves and their uneven political distribution at the global scale (Cordell et al., 2009; Elser and Bennett, 2011). This has focused attention on phosphorus recycling and efficiency in agriculture, including the recognition of soil organic phosphorus as an important resource with the potential to supply crops with phosphorus for many years (Stutter et al., 2012). Several articles in the special issue focus on organic phosphorus cycling in agricultural soils in temperate and tropical latitudes. For temperate soils, an examination of soil phosphorus composition under contrasting agricultural management systems in the United Kingdom reveals marked variation in the proportions of inorganic and organic phosphorus and the chemical nature of the soil organic phosphorus (Stutter et al., 2015). However, this does not appear to reflect differences in phosphorus inputs, because in a separate study the long-term additions of organic fertilizers, including dairy manure, compost, and sewage sludge, to Swiss soils did not greatly alter the amounts or chemical nature of soil organic phosphorus compared to conventional mineral fertilizer additions (Annheim et al., 2015). In the tropics, a study of Colombian pastures reveals that soil degradation reduces organic phosphorus concentrations via a decline in soil organic matter associated with macro-aggregates, demonstrating a link between soil structure and the stabilization of soil organic phosphorus (Nesper et al., 2015). It has conventionally been difficult to examine organic phosphorus cycling in strongly weathered tropical soils such as those in the Colombian pastures, due in part to problems in the use of the isotope dilution method in soils with high phosphate adsorption capacity (Bühler et al., 2003). In this issue, the development of a novel method to quantify trace phosphate concentrations in strongly weathered soils overcomes this problem (Randriamanantsoa et al., 2015), opening the possibility of obtaining information on organic phosphorus mineralization rates for tropical soils.

At the same time as efforts are underway to increase the efficiency of phosphorus use in agriculture, there is ongoing concern about the impact of phosphorus loss from agricultural land on the quality of freshwater ecosystems, and increasing awareness of the role of organic phosphorus in this process (Haygarth et al., 2005; Sharpley et al., 2015). Three articles in the special issue focus on organic phosphorus in freshwater ecosystems. The first uses solution  $^{31}\text{P}$  NMR spectroscopy to examine the chemical nature of organic phosphorus in outflow from

constructed wetlands in Florida, USA, revealing the abundance of labile forms that could contribute to downstream eutrophication (Jørgensen et al., 2015a). The second study reveals the persistence of elevated organic phosphorus concentrations in a Scottish lake following the cessation of point-source phosphorus pollution (Spears and May, 2015). This demonstrates that organic phosphorus cycling can hinder the rehabilitation of polluted freshwater ecosystems by maintaining dissolved phosphorus concentrations for many years following reductions in phosphorus inputs. Finally, organic phosphorus tends to be more mobile in soils than inorganic phosphate and can therefore leach readily through the soil to surface waters (Turner and Haygarth, 2000). This is examined here for organic phosphorus compounds following poultry manure amendments, revealing how organic phosphorus forms are modified during leaching through the soil (Giles et al., 2015).

A major impediment to research on organic phosphorus cycling has been the availability of procedures to detect and quantify organic phosphorus compounds in environmental samples. However, a number of methodological advances have been made in the last decade. Solution  $^{31}\text{P}$  NMR spectroscopy continues to be the primary choice for characterization of organic phosphorus in soils and sediments (Cade-Menun and Liu, 2014), and there is now more precise identification and quantification of compounds. For example, methods have been developed to identify all four natural occurring stereoisomers of inositol hexakisphosphate in a single analysis (Turner et al., 2012) and to quantify soil organic phosphorus compounds by two-dimensional  $^1\text{H}$ - $^{31}\text{P}$  NMR spectroscopy (Vestergren et al., 2012). The utility of solution  $^{31}\text{P}$  NMR spectroscopy as a tool for identification of soil organic phosphorus is reflected in the number of articles involving this technique in the special issue. These include a number of methodological studies, including the development of a technique to selectively extract inositol phosphates from soils using oxalic acid (Jørgensen et al., 2015b), an improvement in signal detection by reducing the soil to solution ratio during extraction of organic phosphorus (McLaren et al., 2015), a new approach to processing proportional data from NMR analysis (Abdi et al., 2015), and an updated peak library to improve identification of signals in  $^{31}\text{P}$  NMR spectroscopy (Cade-Menun, 2015). A novel chromatography procedure is also presented in this issue, involving the determination of both organic phosphorus compounds and organic anions in tropical soils (Waithaisong et al., 2015).

In terrestrial ecology, a recent emphasis on the links between pedogenesis and long-term ecosystem development has focused attention on transformations of organic phosphorus over long timescales and their influence on patterns of plant and microbial communities in the landscape (McDowell et al., 2007; Turner et al., 2007; Vincent et al., 2013). Two articles in the special issue focus on phosphorus transformations during long-term ecosystem development. The first reports detailed information on soil phosphorus transformations along the Cooloola chronosequence in Queensland, Australia (Chen et al., 2015). The pattern of long-term soil phosphorus decline and increasing biological phosphorus limitation at Cooloola is consistent with biogeochemical theory (Walker and Syers, 1976). However, the pre-weathered nature of the parent sand means that the pattern of soil phosphorus chemistry differs from that observed along other long-term chronosequences (Peltzer et al., 2010) and is therefore most similar to the Mendocino terrace chronosequence in California, USA (Izquierdo et al., 2013).

A second article uses stable isotope ratios of oxygen (the  $^{18}\text{O}$ : $^{16}\text{O}$  ratio, expressed as  $\delta^{18}\text{O}$ ) in phosphate to examine phosphorus cycling during long-term ecosystem development. This technique provides information on phosphorus cycling in freshwater and terrestrial ecosystems (Jaisi and Blake, 2014; McLaughlin et al., 2006; Tamburini et al., 2014) and was previously used to examine aspects of microbial phosphorus cycling along a short-term (150 year old) glacial foreland chronosequence in Switzerland (Tamburini et al., 2012). This is extended here to the 6500 year Haast chronosequence in New Zealand, revealing the importance of efficient organic phosphorus cycling in

maintaining phosphorus availability during long-term ecosystem development (Roberts et al., 2015).

Finally, there have been important recent advances in the identification of microbial genes for the synthesis of phosphatases, the enzymes that hydrolyze organic and condensed inorganic phosphorus compounds to release orthophosphate for biological uptake. This work has been conducted primarily in marine environments (e.g. Dyhrman et al., 2006), with little application in terrestrial or freshwater ecosystems. However, an article in the special issue reports that the bacterial gene for alkaline phosphomonoesterase activity (*phoD*) has been examined in soils of a long-term management trial in Canada (Fraser et al., 2015). The abundance of *phoD* corresponded with alkaline phosphatase activity in the soil, being greater in plots receiving organic fertilizer amendments, but the diversity of organisms expressing *phoD* was greater in soils under conventional management (i.e. receiving only mineral fertilizer) in which alkaline phosphatase activity was relatively low. The broader application of this technique in both natural and managed ecosystems will provide important insight into microbial organic phosphorus cycling, particularly as it becomes possible to identify and quantify the many of other classes of phosphatase gene known to occur in the environment.

Collectively, the fifteen articles in this special issue provide insight into current trends and developments in the study of soil organic phosphorus. We hope they will inspire further research on organic phosphorus in the environment and look forward to the next organic phosphorus workshop to be held in the Lake District, UK, in September 2016 (<http://soilpforum.com/2014/10/20/first-announcement-the-international-organic-phosphorus-workshop-lake-district-england-2016/>).

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## References

- Abdi, D., Cade-Menun, B.J., Ziadi, N., Parent, L.-É., 2015. Compositional statistical analysis of soil  $^{31}\text{P}$ -NMR forms. *Geoderma* 257–258, 40–47 (in this volume).
- Annaheim, K.E., Doolette, A.L., Smernik, R.J., Mayer, J., Oberson, A., Frossard, E., Bünnemann, E.K., 2015. Long-term addition of organic fertilizers has little effect on soil organic phosphorus as characterized by  $^{31}\text{P}$  NMR spectroscopy and enzyme activities. *Geoderma* 257–258, 67–77 (in this volume).
- Bühler, S., Oberson, A., Sinaj, S., Friesen, D.K., Frossard, E., 2003. Isotope methods for assessing plant available phosphorus in acid tropical soils. *Eur. J. Soil Sci.* 54, 605–616.
- Cade-Menun, B.J., 2015. Improved peak identification in  $^{31}\text{P}$ -NMR spectra of environmental samples with a standardized method and peak library. *Geoderma* 257–258, 102–114 (in this volume).
- Cade-Menun, B., Liu, C.W., 2014. Solution phosphorus-31 nuclear magnetic resonance spectroscopy of soils from 2005 to 2013: a review of sample preparation and experimental parameters. *Soil Sci. Soc. Am. J.* 78, 19–37.
- Chen, C.R., Houa, E.Q., Condron, L.M., Bacon, G., Esfandbod, M., Olley, J., Turner, B.L., 2015. Soil phosphorus fractionation and nutrient dynamics along the Cooloola coastal dune chronosequence, southern Queensland, Australia. *Geoderma* 257–258, 4–13 (in this volume).
- Cordell, D., Drangert, J.-O., White, S., 2009. The story of phosphorus: global food security and food for thought. *Glob. Environ. Chang.* 19, 292–305.

- Dyhrman, S.T., Chappell, P.D., Haley, S.T., Moffett, J.W., Orchard, E.D., Waterbury, J.B., Webb, E.A., 2006. Phosphonate utilization by the globally important marine diazotroph *Trichodesmium*. *Nature* 439, 68–71.
- Elser, J., Bennett, E., 2011. A broken biogeochemical cycle. *Nature* 478, 29–31.
- Elser, J.J., Bracken, M.E.S., Cleland, E.E., Gruner, D.S., Harpole, W.S., Hillebrand, H., Ngai, J.T., Seabloom, E.W., Shurin, J.B., Smith, J.E., 2007. Global analysis of nitrogen and phosphorus limitation of primary producers in freshwater, marine and terrestrial ecosystems. *Ecol. Lett.* 10, 1135–1142.
- Fraser, T., Lynch, D.H., Entz, M.H., Dunfield, K.E., 2015. Linking alkaline phosphatase activity with bacterial *phoD* gene abundance in soil from a long-term management trial. *Geoderma* 257–258, 115–122 (in this volume).
- Giles, C.D., Cade-Menun, B.J., Liu, C.W., Hill, J.E., 2015. The short-term transport and transformation of phosphorus species in a saturated soil following poultry manure amendment and leaching. *Geoderma* 257–258, 134–141 (in this volume).
- Haygarth, P.M., Condron, L.M., Heathwaite, A.L., Turner, B.L., Harris, G.P., 2005. The phosphorus transfer continuum: linking source to impact with an interdisciplinary and multi-scaled approach. *Sci. Total Environ.* 344, 5–14.
- Izquierdo, J.E., Houlton, B.Z., van Huysen, T.L., 2013. Evidence for progressive phosphorus limitation over long-term ecosystem development: examination of a biogeochemical paradigm. *Plant Soil* 367, 135–147.
- Jaisi, D.P., Blake, R.E., 2014. Advances in using oxygen isotope ratios of phosphate to understand phosphorus cycling in the environment. *Adv. Agron.* 125, 1–53.
- Jørgensen, C., Inglett, K.S., Jensen, H.S., Reitzel, K., Reddy, K.R., 2015a. Characterization of biogenic phosphorus in outflow water from constructed wetlands. *Geoderma* 257–258, 58–66 (in this volume).
- Jørgensen, C., Turner, B.L., Reitzel, K., 2015b. Identification of inositol hexakisphosphate binding sites in soils by selective extraction and solution  $^{31}\text{P}$  NMR spectroscopy. *Geoderma* 257–258, 22–28 (in this volume).
- Lambers, H., Shane, M.W., Cramer, M.D., Pearse, S.J., Veneklaas, E.J., 2006. Root structure and functioning for efficient acquisition of phosphorus: matching morphological and physiological traits. *Ann. Bot.* 98, 693–713.
- McDowell, R.W., Cade-Menun, B., Stewart, I., 2007. Organic phosphorus speciation and pedogenesis: analysis by solution  $^{31}\text{P}$  nuclear magnetic resonance spectroscopy. *Eur. J. Soil Sci.* 58, 1348–1357.
- McLaren, T.I., Smernik, R.J., Simpson, R.J., McLaughlin, M.J., McBeath, T.M., Guppy, C.N., Richardson, A.E., 2015. Spectral sensitivity of solution  $^{31}\text{P}$  NMR spectroscopy is improved by narrowing the soil to solution ratio to 1:4 for pasture soils of low organic P content. *Geoderma* 257–258, 48–57 (in this volume).
- McLaughlin, K., Paytan, A., Kendall, C., Silva, S., 2006. Oxygen isotopes of phosphatic compounds – application for marine particulate matter, sediments and soils. *Mar. Chem.* 98, 148–155.
- Nesper, M., Bünemann, E.K., Fonte, S.J., Rao, I.M., Velásquez, J.E., Ramirez, B., Hegglin, D., Frossard, E., Oberson, A., 2015. Pasture degradation decreases organic P content of tropical soils due to soil structural decline. *Geoderma* 257–258, 123–133 (in this volume).
- Peltzer, D.A., Wardle, D.A., Allison, V.J., Baisden, W.T., Bardgett, R.D., Chadwick, O.A., Condron, L.M., Parfitt, R.L., Porder, S., Richardson, S.J., Turner, B.L., Vitousek, P.M., Walker, J., Walker, L.R., 2010. Understanding ecosystem retrogression. *Ecol. Monogr.* 80, 509–529.
- Randriamanantsoa, L., Frossard, E., Oberson, A., Bünemann, E.K., 2015. Gross organic phosphorus mineralization rates can be assessed in a Ferralsol using an isotopic dilution method. *Geoderma* 257–258, 86–93 (in this volume).
- Roberts, K., Defforey, D., Turner, B.L., Condron, L.M., Peek, S., Silva, S., Kendall, C., Paytan, A., 2015. Oxygen isotopes of phosphate and soil phosphorus cycling across a 6,500 year chronosequence under lowland temperate rainforest. *Geoderma* 257–258, 14–21 (in this volume).
- Sharpley, A.N., Bergström, L., Aronsson, H., Bechmann, M., Bolster, C.H., Börling, K., Djodjic, F., Jarvie, H.P., Schoumans, O.F., Stamm, C., 2015. Future agriculture with minimized phosphorus losses to waters: research needs and direction. *Ambio* 44, 163–179.
- Spears, B.M., May, L., 2015. Long-term homeostasis of filterable un-reactive phosphorus in a shallow eutrophic lake following a significant reduction in catchment load. *Geoderma* 257–258, 78–85 (in this volume).
- Stutter, M.I., Shand, C.A., George, T.S., Blackwell, M.S.A., Bol, R., MacKay, R.L., Richardson, A.E., Condron, L.M., Turner, B.L., Haygarth, P.M., 2012. Recovering phosphorus from soil: a root solution? *Environ. Sci. Technol.* 46, 1977–1978.
- Stutter, M.I., Shand, C.A., George, T.S., Blackwell, M.S.A., Dixon, L., Bol, R., MacKay, R.L., Richardson, A.E., Condron, L.M., Haygarth, P.M., 2015. Land use and soil factors affecting accumulation of phosphorus species in temperate soils. *Geoderma* 257–258, 29–39 (in this volume).
- Tamburini, F., Pfahler, V., Bünemann, E.K., Guelland, K., Bernasconi, S.M., Frossard, E., 2012. Oxygen isotopes unravel the role of microorganisms in phosphate cycling in soils. *Environ. Sci. Technol.* 46, 5956–5962.
- Tamburini, F., Pfahler, V., von Sperber, C., Frossard, E., Bernasconi, S.M., 2014. Oxygen isotopes for unraveling phosphorus transformations in the soil–plant system: a review. *Soil Sci. Soc. Am. J.* 78, 38–46.
- Turner, B.L., Haygarth, P.M., 2000. Phosphorus forms and concentrations in leachate under four grassland soil types. *Soil Sci. Soc. Am. J.* 64, 1090–1099.
- Turner, B.L., Frossard, E., Baldwin, D.S. (Eds.), 2005. *Organic Phosphorus in the Environment*. CAB International, Wallingford, UK.
- Turner, B.L., Condron, L.M., Richardson, S.J., Peltzer, D.A., Allison, V.J., 2007. Soil organic phosphorus transformations during pedogenesis. *Ecosystems* 10, 1166–1181.
- Turner, B.L., Cheesman, A.W., Godage, H.Y., Riley, A.M., Potter, B.V.L., 2012. Determination of *neo*- and *D-chiro*-inositol hexakisphosphate in soils by solution  $^{31}\text{P}$  NMR spectroscopy. *Environ. Sci. Technol.* 46, 4994–5002.
- Vestergren, J., Vincent, A.G., Jansson, M., Persson, P., Ilstedt, U., Gröbner, G., Giesler, R., Schleucher, J., 2012. High-resolution characterization of organic phosphorus in soil extracts using 2D  $^1\text{H}$ – $^{31}\text{P}$  NMR correlation spectroscopy. *Environ. Sci. Technol.* 46, 3950–3956.
- Vincent, A., Vestergren, J., Gröbner, G., Persson, P., Schleucher, J., Giesler, R., 2013. Soil organic phosphorus transformations in a boreal forest chronosequence. *Plant Soil* 367, 149–162.
- Waithaisong, K., Robin, A., Martin, A., Clairotte, M., Villeneuve, M., Plassard, C., 2015. Quantification of organic P and low-molecular-weight organic acids in Ferralsol soil extracts by ion chromatography. *Geoderma* 257–258, 94–101 (in this volume).
- Walker, T.W., Syers, J.K., 1976. The fate of phosphorus during pedogenesis. *Geoderma* 15, 1–19.
- Whitton, B.A., Al-Shehri, A.M., Ellwood, N.T., Turner, B.L., 2005. Ecological aspects of phosphatase activity in cyanobacteria, eukaryotic algae and bryophytes. *Organic Phosphorus in the Environment*. CAB International, Wallingford, UK, pp. 205–241.

Benjamin L. Turner

Smithsonian Tropical Research Institute, Apartado 0843-03092, Balboa,  
Ancon, Panama

Corresponding author.

E-mail address: TurnerBL@si.edu.

Alexander W. Cheesman

College of Marine and Environmental Sciences, James Cook University,  
Cairns, Queensland 4878, Australia

Leo M. Condron

Faculty of Agriculture and Life Sciences, PO Box 85084, Lincoln University,  
Lincoln 7647, Christchurch, New Zealand

Kasper Reitzel

Institute of Biology, University of Southern Denmark, Campusvej 55, DK-  
5230 Odense M, Denmark

Alan E. Richardson

CSIRO Agriculture, PO Box 1600, Canberra, Australian Capital Territory  
2601, Australia