1. Phosphorus Concentrations in Environmental Samples

1.1 Binding forms of phosphorus

1.1.1 P binding forms in soils

Dana Zimmer, Karen Baumann

Even if the total element concentrations should always be determined in environmental samples, the bioavailability or binding form of an element is very often of particular interest. Therefore, different wet-chemical and spectroscopic methods exist to determine the phosphorus forms in environmental samples.

An overview of P binding forms in soils as well as restrictions and difficulties in determination is presented by Cade-Menun and Liu (2013) and is briefly presented here:

In soils, P occurs as organically and inorganically bound P. Inorganic P forms are **orthophosphates**, **pyrophosphates** and **polyphosphates**. At natural pH values in soils, **orthophosphates** exist as **$H_2PO_4^-$** or **HPO_4^{2-}**. **Polyphosphates** are **chains of orthophosphates** with a length of at least two and up to more than 100 orthophosphate groups (**pyrophosphate**). Organic P is subdivided into **orthophosphate monoesters**, **orthophosphate diesters** and **phosphonates**, based on binding of P to C (see also Turner et al 2005). The general structure of the **orthophosphate monoesters** is **$ROPO_3^{2-}$** (with R being an organic residue), with **one orthophosphate per C**. They include sugar phosphates (e.g. glucose 6-phosphate), mononucleotides and inositol phosphates. **Orthophosphate diesters** [**$R1O(R2O)PO^{2-}$**, with R1 and R2 being C-residues] have **two C per orthophosphate**. This includes nucleic acids, phospholipids and lipoteichoic acids. **Phosphonates** are differentiated from other organic P forms because they have a **direct C-P-bond** (no ester bond via O). Their general structure is **$RP(O)(OH)_2$** and includes 2-aminoethylphosphonic acid (AEP), antibiotics such as Fosfomycin and agrochemicals such as the herbicide glyphosate. **Organic polyphosphates** such as nicotinamide adenosine dinucleotide phosphate (NADP) and adenosine triphosphate (ATP) **contain both monoesters and polyphosphate groups**.

There are different methods for characterising P in soils such as wet-chemical (e.g. sequential extractions (e.g. Hedley et al. 1982)) and single extractions, which try to characterise different P binding forms, different bioavailability/P-binding (e.g. DL-extract, oxalate-extract) but also spectroscopic methods (e.g. ^{31}P-NMR), which determine the P binding forms directly. Wet-chemical methods like the sequential P extraction are operationally defined (see also Bacon and Davidson 2008, Rennert 2019) and do not represent the true binding forms in soil. The extracted P pools base on solubility of P compounds in the extracting agents. Additionally, the extracting agents can change the binding forms of the element during extraction (see also Bacon and Davidson 2008, Negassa and Leinweber 2009). When interpreting the results of such extractions, such as the double lactate (DL) extract for estimating plant-available P (estimation necessary P for fertilisation), it is preferred to call it "DL-extractable P" instead of "plant available P".

For sequential extraction procedures such as the Hedley fractionations, the extracts are mainly differentiated colorimetrically (e.g. molybdenum blue) by measuring "inorganic P" (P_i) and calculating "organic P" (P_o) as the difference to total P (e.g. by ICP) . These terms are not precise either, since the colorimetric analysis does not determine all inorganic P. Only the orthophosphate P can be determined, which reacts with the colour reagent. Complex inorganic P forms such as pyrophosphates and polyphosphates as well as colloidal P forms cannot react with the colour reagent and are assigned to the organic P pool although they do not contain C (see also Condron and Newman 2011). Conversely, the low pH value of the colour reagent can degrade organic P and polyphosphates to orthophosphates which in turn appear as inorganic P. For these reasons, the terms "molybdate-reactive P" and "non-reactive P" are the more correct terms (Haygarth and Sharpley 2000, Felgentreu et al. 2018).

References

Bacon JR, Davidson CM (2008) Is there a future for sequential chemical extraction? Analyst, 133, 25–46, DOI: 10.1039/b711896a

Cade-Menun B and Liu CW (2013) 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, DOI: 10.2136/sssaj2013.05.0187dgs

Condron LM, Newman S (2011) Revisiting the fundamentals of phosphorus fractionation of sediments and soils. J Soils Sediments 11, 830–840, DOI: 10.1007/s11368-011-0363-2

Felgentreu L, Nausch G, Bitschowsky F, Nausch M, Schulz-Bull D (2018) Colorimetric chemical differentiation and detection of phosphorus in eutrophic and high particulate waters: advantages of a new monitoring approach. Frontiers in Marine Science 5, article 212, DOI: 10.3389/fmars.2018.00212

Haygarth PM, Sharpley AN (2000) Terminology for phosphorus transfer. Environ. Qual. 29, 10–1, DOI: 10.2134/jeq2000.00472425002900010002x

Hedley MJ, Stewart JWB., Chauhan BS (1982) Changes in inorganic and organic soil phosphorus fractions by cultivation practices and by laboratory incubations. Soil Sci. Soc. Am. J. 46, 970-976, DOI: 10.2136/sssaj1982.03615995004600050017x

Negassa W, and Leinweber P (2009) How does the Hedley sequential phosphorus fractionation reflect impacts of land use and management on soil phosphorus: A review. J. Plant Nutr. Soil Sci. 172: 305–325, DOI: 10.1002/jpln.200800223

Rennert T (2019) Wet-chemical extractions to characterise pedogenic Al and Fe species – a critical review. Soil Res 57, 1–16, DOI: 10.1071/SR18299

Turner BL, Cade-Menun BJ, Condron LM, Newman S (2005a) Extraction of soil organic phosphorus. Talanta 66: 294–306, DOI: 10.1016/j.talanta.2004.11.012

For citation: Zimmer D, Baumann K (*year of download*) Chapter 1.1.1 P binding forms in soils (Version 1.0) in Zimmer D, Baumann K, Berthold M, Schumann R: Handbook on the Selection of Methods for Digestion and Determination of Total Phosphorus in Environmental Samples. DOI: 10.12754/misc-2020-0001