2. Selection of Method

2.4 Effects of drying and storage on P binding forms in environmental samples

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After sampling, environmental samples such as sediments and soils have to be prepared (and stored) before using them for analysis. The way of sample preparation affects the binding forms and extractability of P in the samples. Generally, effects of preparation (e.g. drying) and storage are more pronounced for wet samples with suboxic redox potential and/or higher percentages of organic matter (e.g. digestates, sewage sludge, peat soils, water-rich and/or suboxic, organic-rich sediments, see chapter 2.3) than for relatively dry samples such as from terrestrial mineral soils (e.g. Ajiboye et al. 2004, Bayens et al. 2003, Qi et al. 2014, Rapin et al. 1986, Styles and Coxon 2006).

Potential changes of P forms in solid samples

Generally, the following opportunities are possible for preparation (points (1) to (4)) and storage (points (5) to (6)) of relatively solid samples such as soils:

(1) Usage in naturally wet state according to the redox potential of the sample (if anaerobe under N_2-protective atmosphere , if aerobe in air)
(2) Drying of samples in the air at room temperature
(3) Drying of samples in drying oven (at 40 °, 60 ° or 105 °C)
(4) Lyophilisation
(5) Storage at room temperature after drying
(6) Storage cooled or frozen in wet state

Traditionally, soil samples are dried in the air or in a drying oven (mostly 60 °C) and sieved < 2 mm (fine soil). If the equipment is available, the samples can also be lyophilised. In different experiments, it was verified that **drying**, irrelevant if in a drying oven or by lyophilisation, **and re-wetting** for extraction can shift the P concentrations between P fractions and also change the totally extractable P in comparison to naturally wet samples (Ajiboye et al. 2004, Condron and Newman 2011, Dail et al. 2007, Schlichting and Leinweber 2002, Styles and Coxon 2006, Xu et al. 2011).

It is supposed that the **changed extractability** of dried samples is caused by a **changed particle size** by sieving and grinding of the dried samples (e.g. breaking down of aggregates, increase of surface area), and by microbial processes/transformations during drying (Condron and Newman 2011, Jager and Bruins 1975, Schlichting and Leinweber 2002). Additionally, drying can break down organic substances and cause a lysis of microbial cells releasing P and subsequently changing the available and extractable percentage of P (Khan et al. 2019, Sparling et al. 1985, Srivastava 1998, Turner and Haygarth 2001). Such drying effects are more pronounced in soil samples with a higher percentage of organic matter (such as peat soils) than in mineral soil samples (Styles and Coxon 2006).

By drying at 60 °C, **aging** of **poor crystalline Fe (hydr)oxides** is strengthened, that means that their crystallinity increases (Landa and Gast 1973). Already at 50 °C ferrihydrite is transformed into better crystalline goethite and hematite (Das et al. 2011). This might be the explanation why the percentage of P in the NaOH fraction decreases in sequential extractions of sewage sludge, liquid manure and suchlike, since NaOH mainly extracts P from Fe oxides and organic substances (Ajiboye et al. 2004, Dail et al. 2007). Additionally, the oxidation of anaerobic sediments increases the **crystallinity of Fe and Mn oxides**. For this reason, the percentage of poorer crystallin oxides (stronger binding partners for P and other elements) is shifted to more crystalline oxides, which are weaker binding partners for P (Bordas and Bourg 1998, Rapin et al. 1986). If S is a binding partner in anaerobe samples, the oxidation of the samples and thereby the **oxidation of sulfides** to sulfate can change the bioavailability of S-bound elements as well (Rapin et al. 1986 and chapter 1.1 and 2.3). High S and N concentrations have to be considered, mainly in swine manure, because both can **outgas as H_2S respectively NH_4-N** by oxidation (and drying) and therefore affect P binding forms.

The usage of **naturally wet samples** can be problematic as well, since without sieving the soil samples, **roots** and **soil animals** are in the samples. Their removal is especially complicated for organic rich soil samples because they cannot easily be distinguished from soil matrix (Condron and Newman 2011). For this reason, Condron and Newman (2011) suggest sieving of naturally wet soil or sediment samples through 6 to 10 mm sieves for the removal of coarse material such as stones, roots and mussel shells. Such sample preparation and usage of samples in the naturally wet state can be especially advantageous for the analysis of

potential hotspots such as the rhizosphere (chapter 1.2 and Feng et al. 2005). If samples were taken in a reductive state and **redox-sensitive P forms** (e.g. Fe-P) have to be analysed (Condron and Newman 2011), the redox potential has to be maintained during preparation. This can be realised by a **N_2 protective atmosphere** in **a glove box**.

If samples (irrelevant if in reductive or oxidative state) are **stored** in a **wet state** until analysis, this should be realised only for some days (e.g. at 4 °C in a refrigerator). For a longer time, samples should be frozen (if necessary, by maintenance of redox potential) to reduce microbial transformations (Rapin et al. 1986). In anaerobe samples small changes of binding forms are caused by the freezing of naturally wet samples (Rapin et al. 1986). Oven drying of sewage sludge and liquid manure can cause changes in binding forms and extractability in comparison to frozen and wet samples (Ajiboye et al. 2004, Dail et al. 2007). Besides changes of binding forms, especially for peat samples it has to be considered that drying changes the **wettability** of the samples. That means that a re-wetting of peat samples for extraction can be very problematic.

Recommendations: In order to minimise the effects of drying on P binding forms, environmental samples should either be analysed in naturally wet state (if necessary sieved, parallel dry matter determination) or drying should be as gently and fast (decrease microbial transformations) as possible. Lyophilisation or drying at room temperature (preferably small sample amounts for fast drying) have to be preferred to drying in the drying oven at > 40 °C. Since the effects of drying are more pronounced for samples with high percentages of organic matter, such as peat samples, drying effects should be considered especially for such samples and subsequently whole sample preparations should be adapted as well (use naturally wet or lyophilised samples). Grinding of samples increases homogeneity of samples (potentially lower standard deviation) but also changes extractable P percentages by an increase of the surface area and a break down of aggregates. Therefore, it has to be decided on the basis of scientific question and potential analyses, if grinded or only sieved samples are used.

There is specific expertise about the various environmental samples in the individual working groups of the P-Campus. The working groups Soil Science and Agronomy (both AUF, University of Rostock) especially have

expertise in analytics of samples of **soils, plants, biochar** and **biomass ashes**. The expertise in sampling and **preparation of water and sediment samples** can be found in the working groups of the IOW, the working group Applied Ecology & Phycology (Institute of Biosciences, University of Rostock), especially there also on the Biological Station Zingst, and in the working group Soil Physics (AUF, University of Rostock).

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For citation: Zimmer D, Baumann K (*year of download*) Chapter 2.4 Effects of Drying and Storage on P Binding Forms in Environmental Samples (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