Fourier-transform Infrared (FTIR) Spectroscopy Analysis of Seven Wisconsin Biosolids

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Abstract

This research explores the use of Fourier-transform infrared (FTIR) spectroscopy to better understand the phosphorus characteristics of biosolids. Biosolids from five Wisconsin wastewater treatment plants (Madison, Delafield, East Troy, Mukwonago, and Fort Atkinson) were obtained. From the Madison location, several samples were obtained from different parts of the treatment process – cake, final liquid (labeled as Metrogro), and composted biosolids. FTIR spectra from these samples were compared to P standards to try to identify dominant P species. Several FTIR methods were investigated: attenuated total reflectance (ATR), NaCl salt plates with mineral oil, and pressed KBr pellets. These initial tests indicate that KBr will likely be the most useful. The P standards indicated two main regions where there was a slight but fairly consistent difference between inorganic and organic species in the position of IR peaks.

In the future, comparing the FTIR and ^{31}P NMR results alongside chemical extractions will provide both qualitative and quantitative information that helps describe the inorganic and organic P forms and species in biosolids that have gone through different treatment/production processes. This information could be used to advise farmers applying these biosolids to their fields.

Introduction

- Background
  - Biosolids are land-applied in order to supply nutrients to the soil and to recycle waste.
  - Waste characterization provides insights that allow safe and effective use of various recycled products and wastes.
  - In order to protect surface water quality, biosolid applications in many places have been limited to apply only the quantities that provide the nitrogen and/or phosphorus needed by a crop.
- What are the issues?
  - Eutrophication is accelerated by excess P entering freshwater, and appropriately managing biosolids and other soil amendments can reduce P losses.
  - Differences in P availability from different types of biosolids generated at treatment plants are not well understood, and currently, biosolid differences are not incorporated into the Wisconsin Phosphorus Index.[1]
- Goal
  - To investigate a rapid and simple FTIR method to broadly characterize the species of phosphorus and the ratios of their abundance to predict runoff risk and inform land application rates.

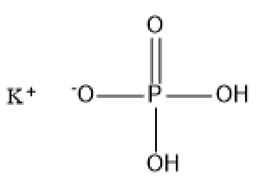
NOTE: All spectra are shown as transmittance—so peaks are pointed down.

Materials

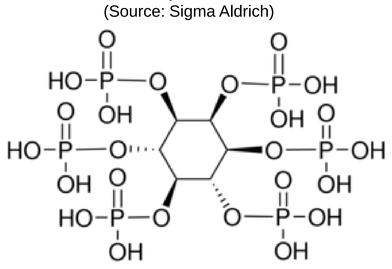
- Bruker (27 Tensor) used for KBr and salt plates
- Mattson (4020 Galaxy FTIR) used for ATR
- IR-grade (>99%) Potassium Bromide (KBr)
- Pellet press with two bolts
- Two NaCl salt plates with mineral oil
- Biosolids from five wastewater treatment plants listed in the abstract
- Inorganic Phosphates
  - KH_2PO_4
  - Na_2HPO_4
  - $CaHPO_4$
  - $NH_4H_2PO_4$
- Organic Phosphates
  - 50% Phytic acid
  - Ribonucleic acid (RNA)
  - D-Glucose 6-phosphate
  - 2-Aminoethyl phosphonic acid
  - Adenosine 5'-triphosphate

Example P Structures

Potassium Phosphate Monobasic
KH_2PO_4



Phytic Acid
(Source: Sigma Aldrich)



Acknowledgments

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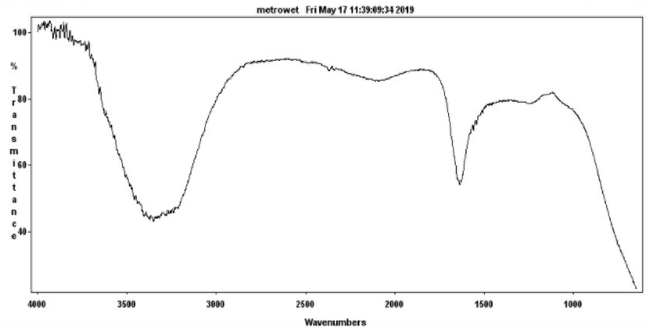
FTIR Methods Comparison

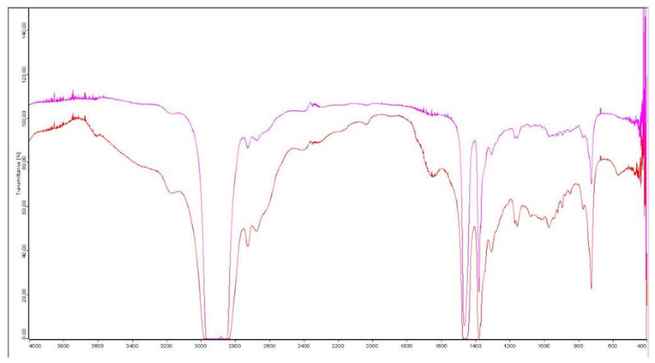
Figure 1. Metrogro via (a) ATR , (b) mineral oil, and (c) KBr

a



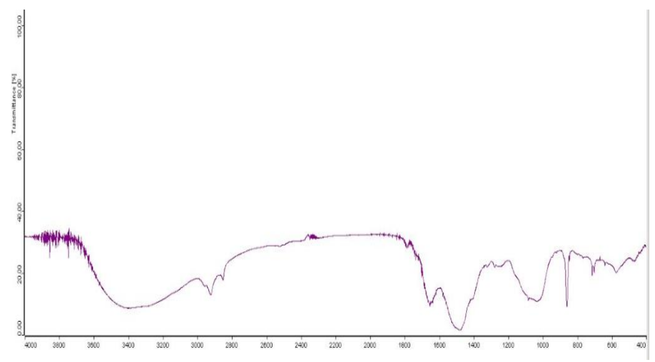
Attenuated Total Reflectance FTIR was the fastest method. The biosolids were placed on top of the ATR crystal and pressed down using a small metal cylinder. Minimal sample preparation is required. However, the ATR spectra seemed to mask certain peaks, and gave less information than the FTIR of KBr pellets.

b



Our second method of FTIR involving salt plates required a greater amount of sample prep. Each biosolid sample was placed on a salt plate with a small layer (2-3 drops) of mineral oil. The sample was sandwiched with another plate and placed into the Bruker to run the FTIR. Shown on the left are spectra of the blank sample with pure mineral oil (pink) and the sample containing Metrogro and mineral oil (red). The noise produced by bond vibrations in mineral oil overpowers the sample peaks, making spectra very difficult to interpret.

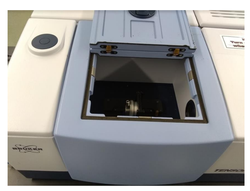
c



The third method used KBr pellets. Biosolid samples and KBr were mixed in a 1:50 ratio by mass. Then, the sample and KBr were ground with a mortar and pestle. The powder was transferred to a metal press and compressed into a translucent pellet using two bolts and wrenches tightening the bolt tips together. The bolts were removed, and the press placed in the FTIR. Sixteen scans are averaged for the spectra shown.

This method gave the most spectral information and was chosen for subsequent analysis.

KBr pellet press



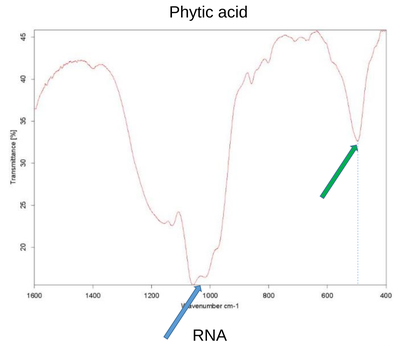
Bruker Tensor 27 (above pictures) used for the second and third methods

FTIR Pure Compounds Comparison

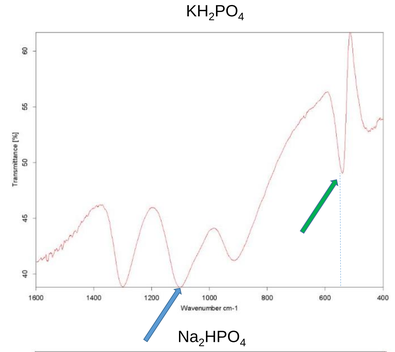
Figure 2. Example organic (left) and inorganic (right) P compounds

Note that the blue arrow points toward P-O asymmetric stretching vibrations, green arrow points toward O-P-O bending

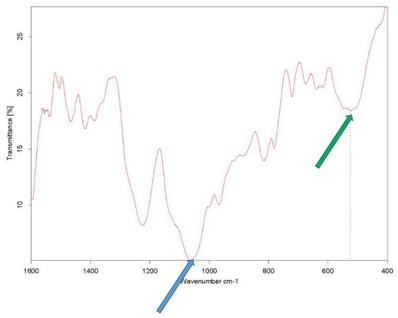
Phytic acid



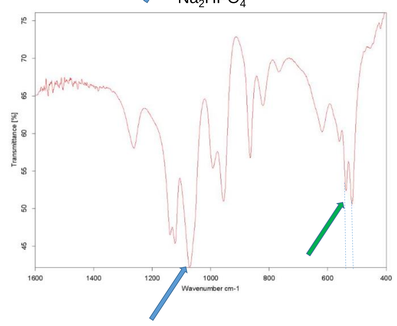
KH_2PO_4



RNA



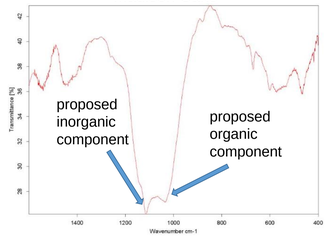
Na_2HPO_4



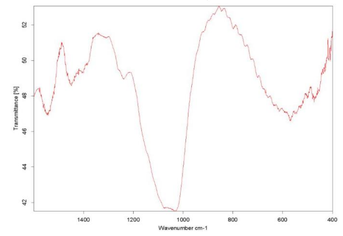
Biosolids Comparison via KBR

Figure 3. Plots of individual biosolids (upper plots) and spiked Metrogro (lower plot)

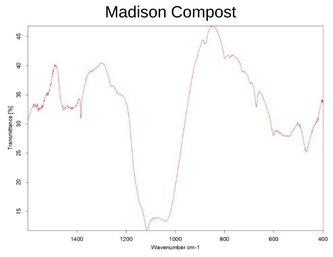
Madison Cake



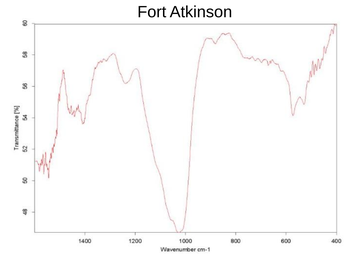
East Troy



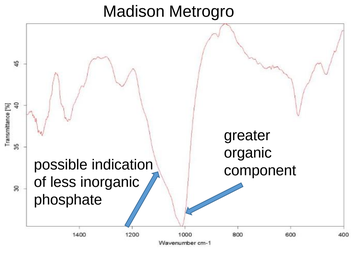
Madison Compost



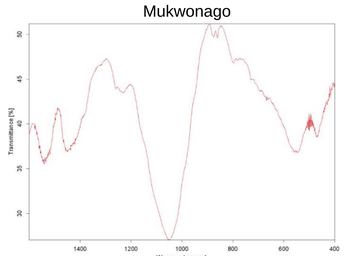
Fort Atkinson



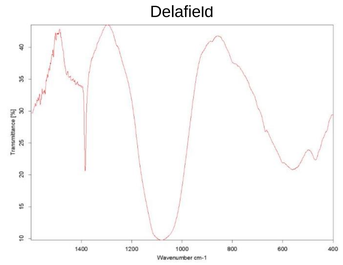
Madison Metrogro



Mukwonago

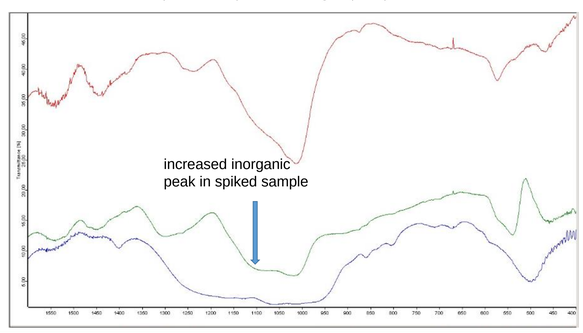


Delafield



Spiked Biosolids

Pure Metrogro (red), Potassium Dihydrogen Phosphate-spiked Metrogro (green), and Phytic acid-spiked Metrogro (blue)



Further Discussion

The two major peaks that appeared in all spectra were the O-P-O deformational bending vibrations (typically 500-670cm^{-1})[2] and the P-O asymmetric stretching vibrations (typically 1010-1080 cm^{-1}).[2] Peaks of phosphates bound to organic groups appeared to shift to a lower frequency (measured in cm^{-1})(see organic/inorganic FTIR comparison on the left). Out-of-phase P-O-C stretches from 920-1088 were observed near the P-O asymmetric vibrations in some organic samples.[2] The ratios of these peaks could indicate relative amounts of inorganic and organic phosphates. Much care (and a healthy dose of humility) and should be exercised in labeling peaks, since it is often unclear as to which peak corresponds to each bond vibration.[3,4]

Conclusion & Future Work

- Of the three FTIR methods investigated, the KBr-pellet method provided the clearest spectra and greatest amount of information.
- Our spectral plots all involved transmittance, in which peaks are negative. For quantitative work on inorganic/organic ratios, absorbance on the y-axis would be more useful, as the peaks would then scale linearly (transmittance involves a logarithmic relationship).
- Work has already begun to correlate the FTIR data with ^{31}P-NMR analysis.
- Based on inorganic/organic peaks, it may be possible to develop a fast, effective IR method which can scan for phosphate species in biosolids – this information can be used to inform land application rates to minimize environmental risk of phosphorus runoff.

References

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2. Jastrzebski, W, Sitarz, M, Rokita, M, Bułat, K. (2011) Infrared spectroscopy of different phosphates structures, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 79:722–727.
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