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Ogunremi, T.

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X-ray Absorption Spectroscopic analysis of raw and processed hog manure

Toju Ogunremi[1], Jeff Cutler[1], Colleen Christensen[2] and Clayton Sparks[3]

[1]Canadian Light Source Inc., 101 Perimeter Road, Saskatoon. SK. S7N 0X4. [2]Feeds Innovation Institute, College of Agriculture & Bioresources, University of Saskatchewan. [3]Clear-Green Environmental Inc., 208-111 Research Dr. Saskatoon. SK. S7N 3R2.

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Abstract

Anaerobic digestion technology is a process that allows livestock producers to generate electricity and heat by digesting manure. Clear-Green Environmental Inc. uses this process to make biogas from hog manure. Raw manure is pumped into a digester where it is digested anaerobically by mesophyllic bacteria. The digested manure is transferred to a dual purpose tank (DPT) which serves as a secondary digester from which the biogas is collected. Carbon is the only nutrient consumed in the digester and the by-product of this process is used in fertilizers. It has not been shown if there is a change in speciation of key elements like nitrogen and phosphorus upon digestion. X-ray Absorption Near Edge Structure spectroscopy (XANES) was used to characterize the nitrogen, phosphorous and iron found in raw and digested hog manure. Two detection modes, Total Electron Yield (TEY) and Fluorescence Yield (FY) were used for data collection. Raw hog manure contained organic nitrogen, phosphates and ferrous iron. Digested hog manure contained organic and inorganic nitrogen, phosphates as well as a mix of ferrous and ferric iron.

Introduction

Hog manure from a storage tank is pumped through a heat exchanger into a mesophyllic anaerobic biodigester where it is continually stirred and held at 37ºC for 20-21 days. In these warm conditions, bacteria present begin to digest carbon, most likely the feed carbon not used in the animal digestive system, which has found its way into the manure stream. The first stage of anaerobic digestion called hydrolysis involves hydrolytic bacteria breaking down organic compounds (carbohydrates, proteins and fats) into fatty acids, alcohol, carbon dioxide, hydrogen, ammonia and sulphides (1). The second stage involves acetogenic bacteria further digesting or breaking down the products from the first stage into acetic acid, hydrogen and carbon dioxide. Following this, methanogenic bacteria convert these products into biogas (1). This process makes the anaerobic digester a complex and changing environment. The digested manure is transferred to a Dual Purpose Tank (DPT) which serves as a secondary digester and is also where the biogas (90% of which is composed of methane and carbon dioxide) is collected. When digestion is complete, the digestate is transferred into a manure lagoon.

X-ray absorption spectroscopy (XAS) is a technique capable of probing *in-situ* the speciation of a particular element in a complex sample in any physical state. XAS provides a unique structural probe not duplicated by other methods. The structural information provided by XAS includes average interatomic distances, the number and chemical identities of neighbors within 5 to 6 Å of a selected atom species as well as the speciation or oxidation state of elements of interest (2). An important advantage of XAS is its application to the non-destructive analysis of complex heterogeneous samples, including manure, whole soils or sediments. Another advantage of XAS is its element specificity. The sensitivity of XAS can be at the hundreds of ppm level of an element, thus it can be used to study the structural environment of an element at trace levels (<2000 ppm) in a chemically complex matrix.

Materials and Methods

Three types of hog manure samples were provided by Clear-Green Inc. These were raw hog manure, partially digested hog manure (digester contents) and digested hog manure (DPT contents). All samples were individually mixed and then filtered using a vacuum pump. The filtrates were dried in a vacuum oven at 50˚C for 36 hours. Dried samples were crushed with a mortar and pestle as finely as possible and evenly mixed. All reference compounds that were not a fine powder were also crushed and mixed with a mortar and pestle.

For hard x-ray analysis (iron K-edge), manure samples were loaded in Teflon sample holders and sealed with Kapton tape. For soft x-ray analysis (nitrogen K-edge, phosphorus K- and L-edges and iron L-edge), the dried samples and reference compounds were mounted on double-sided carbon tape for data collection. The prepared samples were placed in an analysis chamber which was maintained at high vacuum. Two complimentary modes of detection, Total Electron Yield (TEY) and Fluorescence Yield (FY) were used for collection of the XANES spectra. A minimum of two scans per sample was collected. To avoid beam damage, two different spots on each sample were scanned.

Nitrogen K-edge spectra was collected at the Spherical Grating Monochromator (SGM) beamline, 11-ID.1 at the Canadian Light Source Inc. (CLS). The storage ring was operating at 2.9 GeV with a current of 200 mA. The entrance and exit slits were set at 5 and 25 microns respectively giving a photon energy resolving power of ~10,000. The samples were scanned from 395 – 414 eV using the low energy grating and a step size of 0.1 eV. The beamline was calibrated using ammonium chloride with a nitrogen peak position at 407 eV (3).

Phosphorus K-edge data (1s electrons) was collected at the Canadian Synchrotron Radiation Facility (CSRF) located at the Synchrotron Radiation Center (SRC) at the University of Wisconsin using the Canadian Double Crystal Monochromator (DCM) beamline with InSb (111) crystals. The storage ring was operating at 800 MeV and a fill current of 190 mA. Samples were scanned from 2130-2190 eV with a step size of 0.25 eV. Phosphorus $L_{II,III}$-edge data (2p electrons) was collected on the Variable Line Spacing-Plane Grating Monochromator (VLS-PGM) beamline, 11-ID.2 at the CLS. The storage ring was operating at 2.9 GeV with a current of 200 mA. The samples were scanned from 160-130 eV with a step size of -0.1eV. The entrance and exit slits were both set at 100 microns. Both beamlines were calibrated using sodium pyrophosphate ($Na_4P_2O_7$) reference compound with peak positions at 2152.4 eV and 134.93 eV (4) at the K- and L-edges respectively.

Iron K-edge data was collected at beamline X-11B at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory, New York. The storage ring was operating at 2.8 GeV with a current of 200mA. The entrance slit was set at 1x16mm. Reference data was collected in transmission mode whereas the manure sample spectra were collected in FY mode using a Lytle fluorescence detector. Data was calibrated standard iron reference foil. The Iron $L_{II,III}$-edge data were collected at the SGM beamline at the CLS. The storage ring was operating at 2.9 GeV with a current of 200mA. Samples were scanned from 700 – 740eV with a step size of 0.1eV. Data was calibrated using iron (III) oxide with peak position at 710.2 eV (5, 6).

All data were processed using aXis 2000 (March 2005 version, Carl Zimba, Adam & Peter Hitchcock). Individual processed data were compiled into stacked plots using ORIGIN 7.5.

Results and Discussion

Figure 1 shows the N K-edge data for all samples and reference compounds run. The raw manure sample showed a single peak (I) with peak maxima at 402.8 eV. This peak position suggests the presence of an organic form of nitrogen similar to a peptide/amide like bovine albumin or another organic N source. As the raw manure has not been exposed to the digestion process it appears that the unmodified manure contains only organic sources of nitrogen. Peak I can also be observed in the digested manure (Digester and DPT) samples, however, a second peak (II) with peak maxima at 406.85 eV is evident. Peak II for the digester and DPT manure samples has a broad shape with a profile similar to of ammonium chloride. This suggests that peak II is an ammonium salt similar to ammonium chloride indicating the presence of an inorganic N species in digested manure. This shows that the process of bacterial digestion causes the conversion of some organic nitrogen to inorganic form.

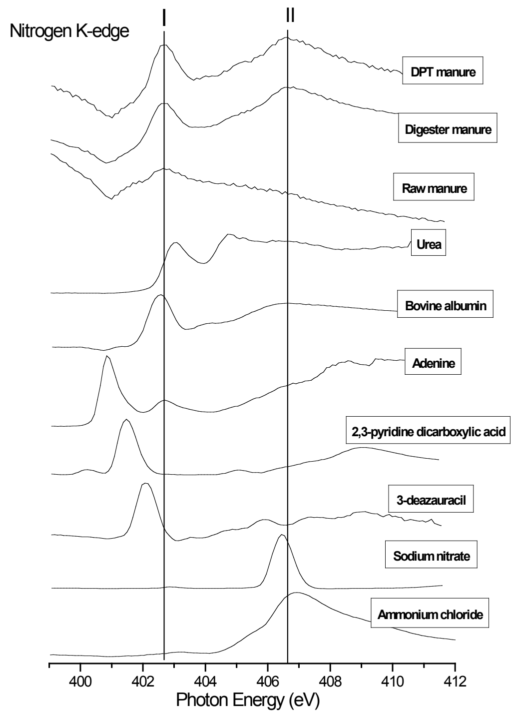

Figure 1. XANES nitrogen K-edge TEY spectra for raw and digested hog manure samples and reference compounds.

A pre-edge peak (line I) is present in the P L-edge spectra of all manure samples (fig 2) at ~136 eV. This feature is also seen in calcium dihydrogen phosphate, sodium hexametaphosphate and sodium acid pyrophosphate spectrum. Apart from this pre-edge peak, the rest of the spectral profiles of these reference compounds are different from those of the manure samples. The spectra of all 3 manure samples appear to be similar. All samples appear to contain phosphates and more reference compounds will need to be run to allow for more specific determination of phosphorus species.

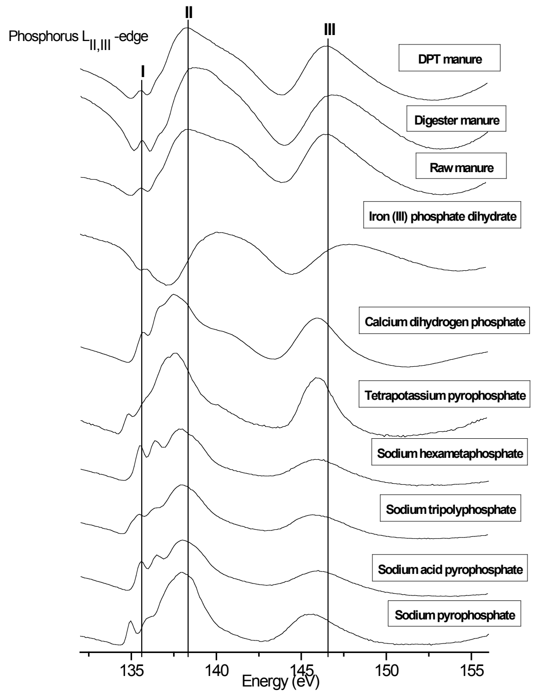

Figure 2. XANES Phosphorus L-edge TEY spectra for hog manure samples and reference compounds. Spectra are background subtracted to allow clearer comparison of spectral features.

The iron L-edge XANES spectra (fig 3) for raw manure showed only one peak with the peak position and profile indicating a single oxidation state of iron (ferrous form). Digester and DPT manure spectral profiles show two peaks. The location and profile of these peaks closely resemble that of iron (III) phosphate dihydrate and iron (II, III) oxide spectra indicating the presence of ferric iron species. This suggests the digestion process causes oxidation of some of the iron species in the manure from ferrous to ferric form.

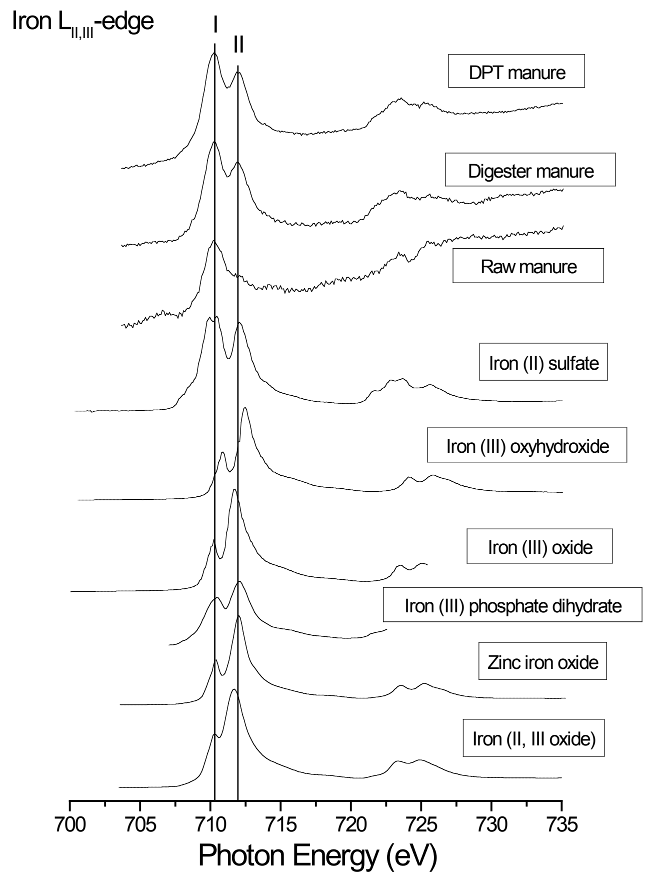

Figure 3. XANES Fe L-edge TEY spectra for hog manure samples and reference compounds.

Conclusions

In summary, application of the synchrotron XANES technique has demonstrated that:

1) Nitrogen in the raw manure sample appeared to be in an organic form. Digested manure from the digester and DPT appear to contain an ammonium salt (inorganic nitrogen) in addition to the organic nitrogen originally present before bacterial digestion. In the Clear-Green digestion process, the manure contents of the Digester and DPT are essentially the same. This will help explain the similarity between these two samples at all the edges investigated in this study.
2) All three manure samples indicate the presence of inorganic phosphates. Phosphates in the raw manure could be bound to calcium, more reference compounds will need to be run to make a more conclusive statement.
3) Iron in raw hog manure appears to be present in ferrous form. Bacterial digestion seems to change the oxidization state producing a mixture of ferrous and ferric forms of iron.

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