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Malley, D.F., B. Trybula, R.D. Ross, and G. Gay. 2000. Evaluating the Use of Near-Infrared Spectroscopy for the Analysis of Biosolids Constituents. Project 99-PUM-6-ET Final Report. Water Environment Research Foundation, Alexandria VA. Document No. D00306WW.

Executive Summary

The application of anaerobically-digested, dewatered municipal sewage sludge, termed biosolids, to agricultural land is a widely-used, cost-effective way of transforming a waste into a resource useful for its plant nutrients and soil conditioning properties. Nevertheless, since they are products of industrial and chemical-based societies, biosolids also contain heavy metals and xenobiotics and, depending upon the treatment process, pathogens.

Increasing public concern about prevention of leaching of nutrients into surface and ground water and accumulation of persistent metals and toxic compounds in soil or crops intensifies the need for environmental monitoring that is accurate, cost-effective, and timely. The cost and the time for conventional laboratory analyses are major constraints on comprehensive monitoring, particularly for materials such as biosolids that do not have appreciable commercial value.

Near-infrared spectroscopy (NIRS) is a 30-year-old technology that can extend conventional monitoring capability significantly. NIRS is molecular spectroscopy, the spectral analysis of intact samples, operating in the wavelength range 780 to 2,500 nm. Substances absorbing light energy in this region are those with covalent bonds between O, H, C, and N and are principally, but not exclusively, organic materials. The technology is used globally for determination of a wide variety of constituents, composition, and functionality in agricultural products, feeds, food, forages, petrochemicals, pharmaceuticals, cosmetics, textiles, polymers, solid wastes, and other materials. Environmental and medical applications are emerging areas.

NIRS extends conventional chemical analytical capability by correlating spectral data with the compositional or functional data from reference analyses on a carefully-selected set of samples - the training set. The process of correlating spectral and conventional data is termed calibration. Once entered into a near-infrared spectrophotometer, calibrations permit the instrument to calculate compositional data from the spectral of future unknown samples of the same type as those in the training set rapidly and inexpensively. The performance of the calibrations in delivering accurate results is monitored by analysing a small proportion of the unknowns by conventional reference methods on an on-going basis. Calibrations are updated as required.

Because it measures intact samples, not only does NIRS require little or no sample preparation, but also it predicts numerous constituents or functions simultaneously and in real time. The instrumentation can be taken to the manufacturing or industrial process, avoiding the time-consuming process of analysing samples in the laboratory. Near-infrared spectroscopy is, thus, not only an analytical tool but also a decision-making tool that can guide how products are used by providing compositional information in a timely manner. The development of mobile NIR instruments for use in the field is expected to extend NIRS capability beyond process monitoring to environmental monitoring.

Although NIRS is most commonly used to predict quantity of organic components of samples, metals may be predicted if they affect the absorption spectrum of water, are bound to spectrally-active substances, or are reliably correlated with spectrally-active substances. For example, metals may be predictable if they are associated with organic matter, oxides, hydroxides, carbonates, or clays that bind or adsorb metals.

The purpose of this study was to explore the feasibility of applying NIRS for the analysis of nutrients and heavy metals in sewage sludge, biosolids, and receiving soil. The samples in the study included sludge from three City of Winnipeg sewage treatment plants (STPs), and from several stages in the treatment process from one plant. This sampling procedure was designed to fulfil a requirement for NIRS of having a range of values for each constituent and to maximise the variability in chemical composition within the training set. Although NIRS analysis of wet, "as is", samples would be most desirable for a monitoring program, dry archived samples were also examined. The analysis of dry samples by NIRS is generally more efficient than for wet samples because constituent concentrations are higher and interference from the strongly absorbing O-H group in water is less. The specific objectives of the study were to:

a. develop and evaluate NIR calibrations for nutrients and metals in four samples:
    i. newly-collected wet sludge from three stages (including biosolids) in the treatment process derived from three STPs (wet sludge)
    ii. dried, archived sewage sludge from three stages in the treatment process derived from three STPs (dry sludge)
    iii. newly-collected soil immediately before and after application of biosolids to agricultural land sampled over a three-month period (field moist soil), and
    iv. dried, archived soil samples from experimental applications of biosolids to agricultural plots during 1992 to 1994 (dry soil)
b. determine errors in the chemical analytical and the NIRS spectral data to better evaluate the success of the calibrations.

Chemical analyses performed on wet sludge samples were percent moisture, percent organic matter, ammonium nitrogen (NH_4-N), total dissolved nitrogen (TDN), suspended N, soluble reactive phosphorous (SRP, essentially PO_4-P), total dissolved P (TDP), suspended P, suspended carbon (C), potassium (K), cadmium (Cd), copper (Cu), chromium (Cr), lead (Pb), nickel (Ni), and zinc (Zn).

A set of dried sludge samples was analyzed for percent organic matter, total Kjeldahl N (TKN), ammonium N (NH_4-N), nitrate N (NO_3-N), phosphate (PO_4-P), K, and sulphate (SO_4-S). A second set was previously analyzed for the heavy metals, Cd, Cr, Cu, Pb, Ni, and Zn.

Field moist soil samples were analyzed for percent moisture, percent organic matter, TKN, NH_4-N, NO_3-N, PO_4-P, K, SO_4-S, Cd, Cr, Cu, Pb, Ni, and Zn. To ensure sufficient range in constituent concentrations, some soil samples were mixed with biosolids in the laboratory. The dried archived soil from the experimental plots was previously analyzed for TKN, NH_3-N, NO_3-N, total P, $NaHCO_3$-extracted P, pH, percent solids, conductivity, and for total and DTPA-extracted Cd, Cr, Cu, Pb, Ni, and Zn. In this study the samples were analyzed for percent organic matter and SO_4-S, and were re-analyzed for TKN.

Near-infrared spectroscopy was performed using a Foss NIRSystems model 6500 scanning visible/near-infrared spectrophotometer (Foss NIRSystems, Inc., Silver Spring Md.) fitted with a standard sample transport or a Rapid Content Sampler (RCA). Software used to operate the instrument and record the spectra as log 1/reflectance at 2 nm intervals was DOS-based near-infrared spectroscopy analysis software (Foss NIRSystems, Inc., Silver Spring Md.). Wet sludge was scanned in a watertight cell with a 2-mm path length from 400 to 2500 nm using the standard sample module. Field moist soil samples were placed in a standard sample cell and scanned from 400 to 2500 nm using the standard sample module.

Dry sludge and soil samples were scanned in borosilicate glass scintillation vials from 1100 to 2500 nm using the RCA.

Calibrations were developed between the spectral data and the reference chemical data separately for each constituent in each of the four types of samples. Calibrations were developed using the step-wise multiple linear regression option of NSAS. The spectral data were pre-treated using a variety of combinations of data smoothing and derivatization.

The success of calibrations was judged according to statistical criteria, including the magnitude of the coefficient of determination, r^2, between predicted values for the constituent and the reference values. A second criterion, termed RPD, was the ratio of the standard deviation of the constituent values to the standard deviation of the residuals, i.e., differences between predicted values and reference values. A third criterion, termed RER, was similar to the RPD, except that the ratio was the range of the constituent values to the standard deviation of the residuals.

Using multivariate analysis software, Unscrambler, principal component analysis of spectral and constituent data provided information on the relationships among samples and among constituents, and provided information on the spectral basis of the prediction for numerous constituents.
Calibrations developed for the wet sludge and biosolids (n = 80) had r^2 values between 0.89 and 0.99 for all constituents. Normally, r^2 values of this magnitude indicate excellent calibrations, but in this case the range of constituent values was large related to the large range in water content of sludges and biosolids. For some of the constituents, either the low or the high constituent values or both were not well-predicted by NIRS. The sludges had high water content (96%-98%) and low constituent values whereas the biosolids had low water content (76%) and high constituent values. Calibrations were repeated for the wet sludges only (n = 60). Good calibrations were developed for percent moisture, percent organic matter, and suspended C with r^2 of 0.89 to 0.95. Calibrations developed for suspended N, Cr, Cu, and Pb were good with r^2 of 0.85 to 0.89. The calibrations for NH_4-N and Cd were useful with r^2 of 0.79 and 0.75, respectively. Calibrations for TDN, total N, suspended P, Ni, and Zn were statistically significant with r^2 of 0.5 to 0.6, but less useful. Soluble reactive P, TDP, and K were not predictable in this set of sludge samples. The sample set of biosolids (n = 20) was too small to perform calibrations. Nevertheless, the calibrations for the set of 80 samples gave predicted values for percent moisture, percent organic matter, NH_4-N, Cd, Cu, Pb, Ni, and Zn that suggested that NIRS may be useful for predicting these constituents in biosolids.

In dry sludges (n = 84), percent organic matter and NH_4-N were predicted successfully with r^2 around 0.90. Phosphate and K were predicted marginally to usefully with r^2 of 0.64 and 0.71, respectively. Sulfate was not predictable. In the second set of dry sludges (n = 101), good calibrations were developed for Cd, Cu, Pb, and Ni with r^2 of 0.79 to 0.85. The calibration for Cr was useful ($r^2 = 0.72$), but that for Zn was marginal ($r^2 = 0.56$).

In the field moist soil (n = 82) amended with biosolids during field application or in the laboratory, good calibrations were developed for TKN, NH_4-N, PO_4-P, Cd, Cu, Cr, Pb, and Zn with r^2 from 0.81 to 0.95. The calibration for percent moisture was useful at $r^2 = 0.72$. Those for NO_3-N, K, SO_4-S, and Ni were marginal with r^2 of 0.44 to 0.52. Percent organic matter was not predictable. For the dry soil (n = 125), results for organic matter and N fractions were better than for the field moist samples, with percent organic matter and TKN predicted with r^2 of 0.91 to 0.98. Calibrations for conductivity and pH were useful with $r^2 \sim 0.70$ but percent solids and SO_4-S were predicted less well with r^2 of 0.41 to 0.52. Nitrate-N was not predictable. Calibrations for total P and for $NaHCO_3$-extractable P were marginal at $r^2 \sim 0.65$. Among the metals, Ni was predicted best with r^2 of 0.87, and Zn was predicted with r^2 of 0.7, but the metals, Cr, Cu, Pb were predicted poorly with r^2 of 0.4 to 0.5. Diethylene triamine pentaacetic acid (DTPA)-extracted metals tended to be predicted more poorly than the total metals, except that a useful calibration with r^2 of 0.73 was developed for DTPA-Cd.

In summary, NIRS analysis of the samples of sludges and biosolids studied here was feasible for measuring most of the N content (i.e., NH_4-N and suspended N), organic matter content expressed as percent organic matter or suspended C, and moisture. It was not useful for the estimation of the other major nutrients, P and K. Among the heavy metals, Cd, Cu, and Pb were measurable by NIRS in the wet samples but results were mixed for Cr and Zn. By drying the samples, some analytical advantage was obtained. Ammonium-N was predicted more precisely and Ni was predictable. In the field moist soils before and after receiving addition of biosolids, NIRS appeared feasible for measuring for the nutrients, total N, NH_4-N, and PO_4-P, but not NO_3-N, K, SO_4-S, or percent organic matter. The heavy metals, Cd, Cu, Cr, Pb, and Zn but not Ni were measurable by NIRS. Drying of the soil conferred some analytical advantages, particularly for the measurement of percent organic matter, and Ni.

This study demonstrated that rapid, simultaneous, real-time, cost-effective monitoring of N, organic matter, moisture, Cu and Pb in “as is” (wet) sewage sludge and biosolids appears feasible using NIRS. More work needs to be done to determine whether Cd, Cr, Ni, and Zn can be predicted with acceptable reliability. Results of this study suggest that the nutrients, P and K will not likely be predictable in sludges with NIRS. More work is required to develop and evaluate NIR calibrations specifically for the biosolids. The technology shows potential as well to estimate N, P, Cd, Cu, Cr, and Pb on field moist soil. This could be useful to evaluate background levels in agricultural slated to receive biosolids additions, and in soils after amendment. Analysis by NIRS of dried sludge, biosolids and soil samples prepared for laboratory analysis could provide information of additional constituents and assist in the selection of samples for labor-intensive laboratory analysis.

This is believed to the first attempt to apply NIRS for the analysis of domestic sewage sludge and biosolids-amended soils. Evidence from this study suggests that NIR technology could replace a proportion of conventional laboratory analysis with a lower cost alternative for the monitoring of N and some heavy metals in biosolids and soils. Moreover, NIRS produces timely analytical results that could alter field operations to modify biosolids application rates, to match biosolids composition and soil properties, and to allow amendment of biosolids with inorganic nutrients to provide a more balanced fertilizer. Reliable, timely data on the composition of biosolids and environmental data on the fate of constituents in biosolids applied to agricultural land may increase the extent of public support for the practice.