Emerging possibilities for near infrared spectroscopy to contribute to environmental analysis

D.F. Malley

PDK Projects, Inc., 365 Wildwood Park, Winnipeg, MB R3T 0E7, Canada

Introduction

Near infrared (NIR) spectroscopy is potentially a powerful and revolutionary technology for environmental analysis. Near infrared technology is supported by a large body of theoretical knowledge and results from applications (Council for NIR Spectroscopy Bibliography of over 15,000 citations). The technique is well developed with easy-to-use, highly dependable instruments, but at the same time it is evolving, particularly with the production of more portable and rapid instruments and more powerful and flexible software. NIR is used globally in numerous industries for commodity analysis. Its desirable features include accuracy, precision, discrimination capacity, speed and adaptability to various operating circumstances, including harsh or hazardous conditions.

This paper (a) examines the unique capabilities of NIR that make it a candidate method for environmental analysis, (b) identifies barriers to the use of NIR and (c) explores several key environmental problems to which NIR can contribute unique analytical capability.

Capabilities of NIR for environmental analysis

Near infrared spectroscopy is largely unknown in the field of environmental chemistry and monitoring, despite the fact that numerous other spectroscopic techniques are widely used (Table 1). Even in soil analysis, where the research literature on NIR extends over four decades, NIR is not yet routinely used.

A number of field instruments exist that are used to continuously monitor various parameters including temperature, pH, conductivity, turbidity, suspended solids, salinity, dissolved O_2, redox potential and humidity. Near infrared spectroscopy shares many of the features of other portable technologies that operate in the field and, in addition, brings unique capability to analyse the compoposition of largely organic substances in and functional properties of samples (Table 2).

Table 1. Some laboratory instrumentation used commonly for environmental analytical chemistry.

Acid-base titrations	Mass spectroscopy
Oxidation–reduction	Atomic absorption spectroscopy
UV-vis spectrophotometry	Gas chromatography
Infrared spectrometry	High performance liquid chromatography
Nuclear magnetic resonance spectroscopy	Electroanalytical methods

Table 2. Features of NIR spectroscopy relevant to environmental analysis.

Portability	Non-destruction of the sample; availability for future analysis; suitability for live material
Speed	Analysis of intact sample matrices
Real-time analysis	Weather resistance
Simultaneous prediction of multiple constituents	Simplicity of the method
Qualitative and quantitative parameter	Constancy of the method
Composition and function	Stability of instrument performance
	Cost-effectiveness for large sample sets

Field-portable NIR instruments have been newly developed or adapted from laboratory instruments. A moving field sensor was developed to operate in-furrow in agricultural fields for measuring soil organic C.[1] A Bran+Luebbe InfraProver System was operated on board a vessel in the river Nieuwe Merwede, The Netherlands. Cores were taken from the sediment, sectioned and scanned on board for the prediction of dry solids content, organic matter content in various particle size fractions and density.[2] Subsequently, the instrument was placed in a water-tight housing and deployed in the water column with a fibre-optic probe inserted into the sediment for *in situ* determinations (W.R. Doorenweerd and G.L.J. Haaij, Delta Consult bv, The Netherlands, personal communication). Two instruments developed for on-the-go analysis of agricultural crops during harvest, the Textron/Case NH ProSpectra [3,4] and the Zeiss Corona spectrometers,[5] have been mounted on a pick-up truck to create a mobile NIR laboratory for on-site analysis of hog manure.[6]

Barriers to the use of NIR in environmental analysis

Although there are a number of challenges to the use of NIR for environmental analysis (Table 3), it is probable that the lack of familiarity of environmental chemists and regulators with NIR is the ma-

Table 3. Barriers to the use of NIR spectroscopy in environmental analysis.

Not taught in university Chemistry programs, where most environmental chemists and environmental technicians are trained.	Need to calibrate for samples of each type
Virtually unknown to government scientists, regulators, consultants, and academics	Need to calibrate for each make and model of instrument
Indirect nature of the predictions raises scepticism; acceptance requires a paradigm shift in thinking	Difficulty of identifying the major variables affecting extrapolability of calibrations. What is an appropriate "training set"?
If predictions are poor, NIR is blamed, not reference analyses	The high cost of calibration for small sample sets makes it not useful for small sample sets
Need to calibrate for each constituent	Capital outlay for instrumentation in addition to maintaining conventional analytical capability

jor explanation for the present low usage of NIR. This stems from the absence of NIR in the chemistry curriculum in most universities based on a prevalent opinion held in academia that the NIR region is difficult to explain from a spectroscopic viewpoint and not of much use for analysis.

In practice, it is likely that the largest future challenge to the widespread use of NIR for environmental analysis will be the calibration process. Most NIR determinations in environmental samples will be for naturally-occurring organic matter (NOM) or for properties influenced by or correlated with NOM. The composition of NOM and the factors affecting its variability over time and space are poorly known. Therefore, the identification of an appropriate "training set" for environmental applications will require care.

Global environmental issues

Many crucial environmental issues today have organic substances at their core. These include:
(a) nutrient management

- manure and compost
- biosolids
- protection of aquatic ecosystems

(b) climate change
- carbon inventories

(c) oil and gas industry environmental impacts
- total petroleum hydrocarbons

Manure and compost

Degradation of land and surface and ground water by an overabundance of nutrients is one of the oldest and most widespread of pollution problems. Natural processes are estimated to incorporate about 140 million tons of nitrogen into the terrestrial nitrogen cycle every year. Human activity has doubled that amount.[7] The management of N and P in manures and biosolids can potentially be greatly assisted by NIR analysis.

Animal manure and compost, i.e. animal and plant wastes in the process of biodegradation, are by-products of agriculture that contain nutrients useful to crops. If managed properly, their application to agricultural land potentially solves a waste management problem and replaces some of the inorganic fertilizer that would otherwise be used. Nevertheless, the high variability in nutrient composition of manure and compost from one operation to another and with time makes reliable loading of nutrients to land difficult. Hog manure can be particularly variable in composition even during the pump-out of a manure store, largely because the particulate material containing most of the P and metals is heavy and difficult to keep in suspension. Over the 8-day pump-out of a two-celled earthen manure store in Manitoba, Canada, total N ranged over 3.5-fold and total P over 20-fold.[8]

NIR is potentially applicable to on-site determination and control of nutrient loading during manure and compost application. Progress is being made using laboratory instruments such as the Foss NIRystems Inc. model 6500 visible/near infrared scanning spectrophotometer towards documenting capabilities of NIR analysis of hog manure,[9–11] cattle manure,[10,12–14] cattle manure compost,[15,16] livestock manure compost[17] poultry manure[18] and unspecified compost.[19] Almost all studies reported that NIR predicted moisture highly successfully and organic matter or solids, ammonium-N, organic N and total N well or reasonably well. Phosphorus was generally predicted poorly, except in several of the hog manure studies[9,11] and one compost study,[19] where it was predicted very successfully. The prediction of K was inconsistent. The field-portable instruments, ProSpectra and Corona, show promise for the in-stream, real-time analysis of hog manure during land application.[6] As part of a manure delivery

system with GPS and GIS, NIR could accurately monitor nutrient loading to land, balance N : P by the addition of inorganic nutrients and deliver a custom fertilizer application. Challenges to making this work including sample presentation and development of calibrations.

Biosolids

As for manure and compost, applying anaerobically-digested, dewatered municipal sewage sludge, termed biosolids, to agricultural land is a widely-used, cost-effective way of disposing of this waste and making use of the organic matter, N and P that it contains. The UK and the US produce one million and seven million tonnes of biosolids, respectively, every year and apply about half of it to agricultural land.

When biosolids are applied to land, the most important constituents are the macro-nutrients, N, P and K and the heavy metals Cd, Cr, Cu Pb, Ni and Zn that may, potentially, accumulate to toxic levels from repeated application. On the other hand, when biosolids are land-filled, the organic matter content is of concern since C may be biodegraded in the landfill to produce dangerous methane. In a study involving biosolids from the City of Winnipeg, MB, Canada, moisture and organic matter content were predicted successfully, NH_4–N and suspended N were predicted marginally well, but P and K were not predictable.[20] Cadmium, Cu, Pb and Zn were predicted moderately well, likely as a result of binding to the organic matter or clay present in the biosolids.[20]

Aquatic ecosystem monitoring

Water quality

Water quality in lakes can be impacted by the release of wastes by human activities into air, land and water. NIR was found to be highly successful in measuring the concentrations of C, N and P in the suspended particulates (seston) in lakes.[21,22] This technique can monitor changes in the mass of N and P with changes in nutrient loading. NIR analysis of seston has been found to be related to total organic C, total P and pH of the lake water sampled at the same time.[23] NIR spectra from surface (0–1 cm depth) sediments in 58 Swedish lakes reflected water quality over the previous four years for total P, pH and total organic C.[24] This was repeated on Canadian lakes where suspended C and suspended N in lake water in the prior two years were predicted based on NIR analysis of the surface (0–1 cm) sediment.[25] In a study of sediment cores from Swedish lakes, the NIR spectra were used to predict pH in the lake water prior to acidification.[26]

Sediment quality

NIR spectroscopy has been highly successfully used for the prediction of total C, carbonate, organic C and N in lake sediments from four Canadian lakes ranging over more than 18° latitude[27] but P was predicted only marginally well. Phosphorus was predicted very successfully in sediments from eutrophic German Lake Arendsee.[28] Background concentrations of heavy metals, Fe, Mn, Zn, Cu, Pb and Ni in sediments from a pristine Canadian lake were predictable, apparently because of their association with organic matter.[28] Cadmium, experimentally added to the same lake was not successfully predicted in the sediment, either because its concentration was too low or because its association with the organic matter was much shorter than for the naturally-occurring metals.[29]

An elegant study of a small Swedish lake (0.5 km^2) of known bathymetry, involved only intensive sampling of surface sediments, drying and scanning of the samples, ashing of the samples and principal component analysis of the spectral data. Variance due to water depth and organic matter content was removed from the variance in the first principal component. The remaining variance in PC1 reflected organic matter quality. When the PC1 scores were mapped on the lake, the influence of natural

inlets and outlets, of the run-off from human habitation and of clear-cutting on the shore on organic matter quality were clearly seen.[29]

Climate change

The most serious environmental problem facing mankind today is global climate change associated with increases in emissions from human activity of greenhouse gases, CO_2, CH_3, N_2O and chlorofluorocarbons (CFCs) into the atmosphere well above natural levels. The Kyoto Protocol, negotiated in Japan in 1997, commits industrialised nations to decrease greenhouse gas emissions between 2008 and 2012. As an alternative to some of the reduction in greenhouse gas emissions, some nations are proposing to take "credit" for large stores of C such as forests and soils that they have within national boundaries.[30] As well, they propose, through resource management, to use forests and soils as sinks to remove or sequester C from the atmosphere.[31]

Carbon quantity

Practical, cost-effective methods operating on a landscape scale are needed to determine the inventories of stored C and changes in C under management strategies. Carbon in soil is highly variable on a small-scale with both horizontal distance and topography and with depth. For example, soil from a 5.6 ha field in the Black Soil Zone of Manitoba, Canada varied in organic C from 0.38 to 4.05% d.w. in all A horizons combined and from 0.92 to 4.05% d.w. in the Ah horizon alone.[32] NIR is probably the only technique that is sufficiently cost-effective to allow the large numbers of samples to be measured that would be required to determine the size of and dynamic changes in C inventories.

Precision of NIR for measuring organic matter or C is comparable to the conventional Walkley Black or Dumas combustion methods. Using NIR, a calibration model developed for the above Manitoba soil samples between the chemically-determined organic C and the NIR spectral data predicted this constituent with an error of ± 0.33% organic C (range 0.38–4.05 %).[33] In a study on US soils, organic C (range 0.6 to 2.8%) was predicted by NIR with an error of ± 0.1% organic C.[34]

Although most analysis for organic matter or organic C with NIR has been on dried samples, the greatest benefit from NIR would be achieved if samples could be analysed on-site without costly sample transport, documentation, storage and analysis in the laboratory. Carbon could be analysed at the time of field sampling and results mapped as they were obtained. Field moist soil has been analysed by NIR. Percentage organic matter (range 0.1 to 40.6%) in field moist clay and peaty soils was predicted with an error of 3.32% organic matter (D.F. Malley and R.S. Currie, unpublished data). Soil organic C (range 0.3 to 2.5%) was measured in a group of US field moist soils with an error of 0.25% organic matter.[1]

Carbon quality

Determining the permanence of the C sequestered or stored in agricultural and forest ecosystems is its chemical nature or quality. Conventional methods for the determination of C quality are even more impractical to apply on a landscape scale than are laboratory methods for organic matter or C content in soil and litter. With NIR, carbon quality can be determined simultaneously with organic matter or C quantity. Total N, lignin and cellulose contents of forest foliage of 13 different species have been successfully determined with NIR.[35] Carbon, N, ash content, acid-detergent fibre and acid–detergent lignin were successfully determined in the litter of eight species of evergreen and deciduous broad-leafed trees, conifers and shrubs using NIR.[36] Measures of decomposition in leaf litter such as C/N ratios, lignin/N ratios have been predicted with NIR.[37] The effects of clear cutting forests with and without prescribed burning on humus quality, total microbial C and substrate-induced respiration

were studied with NIR.[38] The usefulness and limitations of NIR to determining various C fractions in litter and soil have been reviewed.[39]

Petroleum hydrocarbons

Petroleum hydrocarbons (PHCs) represent the most wide-spread soil contaminants in many countries. They create a fire or explosion hazard, threaten human health, soil quality, drinking water quality, aquatic ecosystems and can be toxic to plants and animals. NIR is used quite widely for process control and product quality monitoring in oil refineries.[40] If successful for the determination of PHCs in soil, NIR would be very useful for the delineation and assessment of contaminated sites, particularly in remote areas where the need for conventional chemical analyses in laboratories results in costly delays. It may also by useful for monitoring natural recovery or remediation of contaminated sites.

Prediction of petroleum hydrocarbon contamination in soil and sand has been explored using soil and sand spiked with gasoline, diesel, motor oil and synthetic hydrocarbon mixtures. The determination of the hydrocarbons appeared to be more feasible in sand than in soil.[41] Diesel fuel contamination of soil has been predicted by NIR marginally well, using solid, phase micro-extraction–gas chromatography as the reference method for the determination of the hydrocarbons.[42]

Conclusion

A number of features combine to make NIR spectroscopy the most cost-effective method of analysis to emerge during the last three decades. Although NIR is presently poorly known among environmental scientists, consultants, technicians and regulators, the body of literature and experience with the technique is growing quickly. The cost of purchasing instruments, in addition to maintaining conventional chemical analytical capability, is a potential barrier when budgets for environmental monitoring and research are tight. Environmental scientists operating in a multi-disciplinary, cooperative environment with establishments such as agricultural industries or research stations may have an opportunity to try the technology before committing to a major purchase.[43] Nevertheless, the capital cost of an instrument may be roubped in a relatively short period of time, in cases where NIR significantly reduces labour or commercial laboratory costs. As NIR comes into wider use, such as for the analysis of C quantity and quality in relation to C inventories and sequestration, it is expected to lead to improved understanding of the composition, dynamics and variability of NOM. As it is in other fields, NIR in environmental analysis will be a tool to conduct routine analyses more efficiently and a stimulus to the development of new analytical capabilities not presently possible.

References

1.   K.A. Sudduth and J.W. Hummel, *Transactions of the ASAE* **36,** 1571 (1993).
2.   P.W.R. Doorenweerd and G.L.J. Haaij, International Conference on Contaminated Sediments: Restoration and Management. Rotterdam, The Netherlands, 7-11 September. Preprints, Volume II, p. 1045 (1997).
3.   Anonymous, *Case IH Canadian Farming*, Fall, p. 4 (1999).
4.   P. Williams, *NIR News* **11(3),** 3 (2000).
5.   M. Rode, Abstract #O7-2 in Abstracts and Program of NIR-2001: *Changing the World with NIR*, 10th International Conference on near infrared Spectroscopy, Kyongju, Korea. 10-15 June (2001).
6.   P.D. Martin and D.F. Malley, in Proceeding sof the Livestock Options for the Future Conference, Winnipeg, MB, Canada, 25–27 June (2001).

7. L.R. Brown, C. Flavin, H. French and others, *State of the World 2000*. The Worldwatch Institute. W.W. Norton & Co., New York, USA (2000).
8. D.F. Malley and P.D. Martin, in *Proceedings of the Livestock Options for the Future Conference*, Winnipeg MB, Canada 25–27 June (2001).
9. D.F. Malley, R.G. Eilers, E. Rempel, M. Van Walleghem and P.D. Martin, in *Manure Management'99: Proceedings of a Tri-provincial Conference on Manure Management*. Saskatoon, SK, 22–24 June, p. 633 (1999).
10. A. Millmier, J. Lorimor, C. Hurburgh Jr, C. Fulhage, J. Hattey and H. Zhang, *Transactions of the ASAE* **43,** 903 (2000).
11. D.F. Malley, L. Yesmin and R.G. Eilers, *Soil Sci. Soc. Amer. J.* **66,** (in press).
12. T. Asai, S. Shimizu, T. Koga and M. Sato, *Nippon Dojo Hiryogaku Zasshi* **64,** 669 (1993).
13. J.B. Reeves, III and J.S. Van Kessel, *J. Near Infrared Spectrosc*. **8,** 151 (2000).
14. J.B. Reeves, III and J.S. Van Kessel, *J. Dairy Sci.* **83,** 1829 (2000).
15 M. Nakatani and Y. Harada, *Japanese J. Soil Science & Plant Nutrition* **66,** 422 (1995).
16. M. Nakatani, Y. Harada, K. Kaga and T. Osada, *J. Japanese Soil & Fertil. Soc.* **66,** 159 (1996).
17. T. Kinoshita, A. Ichikawa and T. Kotah, *Aichi-ken Nogyo Sogo Shikenjo Kenkyu Hokoku* **29,** 305 (1997).
18. J.B. Reeves, III, *J. Ag. Fd. Chem.* **49,** 2193 (2001).
19. J.-J. Nam, K.-Y. Jung and S.-H. Lee, *Near Infrared Spectroscopy: Proceedings of the 9th International Conference*, Ed by A.M.C. Davies and R. Giangiacomo. NIR Publications, Chichester, UK, p. 613 (2000).
20. D.F. Malley, B. Trybula, R.D. Ross and G. Gay, *Evaluating the use of near infrared spectroscopy for the analysis of biosolids constituents.* Project 99-PUM-6-ET, Water Environment Research Foundation, Alexandria, VA. D00306WW (2000).
21. D.F. Malley, P.C. Williams, M.P. Stainton and B.W. Hauser, *Can. J. Fish. Aquat. Sci.* **50,** 1779 (1993).
22. D.F. Malley, P.C. Williams and M.P. Stainton, *Water Res.* **30,** 1325 (1996).
23. E. Dåbakk, M. Nilsson, P. Geladi, S. Wold and I. Renberg, *Wat. Res*. **34,** 1666 (2000).
24. M. Nilsson, E. Dåbakk, T. Korsman and I. Renberg, *Environ. Sci. Technol.* **30,** 2586 (1996).
25. P.D. Badiou, D.F. Malley, M.J. Paterson and M.P. Stainton, *Proceedings for the 43nd Annual Meeting of the Manitoba Soil Science Society*, January 25–26, p. 54 (2000).
26. T. Korsman, M. Nilsson, J. Ohman and I. Renberg, *Environ. Sci. Technol.* **26,** 2122 (1992).
27. D.F. Malley, L. Lockhart, P. Wilkinson and B. Hauser, *J. Paleolimnol.* **24,** 415 (2000).
28. D.F. Malley, H. Rönicke, D.L. Findlay and B. Zippel, *J. Paleolimnol*. **21,** 295 (1999).
29. D.F. Malley and P.C. Williams, *Environ. Sci. Technol.* **31,** 3461 (1997).
30. T. Korsman, M.B. Nilsson, K. Langren and I. Renberg, *J. Paleolimnol.* **21,** 61 (1999).
31. D. Anderson, R. Grant and C. Rolfe, *Taking Credit: Canada and the Role of Sinks in International Climate Negotiations*. David Suzuki Foundation and West Coast Environmental Law, 86 pp. (2001).
32. G.R. Manning, Master of Science Thesis, Department of Soil Science, University of Manitoba, Winnipeg MB, Canada (1999).
33. P.D. Martin, D.F. Malley, G. Manning and L. Fuller, *Can. J. Soil. Sci.* (accepted for publication).
34. G.W. McCarty and J.B. Reeves, III, in *Assessment Methods for Soil Carbon*, Ed by R. Lal, J.M. Kimble, R.F. Follett and B.A. Stewart, *Adv. Soil Sci*. Lewis Publishers, Boca Raton, USA, p. 371 (2001).
35. T.M. McLellan, J.D. Aber, M.E. Martin, J.M. Melillo and K.J. Nadelhoffer, *Can. J. For. Res*. **21,** 1684 (1991).
36. R. Joffre, D. Gillon, P. Dardenne, R. Agneessens and R. Biston, *Ann. Sci. For.* **49,** 481 (1992).

37   D. Gillon, R. Joffre and P. Dardenne, *Can. J. For. Res*. **23,** 2552 (1993).

38. J. Pietikäinen and H. Fritze, *Soil Biol. Biochem*. **27,** 101 (1995).

39. B. Ludwig and P.K. Khanna, in *Assessment Methods for Soil Carbon*, Ed by R. Lal, J.M. Kimble, R.F. Follett and B.A. Stewart, *Adv. Soil Sci*. Lewis Publishers, Boca Raton, USA, p. 361 (2001).

40. J. Workman, Jr, *J. Near Infrared Spectrosc.* **4,** 69 (1996).

41. H.W. Zwanziger and H. Förster, *J. Near Infrared Spectrosc*. **6,** 189 (1998).

42. D.F. Malley, K.N. Hunter and G.R.B. Webster, *J. Soil Contamin*. **8,** 481 (1999).

43. W.J. Foley, A. McIlwee, I. Lawler, L. Aragones, A.P. Woolnough and N. Berding, *Oecologia* **116,** 293 (1998).