

## Objective Selection of Sediment Samples using Near-infrared Spectroscopy

**Summary** NIR spectra contain information about the whole sample matrix that reflects the quantity and nature of such components as naturally-occurring organic matter and clays. Where these components influence the binding or behaviour in sediments of constituents of interest, such as trace contaminants, that are costly to analyze, this information may be useful in the selection of samples for these analyses. This information requires no reference data and is available through chemometric techniques such as principal component analysis. Objective selection of samples for further testing is expected to provide a more representative set of samples than random selection.

The method of objective sample selection is demonstrated using an example from a study of environmental impacts of the 1997 Red River "Flood of the Century". In 1997, the Red River Valley in Minnesota, North Dakota, and Manitoba experienced the worst flood in over 100 years, producing the "Red Sea", up to 40 km wide and 180 km long. This inundated cities, towns, and farms, and deposited tonnes of nutrients and persistent contaminants to the sediments of the south basin of Lake Winnipeg.

**Surface sediments** (0 - 0.5 cm) were collected from the south basin in a study on contaminant impacts on the basin ecosystem (Stewart et al. 1999). Samples (n=33) were collected along three parallel transects, A, B, and C, extending from the mouth of the Red River northward 52 km into the lake. They were later analyzed for nutrients, 12 heavy metals, >25 organochlorines (pesticides, herbicides, PCB, DDT) and >45 polycyclic aromatic hydrocarbons and alkenes.



**Samples** were dried and scanned using a Foss NIRSystems model 6500 visible/NIR scanning spectrophotometer from 1100 to 2500 nm using Near-Infrared Analysis Software. The spectral data were transformed to the first derivative to reduce the effect of differences in particle size among samples. Principal component analysis of the spectral data was performed using The Unscrambler® 7.6 multivariate statistical analysis software.

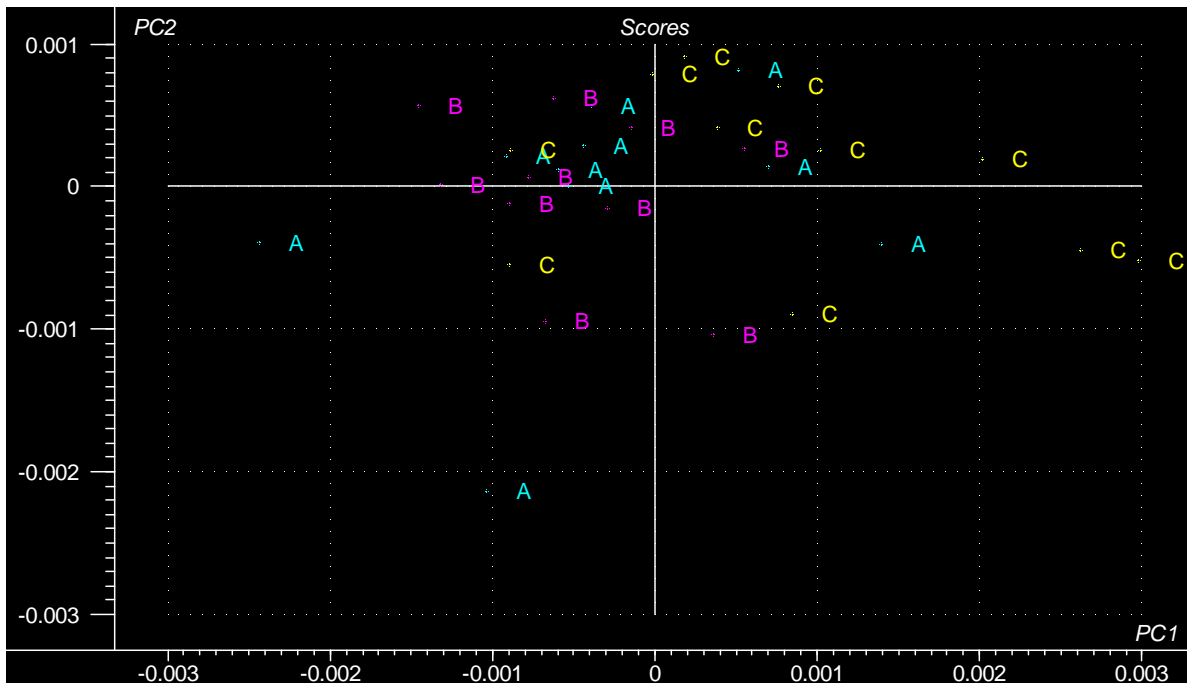


Fig. 1. Scores of the sediment samples on the first two principal components explaining the variability in spectral data. Samples from the transects, "A", "B", "C" are colour-coded.

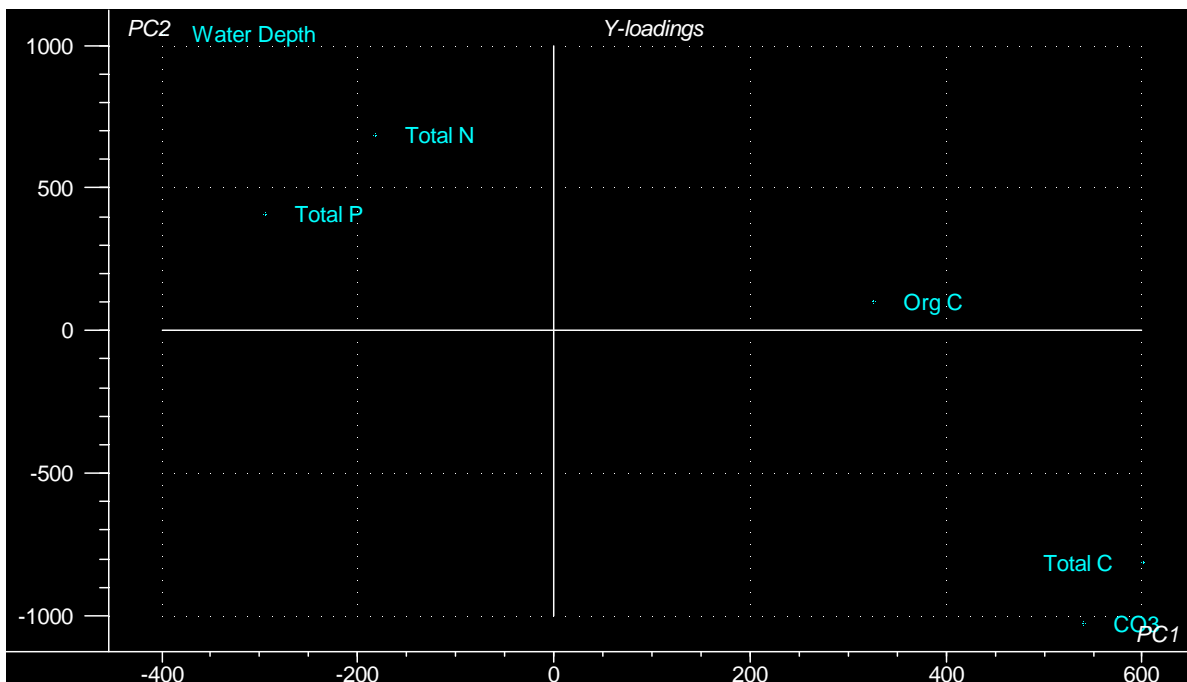


Fig. 2 Loadings of several constituents and parameters on PC1 and PC2 from PLS2 analysis

**Figure 1** is a two-dimensional scatter plot of scores for the first two principal components (PC1 and PC 2) for 33 samples. The closer the samples are in the scores plot, the more similar they are with respect to PC1 and PC2. Conversely, samples far away from each other are different from each other. In this example, reference data for nutrients and water depth were available and give insight into compositional differences influencing the distribution of samples in Fig. 1.

**Reference data** were combined with the spectral data (first derivative) in a partial least squares regression analysis (PLS2) using The Unscrambler® 7.6. Figure 2 shows the loadings of the nutrients and water depth on the first two principal components. An inverse relationship between water depth and carbonate content is shown. Figures 1 and 2 can be viewed together. Samples in a quadrant in Fig. 1 were generally high in a constituent that loaded in the same quadrant in Fig. 2. Thus, the samples in the upper left quadrant in Fig. 1 would be high in N and P. Fig. 2 shows that the contents of carbonate, total carbon, organic carbon, and spectrally-active factors correlated with water depth more strongly influenced sample scores in Fig. 1 than did contents of phosphorus and nitrogen that were closer to the center of the plot.

**In conclusion**, the spectral data alone, displayed using principal component analysis, offer a means to select samples that represent the variability present and to avoid analyzing a large number of similar samples.

When the spectra are combined with compositional data on the samples that can be predicted by NIRS such as carbon or nutrient contents, selection of samples for further analysis can be targeted to more specific parameters such as variability in organic matter content.

## References

Stewart, A.R., G.A. Stern, W.L. Lockhart, A. Salki, M.P. Stainton, B.N. Billeck, R. Danell, J. Delaronde, N.P. Grift, T. Halldorson, K. Koczanski, A. MacHutcheon, B. Rosenberg, D. Savoie, D. Tenkula, G. Tomy, and A. Yarchewski. 1999. Influence of the 1997 Red River flood on contaminant transport and fate in southern Lake Winnipeg. Report to the International Red River Basin Task Force. 41 p + 3 Appendices.

## Authors

Dr. Diane Malley

PDK Projects, Inc., Winnipeg MB and Nanaimo B.C. Canada

Copyright © PDK Projects, Inc. 2006

PDK Projects, Inc. is incorporated in Manitoba and registered in B.C.

Business Office: 5072 Vista View Crescent, Nanaimo B.C. Canada

Tel: 250-751-8890 Fax: 250-751-8225

Laboratory: #2 – 12 McGillivray Place, Winnipeg MB R3T 1N4

Email: [dmalley@pdkprojects.com](mailto:dmalley@pdkprojects.com)

[www.pdkprojects.com](http://www.pdkprojects.com)