

Surrogate Correlations and Near-Infrared Diffuse Reflectance Sensing of Trace Metal Content in Soils

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Abstract Near-infrared diffuse reflectance sensing (NIRS) of soils has been the object of considerable interest and research in the last few years. This has been motivated by the prospect that this method seems to provide a cheap, convenient alternative to conventional, time-consuming methods for the measurement of a wide range of soil parameters. In particular, various authors have advocated that NIRS could be used to measure

rapidly and non-destructively the concentration of trace metals in surface soils. Correlation analyses between NIRS spectra and trace metal concentration have yielded inconclusive results to date, suggesting that trace metal concentration may belong to a class of “tertiary” soil parameters, linked to NIRS spectra through “surrogate”, or indirect, correlations, involving some other primary or secondary parameter like clay or organic matter content, to which NIRS spectra are very sensitive. To assess the validity of this surrogate correlation hypothesis in the case of trace metals, experiments were carried out with soil samples varying only in the amount of trace metals they contain. Field-aged Hudson and Arkport soil pots spiked with Cu and Zn, freshly spiked samples of the same soils, and samples of a metalliferous peat soil from Western New York naturally rich in Cd and Zn were subjected to NIRS under laboratory conditions. Detailed analysis indicates that the NIR spectrum is sensitive to sample handling, including the orientation of the samples in the NIRS instrument, but that, at the same time, there is no discernable effect of the presence of trace metals on any part of the NIR spectrum. These results provide strong experimental support to the hypothesis of “surrogate” correlation for trace metals, and indicate that trace metals, even in severely contaminated soils, should not interfere with the NIR sensing of primary or secondary parameters, like organic matter content. Further work is needed to determine if this feature of NIR spectra extends to other soil chemical parameters.

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1 Introduction

In the last decade, near-infrared diffuse reflectance sensing (NIRS) of soils has been the object of significant interest, with research on this promising spectroscopic technique continuing unabated. Some researchers see it as a fast, relatively inexpensive alternative to traditional laboratory methods for the determination of a wide range of soil parameters. Other prospects for the technique include the design of new “proximal” sensors in support of precision agriculture, and a practical way to assess a range of soil parameters via satellite-based sensors.

In spite of a number of clear failures (e.g., Genú and Demattê 2006), some authors have suggested that the range of soil parameters that could be effectively evaluated via NIRS includes the concentration of various chemical elements like phosphorus, potassium, sodium, calcium, and total nitrogen (e.g., Ludwig et al. 2006; Maleki et al. 2006; Mouazen et al. 2006). In particular, in polluted sediments and soils, e.g., in brownfields or in agricultural fields amended with sewage sludge, NIRS has been advocated as a feasible method for the rapid determination of trace metal content (Malley and Williams 1997; Kemper and Sommer 2002; Moron and Cozzolino 2003; Font et al. 2004; Siebielec et al. 2004; Wu et al. 2005a, b; Genú and Demattê 2006). Malley and Williams (1997) scanned freshwater sediments between 1,100 and 2,500 nm and obtained high r^2 values between NIR-predicted and chemically analyzed metal concentrations of 0.91 for Cu, 0.93 for Zn, 0.81 for Pb, and 0.88 for Ni, but a lower r^2 value for Cd (0.63). Kemper and Sommer (2002) measured the visible to near-infrared reflectance (350–2,400 nm) of soils in Spain contaminated with pyritic sludge and exhibiting high concentrations of a number of trace metals. They found the best r^2 values for Hg (0.96), Pb (0.93), and Sb (0.93). Results for Cd (0.51), Cu (0.43), and Zn (0.24) were not statistically significant. In 332 samples of agricultural soils from Uruguay, Moron and Cozzolino (2003) carried out a modified partial least square analysis of NIR spectra and found calibration r^2 values of 0.87 for Cu and 0.72 for Zn. Font et al. (2004) analyzed 100

samples from the same area of Spain studied by Kemper and Sommer (2002), and obtained much better calibration r^2 values for Cu (0.76) and Zn (0.87). Siebielec et al. (2004) analyzed chemically and via NIR spectroscopy 70 soil samples from a metal mining region in Poland, exhibiting a wide range of concentrations of Zn, Pb, and Cd. They obtained r^2 values of 0.84 for Ni, 0.67 for Zn, 0.61 for Cu, 0.54 for Cd, and 0.45 for Pb. After removal of data points identified as “calibration outliers”, these statistics improved (e.g., to 0.75 for Cu and 0.84 for Zn). In 120 samples of moderately contaminated suburban soils near Nanjing (China), Wu et al. (2005a) obtained prediction r^2 values of 0.86 for Ni, 0.76 for Cr, 0.62 for Cu, 0.59 for Hg, 0.66 for Pb, and 0.62 for Zn.

These conflicting experimental observations, for example with r^2 values for Cu in some cases very significant, at 0.91 (Malley and Williams 1997), or not significant at all, at 0.43 (Kemper and Sommer 2002), raise questions about the nature of the correlation between NIR spectra and the trace metal content of soils and sediments. Several authors (e.g., Malley and Williams 1997) assert that pure metals do not absorb electromagnetic radiation significantly in the NIR region. Others (e.g., Wu et al. 2005b) consider that trace metals do not have identifiable spectral features when they are present in soils at trace levels, leaving it somewhat open as to whether things might be different at higher concentrations. Unfortunately, at this juncture, there is no experimental evidence confirming that trace metals present in soils either do or do not lead to diagnostic features in NIR spectra; most authors do not report individual spectra, or when they do, it is clear that spectra are also affected by other, compounding parameters.

Nevertheless, in spite of a lack of concrete evidence, an implicit consensus seems to have emerged in the literature (e.g., Wu et al. 2005a, b; Siebielec et al. 2004) that NIRS does not measure trace metals directly, but may provide indirect measurements, due to the fact that NIRS is affected by soil parameters, like organic matter, sulfide, carbonate, or oxide content, which are controlling the amount of trace metals that a soil is able to retain. Thus, calibrations that one might develop between NIR spectral data and trace metal concentrations in soils would be example of what Shenk et al. (1992) termed “surrogate calibrations”. Following this perspective, one might rank soil parameters into

“primary”, “secondary”, and “tertiary” classes, depending on whether the parameters, respectively, lead to well-identified regions of absorption in the NIR spectrum, lead only to overall changes in the spectrum over the whole visible/near-infrared range, or lead to no noticeable feature at all in any part of the spectrum. According to this classification, soil moisture would be a primary parameter, whereas organic matter would be a secondary one. Trace metal content would then be a tertiary parameter, predictable from NIR spectra only because it is somehow correlated with a primary or secondary parameter. However, this hypothesis remains to be confirmed.

In this general context, the key objective of the research described in this article was to assess the extent to which the surrogate calibration hypothesis applies to the case of trace metal content in soils; in other words, whether trace metal content can be classified as a tertiary parameter for NIRS. This objective was tackled by subjecting to NIRS a number of soil samples that either naturally or artificially have very different trace metal concentrations, but otherwise do not differ significantly in any other way. The materials tested included different samples of peat soil, naturally rich in Cd and Zn, samples of mineral soils spiked with Cu and Zn in different proportions and field-aged in pots, as well as freshly spiked samples of the same soils. A preliminary step in the research consisted of alleviating as much as possible various sources of measurement imprecision associated with the handling of the samples, in particular, its orientation relative to the spectrometer, in order to allow a reliable comparison among spectra.

2 Materials and Methods

2.1 Field-Aged Metal-Spiked Soil Samples

A silt loam soil (Hudson series, classified as fine, illitic, mesic Glossaquic Hapludalf) was collected from the surface layer of an agricultural research field on the Cornell University Campus in May 2003 (Soil Survey Staff 2006). The soil was thoroughly mixed and stored in sealed plastic bins. Six subsamples were collected from the bins to determine their moisture content. Twenty-five samples of the soil were then spiked with copper (Cu)

and zinc (Zn) by spreading them out on a plastic sheet and spraying them with various amounts of 0.5 M ZnSO₄ and CuSO₄ solutions to achieve targeted concentrations of 0, 50, 100, 200, and 400 mg kg⁻¹ (dry weight) independently for Zn and Cu (Table 1). An appropriate amount of deionized water was added to the solution sprayed on each soil sample, to ensure that the same volume of liquid was applied to all soils, regardless of treatment. The spiked soil samples were turned three times during the spray application and then placed in a V-mixer for 5 min to completely mix the treated soil. Approximately 8.8 kg of each moist, treated soil sample (6.88 kg dry weight) was put into a 24-cm-diameter by 22-cm-tall plastic pot that had been prepared by placing a piece of polyester landscape fabric on the bottom to hold the soil in place while allowing solution to leach through.

A second set of 25 Cu- and Zn-spiked soil samples was prepared simultaneously using a sandy loam soil (Arkport series, classified as coarse-loamy, mixed, active, mesic Lamellic Hapludalf), collected and treated in June 2003, following the same procedure described above. Each pot in the Arkport series contained 10 kg of moist soil (8.26 kg dry weight).

The 50 Hudson and Arkport soil pots were brought back to the field in June 2003, and were sunk into holes dug for the pots so that the soil surface in the pots was level with the soil surface in the field. These metal-spiked soil pots were then allowed to age under field conditions. Subsequent total soil metal analyses showed that the Cu concentration in the Arkport soil thought to be treated with 200 mg kg⁻¹ Cu only (i.e., with no added zinc) was the same as that in the 100 mg kg⁻¹ Cu treatment, indicating an error in the spiking process for this one level of Cu. Therefore, the data obtained from the Arkport soil amended with 200 mg kg⁻¹ Cu were treated as a replicate of the 100 mg kg⁻¹ Cu treatment in all analyses.

All pots were seeded with six soybeans seeds (cv. Pioneer 91 B91) in June 2003. The plants were harvested in late summer, but the pots and soil remained in the ground. In June 2004 and 2005, soybeans were again planted in the pots. At harvest time in 2005, soil samples were collected from each pot and air-dried. Aggregates were crushed with a mortar and pestle into a powder that was passed

Table 1 Total concentrations of Cu and Zn in the soils spiked with combinations of the two metals (the soil in the pots was sampled and analyzed, 2 years after installation in the field)

		Added copper concentration (mg kg ⁻¹)										
		0		50		100		200		400		
		Cu	Zn	Cu	Zn	Cu	Zn	Cu	Zn	Cu	Zn	
Added zinc concentration (mg kg ⁻¹)	0	Arkport	14.3	83.5	56.9	91.6	105	86.9			389	86.1
		Hudson	13.2	83.5	46.9	85.4	85.6	85.2	150	85.8	306	83.0
	50	Arkport	17.2	131	61.3	130	104	126	188	122	385	131
		Hudson	14.8	121	48.4	116	93.2	118	169	121	288	118
	100	Arkport	17.0	165	59.0	173	106	172	200	162	378	154
		Hudson	15.6	156	48.7	157	85.3	155	157	156	311	147
	200	Arkport	18.1	249	57.7	243	108	250	182	233	399	235
		Hudson	15.8	232	52.4	238	84.8	221	170	234	319	222
	400	Arkport	17.5	409	59.7	403	109	402	195	387	388	369
		Hudson	14.9	357	51.3	378	79.7	356	162	353	305	350

through a 2-mm stainless-steel sieve to remove large gravel and/or roots. Important characteristics of the soils, including pH, organic matter (OM) content, cation exchange capacity (CEC), and texture, were measured using the bulk control subsamples. Specifically, soil pH was determined in deionized–distilled water (1:1 weight:weight), with the pH values of the Arkport and the Hudson soil series being 5.63 and 5.86, respectively. The OM content of the soils, estimated by weight loss upon ignition, was 4.10% for the Arkport and 3.84% for the Hudson series. Texture analysis was performed by the pipette method, showing that the Arkport soil had 2% clay, 62.1% sand, and 35.9% silt, whereas the Hudson soil consisted of 15% clay, 16% sand, and 69% silt. The CEC of the soils, estimated by measuring the amount of Ca²⁺ and Mg²⁺ displaced from exchange sites by a BaCl₂ solution, was 6.28 cmol kg⁻¹ for the Arkport and 12.5 cmol kg⁻¹ for the Hudson soil. The amount of Zn and Cu loaded in these soils appeared to have very little impact on the soil properties after 1 year of equilibration under field conditions. This conclusion is reached by comparing the soil pH and OM contents in the control to those in the soil treated with the highest metal loadings (Cu and Zn 400 mg kg⁻¹). Subsamples of each spiked soil were microwave digested in hydrofluoric acid (EPA 3052) and analyzed by inductively coupled plasma (ICP) emission spectrometry (SPECTRO CIROS^{CCD}; SPECTRO Analytical Instruments Inc., Mahwah, NJ, USA) for

determination of total Zn and Cu, among other elements. The total concentrations of Cu and Zn in the soil subsamples collected in October 2005 are listed in Table 1.

2.2 Freshly Spiked Soil Samples

Spiked soil samples were prepared by spraying five 25-g subsamples of each of the two control (non-spiked) soils collected in Oct. 2005 (thinly spread across the bottom of large plastic weighing boats) with a solution of ZnSO₄ and CuSO₄ to yield soils with additional 0, 400, 800, 1,600, and 3,200 mg kg⁻¹ of Cu and, independently, equivalent amounts of Zn. An appropriate amount of deionized water was sprayed on the soils so that each soil received the same volume of liquid. The solutions were applied slowly to avoid ponding on the soil surface. After air drying, the samples were pulverized and homogenized in a mortar and pestle, passed through a 2-mm sieve, and stored in 100-mL polyethylene bottles until needed.

2.3 Metalliferous Peat Soils from Western New York

Samples of six peat soils with naturally elevated Zn and Cd concentrations were obtained from the Manning peatland region of western NY. The samples were collected, mixed, and stored in a field-moist state in large plastic bags until needed, as described by

Martínez et al. (2002). Total Zn and Cd concentrations of these six original peat samples were determined on air-dried subsamples of the peat soils by microwave HF digestion and ICP emission spectrometry.

Based on these measurements, five new samples were created by blending and thoroughly mixing portions of the original six field samples. This technique resulted in a series of 11 metalliferous peat soils with concentrations of Zn that increase in an approximately geometric progression (Table 2). The resulting materials were stored in 100-mL polyethylene bottles until needed. For the hyperspectral analyses, the peat samples were air-dried, crushed in a mortar and pestle, and passed through a 2-mm sieve.

2.4 Sample Packing and Bulk Density

To carry out the hyperspectral analysis, soil samples were placed in 47-mm-diameter air-tight Petri dishes (Fisher brand; Fisher Scientific, Pittsburgh, PA, USA). The volume of the Petri dishes ($13.02 \pm 0.14 \text{ cm}^3$) was determined gravimetrically by filling the bottom half of the dish with deionized–distilled water. The soil samples were weighed into the Petri dish to assure a constant bulk density within each soil series of 1.31, 1.00, and 0.38 g cm^{-3} for the Arkport, Hudson, and Elba samples, respectively.

2.5 Hyperspectral NIR Analyses

The different samples were analyzed with a Fieldspec[®] Pro near-infrared (NIR) spectroradiometer (model FSP 350-2500P; Analytical Spectral Devices; Boulder, CO,

USA) in the wavelength range of 1,000–2,500 nm. Diffuse reflectance spectra were collected with a light source located 2 cm over the bare soil surface. For each sample, ten spectra were collected, then the sample was rotated randomly and ten more spectra were collected. The process was repeated once more for a total of 30 spectra (ten at each orientation). This rotation of the sample was deemed necessary to compensate for any bias that may be caused by the marked heterogeneity of the light source (Fig. 1).

At the beginning of each analytical session, the instrument was optimized according to the instructions in the manual. A dark current measurement was made. Then a white standard (Spectralon II; Labsphere, Inc., North Sutton, NH, USA) was analyzed and the instrument optimized. The Spectralon II white standard was then treated as a sample and 30 spectra were collected. The procedure was repeated for two internal laboratory standards: kaolinite clay (H-1, Murfreesboro, Arkansas; Ward's Natural Science, Rochester, NY, USA) and mineral soil from NY State identified as Soil 6709-17. The Spectralon II standard was inserted after every five to six samples to verify that its spectrum had not significantly shifted from that collected at the beginning of the run. After every series of samples associated with a given soil, spectra were again collected for the three standard samples. Spectra were also collected for the standards at the end of every session

Table 2 Zn and Cd concentrations in metalliferous peat soils

Sample #	Zn (mg kg^{-1})	Cd (mg kg^{-1})	Source
1	155	1.48	Field
2	335	1.54	Blended
3	671	1.66	Blended
4	1,355	1.90	Field
5	2,767	3.47	Field
6	3,435	5.05	Field
7	3,777	4.89	Field
8	5,411	8.50	Blended
9	6,767	10.9	Blended
10	8,122	13.2	Blended
11	9,082	14.9	Field



Fig. 1 Photograph of the light spot produced by the Fieldspec[®] Pro near-infrared (NIR) spectroradiometer, showing that it is spatially uneven

to ascertain the absence of instrumental drift during the measurements.

2.6 Statistical Analysis

To determine if sample rotation had a significant influence on observed NIR spectra, the ten replicate reflectance measurements obtained at each position of the sample at each wavelength were compared via analysis of variance. The use of a method of “analysis of variance by ranks”, also known as the non-parametric Kruskal–Wallis test (Kruskal and Wallis 1952; Zar 1999), obviated the need to check for normality. In cases where this test resulted in a rejection of the null hypothesis (H_0 =equality of the means of the reflectance signals at the three sample positions), at a specified significance level (e.g., $\alpha=0.01$), a different test was run to determine the groups of replicate measurements among which significant differences occurred. This second test involves non-parametric Tukey-type multiple comparisons among means (Zar 1999), using the Nemenyi test.

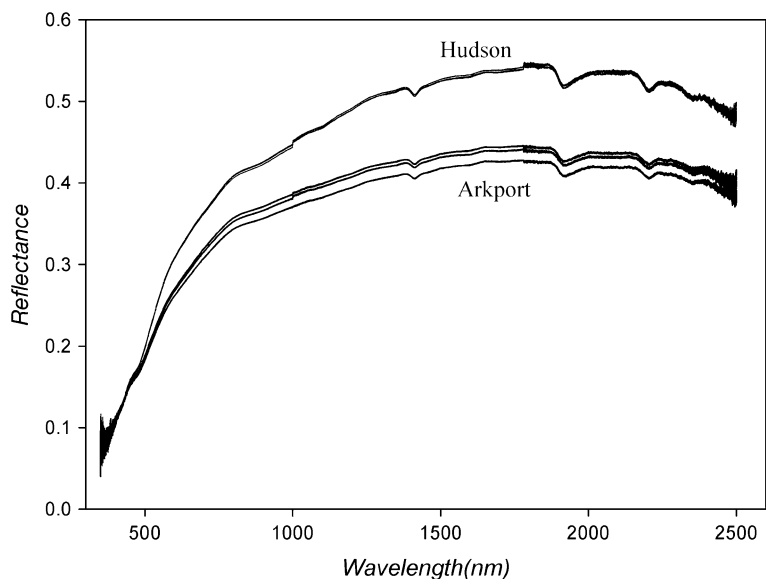
Comparisons among experimental spectra obtained for samples within a given soil series are made using the same procedure, i.e., using the non-parametric Kruskal–Wallis test followed by non-parametric Tukey-type multiple comparisons. This procedure was applied to the original spectra and to transformed data resulting from the application of several spectral preprocessing

techniques. The original reflectance (R) data were first transformed into absorbance [$A = \log_{10}(1/R)$] and Kubelka–Munk units [$KM = (1 - R)^2/2R$]. The first and second derivatives were then calculated using Savitzky–Golay smoothing with a cubic spline fit of the spectral responses (reflectance, absorbance, and KM) (Savitzky and Golay 1964).

3 Results and Discussion

Reflectance measurements appear to be affected differently by the rotation of the samples, depending on the soil considered (Fig. 2). Superposition of all ten replicate spectra, for the three sample orientations considered, leads to very little scatter for the Hudson and Elba soil samples, as a rule. By contrast, for a number of the Arkport soil samples, the three groups of ten replicates tend to be more distinct, and in some cases, as illustrated in Fig. 2, are significantly different from each other (at the 0.01 probability level) at almost all wavelengths, except at the extreme ends of the spectral range considered (below 500 nm and above 2300 nm). Visual inspection did not reveal any clear morphological reason for this significance of rotation in the case of the Arkport samples. It was therefore decided that the mean of the 30 individual spectra obtained for each sample would be systematically computed and used in further analyses. Not unexpectedly, the resulting mean spectra are associated with

Fig. 2 Illustration of the effect of sample rotation on the visible/near-infrared reflectance spectra of representative samples of the Hudson (sample 0–200, dry) and Arkport (sample 0–0, 11.2% moisture) soils. *Thin solid lines* are plotted for each of the 30 replicate measurements for each soil sample, corresponding to ten replicate measurements for three different orientations of the sample relative to the spectrometer



narrow confidence intervals in the Hudson and Elba soils, and with noticeably broader ones in the Arkport soils (Fig. 3).

Whether one goes down along columns, or follows laterally along rows in Table 1, the same type of graph is obtained for the changes in reflectance in the visible/near-infrared range. In Fig. 4a, the concentration of Zn increases progressively from 0 to 400 mg kg⁻¹, whereas that of Cu remains constant. The spectra for the five cases differ significantly from each other (at the 0.01 probability level), except the 400–0 and 400–200 spectra that are significantly different from each other only in selected subranges. For most of the spectral range in the near-infrared (beyond 700 nm), the spectra seem to be translationally invariant, vertically. However, this translation does not follow the Zn concentration monotonically. In order of increasing reflectance, the samples are ranked as 400–100 < 400–50 < 400–0 < 400–200 < 400–400, which seems to be random, unless one accepts the perspective that reflectance at first decreases with increasing Zn content from 0 to 100 mg kg⁻¹, then increases drastically for Zn content of 200 and 400 mg kg⁻¹ to reach reflectance levels higher than the control one with no Zn. However, this pattern does not hold for other columns or rows of Table 1. For example, for the series with no Zn and varying levels of Cu (Fig. 4b), the samples are ranked as 50–0 < 100–0 < 200–0 < 400–0 < 0–0 in order of increasing reflectance. Furthermore, the top spectrum in Fig. 4b,

for the control (0–0 case), coincides almost perfectly with the 400–400 spectrum in Fig. 4a. All spectra for the Hudson soil fit in the band between the 400–400 and 400–100 spectra in Fig. 4a, with no noticeable pattern of any kind between these two extremes in relation to either Cu or Zn concentration.

Similar observations are made in the Arkport soil samples, except that, in this case, as suggested by the broader confidence intervals in Fig. 3, fewer of the mean spectra are significantly different from each other. Typically only the extreme spectra, associated with the highest and lowest reflectances along a given column or row of Table 1, are significantly different from each other (at the 0.01 probability level). For example, in the sequence associated with the 400 mg kg⁻¹ Cu column in Table 1, only the spectrum with the lowest reflectance (400–50) and the one with the highest reflectance (400–100) differ significantly from each other, while any other pair of spectra is statistically indiscernible (Fig. 5a). In fact, the other three spectra (for the 400–0, 400–200, and 400–400 samples) are virtually superposed for much of the spectral range considered, except near 1,500 nm. The same situation occurs for the sequence with no Zn (Fig. 5b). In this case, the lowest reflectance is found for the 50 mg kg⁻¹ Cu sample, whereas the highest one is obtained for the 200 mg kg⁻¹ Cu sample. In between, the spectra are ranked in order of increasing reflectance as 50–0 < 0–0 < 100–0 < 400–0 < 200–0, which indicates that the mean spectra do not follow

Fig. 3 Illustration of the effect of sample rotation on the visible/near-infrared reflectance spectra of representative samples of the Hudson (sample 0–200), Arkport (sample 0–0), and Elba (sample 11) soils. The *thick solid lines* correspond to the means of 30 replicates for each soil, and the *thin lines* represent the mean plus or minus one standard deviation

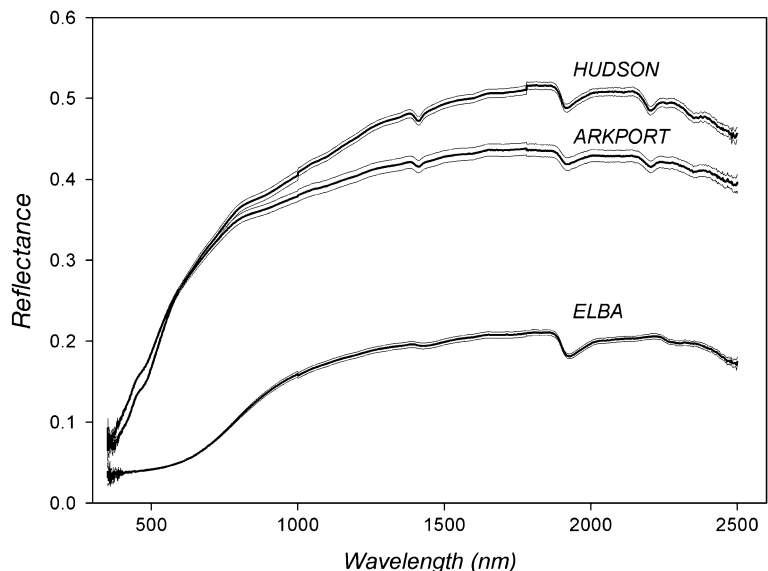
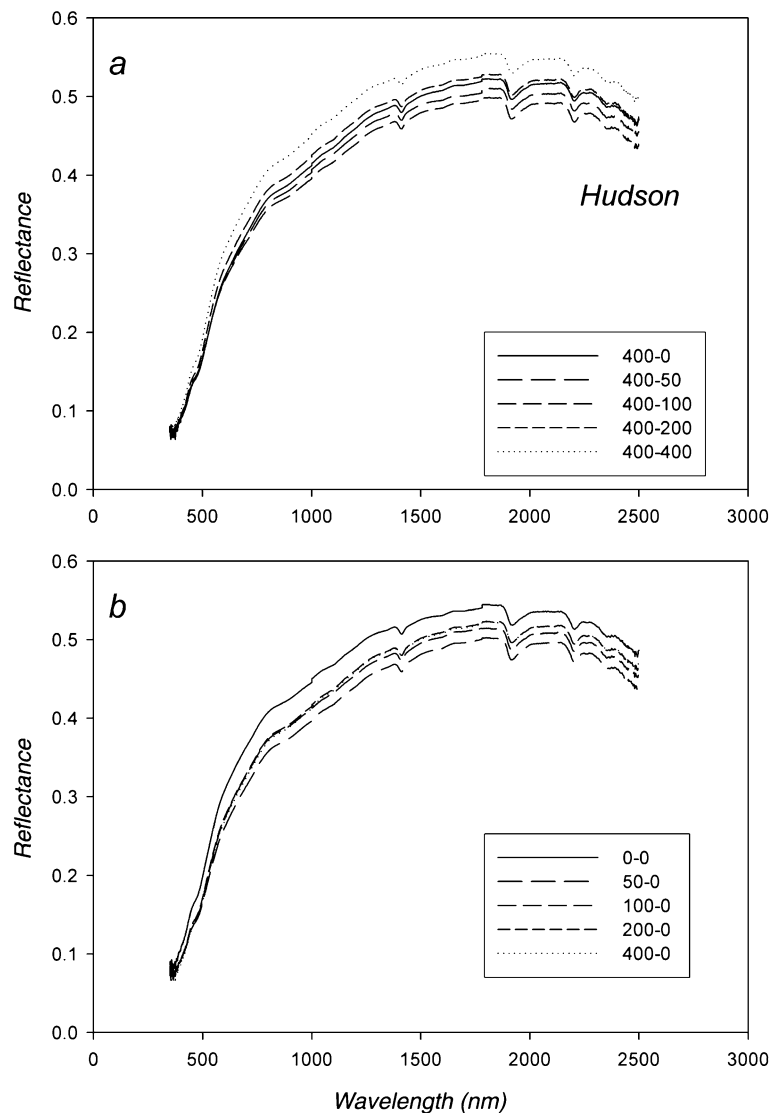


Fig. 4 Relationship between reflectance and wavelength in the visible/near-infrared for representative Hudson soil samples containing **a** 400 mg kg⁻¹ of Cu and varying concentrations of Zn between 0 and 400 mg kg⁻¹, and **b** varying concentrations of Cu between 0 and 400 mg kg⁻¹ and no Zn



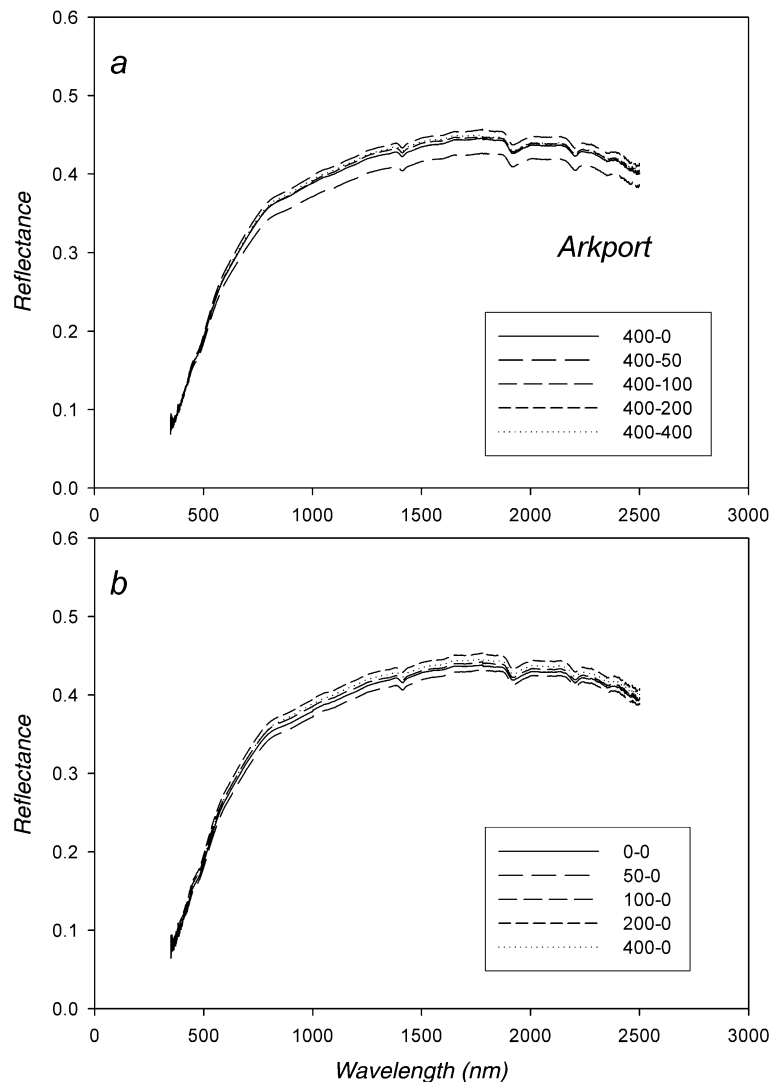
the soil Cu concentration in any way. Again, overall, as with the Hudson soil, the spectra for the different Cu–Zn combinations in the Arkport samples appear to fall in a relatively narrow band, within which there does not seem to be any noticeable pattern.

Even when soil samples with equal concentrations of Cu and Zn ranging from 0 mg kg⁻¹ to a highly contaminated 3,200 mg kg⁻¹ are considered (Fig. 6), there is no observable pattern in the reflectance spectra. In the Hudson soil samples, for example, the spectra are ranked 0–0 < 100–100 < 50–50 < 200–200 < 1,600–1,600 < 400–400 < 3,200–3,200 < 800–800 in increasing order of reflectance (Fig. 6a), whereas in the Arkport soil samples, reflectance increases in the

order 0–0 < 1,600–1,600 < 50–50 < 100–100 < 400–400 < 200–200 < 3,200–3,200 < 800–800 (Fig. 6b). Only the metal concentrations corresponding to the spectra at the high and low end coincide for the two soils, which given the random pattern of the rest of the spectra may be coincidental rather than significant. This indicates that NIRS is not sensitive to the presence of Cu and Zn in soils even at concentrations well beyond the trace levels (<100 mg kg⁻¹) generally seen in soils.

Furthermore, unlike chemical extraction analyses, which report large differences in the metal extractability of long-contaminated or field-aged soils and soils that have been recently spiked with metal salts in

Fig. 5 Relationship between reflectance and wavelength in the visible/near-infrared for representative Arkport soil samples containing **a** 400 mg kg⁻¹ Cu and varying concentrations of Zn between 0 and 400 mg kg⁻¹, and **b** varying concentrations of Cu between 0 and 400 mg kg⁻¹ and no Zn



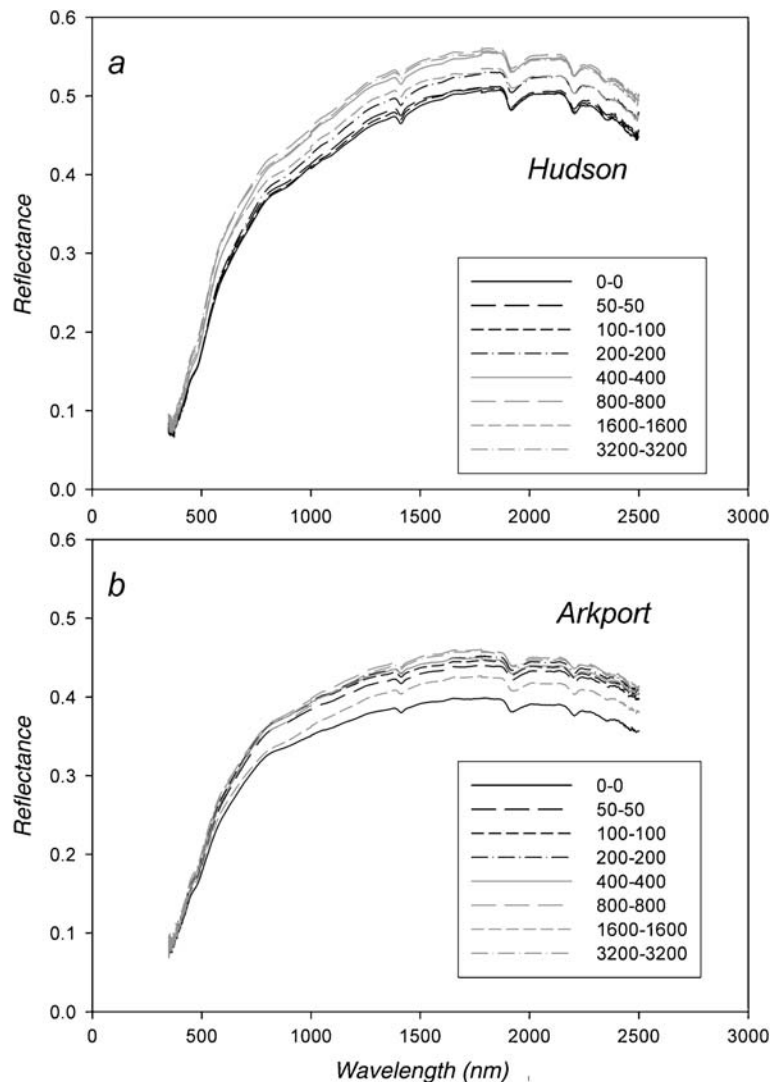
the laboratory at equivalent metal loadings (Kim 2006), there is no obvious difference or pattern in the reflectance spectra of the two types of metal-contaminated soils used in this study (Fig. 6). As indicated in Fig. 7, the variation between the reflectance spectra of soils freshly spiked with Cu and Zn and the field-aged metal-contaminated soils is not significantly different from the variation between replicate samples of the same soil.

Metals in soils may be present in many different forms. They may, for example, be part of mineral structures, be covalently bonded to specific sorption sites or weakly held at non-specific exchange sites on soil mineral or organic surfaces, or be precipitated on soil surfaces (e.g., Jacobson et al. 2005a, b, 2007;

Qureshi et al. 2003). The processes are significantly influenced by the type of soil, the nature of the metal, and the amount of the metal loaded. In the freshly spiked soils with Cu and Zn metal loadings of 400–3,200 mg kg⁻¹, for example, it is expected that non-specific mechanisms such as precipitation and cation exchange govern the chemical forms of the metals (Kim 2006). The random pattern of the reflectance spectra for the freshly spiked samples (Fig. 6) suggests that no diagnostic features are associated with the presence of precipitated salts, at least up to a total of 6,400 mg kg⁻¹ in soil.

In the field-aged metal-spiked soils, on the other hand, we would expect a certain degree of time-dependent change in the metal chemistry due to the

Fig. 6 Relationship between reflectance and wavelength in the visible/near-infrared for increasing concentrations of Cu and Zn ($0\text{--}3,200\text{ mg kg}^{-1}$ for each metal) in **a** Hudson and **b** Arkport soils. The entries in the index correspond to different Cu and Zn contents

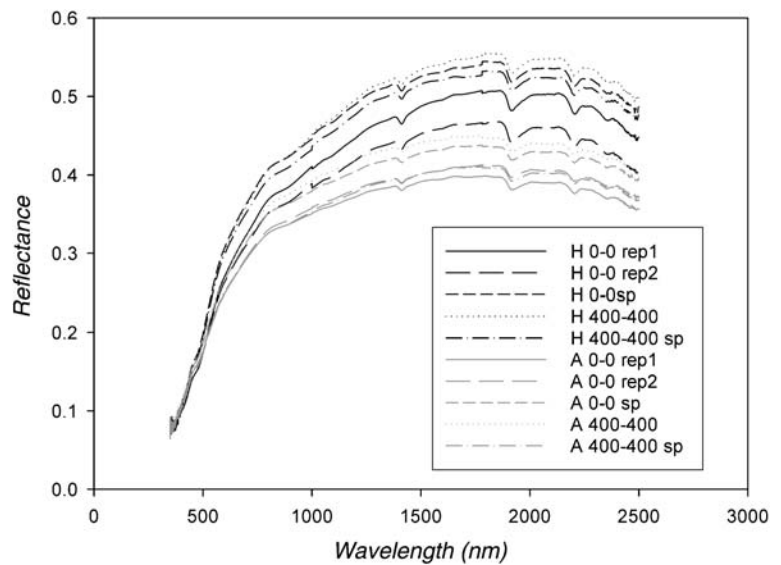


redistribution of Cu and Zn to less accessible sorption sites over time. This is consistently supported by results obtained from both chemical analyses and bioassays using the same soils (Kim 2006). In the NIRS spectra (Fig. 6), however, there is no differentiating feature or pattern that distinguishes between the metal loading and sorptive processes. Thus, the random pattern of the spectra in Fig. 6 indicates that there is no diagnostic feature associated with the chemical form and/or distribution of Cu and Zn in the Arkport and Hudson mineral soils.

Even when air-dried, the very hydrophilic Elba soil contains a sizeable amount of moisture. The presence of water causes strong absorbance in a very characteristic region of the spectra, at about

1,900 nm (Fig. 8), unlike in the Hudson and Arkport soils where this absorbance is far less prominent. In other respects, however, the various spectra for the Elba soil exhibit many of the same features already found in Figs. 4 and 5. As in previous graphs, the spectra in Fig. 8 do not follow any particular order that would be consistent with the amount of Zn and Cd present in the samples. At a wavelength of 1,500 nm, the ranking in the order of increasing reflectance is $4 < 11 < 1 < 8$. The latter two spectra are not significantly different from each other over most of the range of wavelengths considered. In fact, these top two spectra cross over at approximately 1,750 nm, causing the order of the spectra to be even more haphazard.

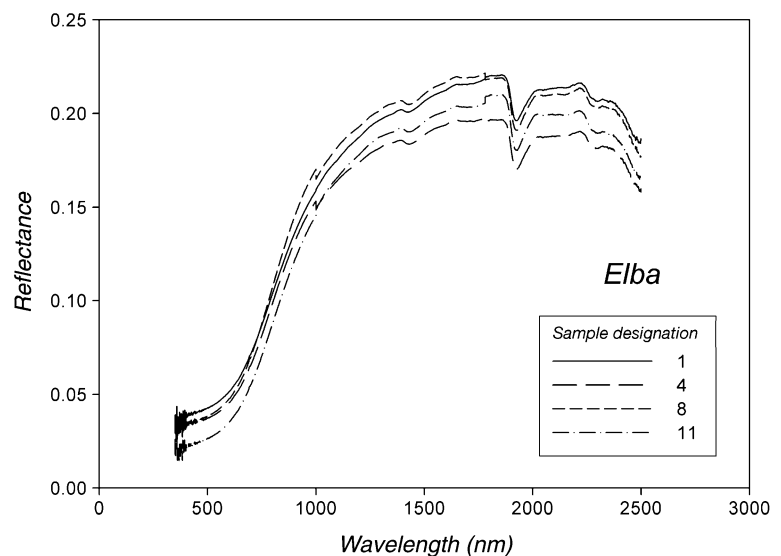
Fig. 7 Relationship between reflectance and wavelength in the visible/near-infrared for the Hudson and Arkport soils freshly spiked with Zn and Cu, and for the soils containing aged metals. The entries in the index correspond to different Cu and Zn contents. The suffix “sp” denotes freshly spiked soils



One might argue with the above analysis of the original NIR spectra of the different samples that in spite of the lack of a pattern among the spectra that would be consistent with the content of the soils in Zn, Cu, or Cd, there may still be some subtle differences in the shape of the spectra in specific regions, which can only be revealed by computing first derivatives, via wavelet analysis, or through a combination of these two approaches. None of the spectral transformations that were carried out, however, suggested any such fine detail. The two graphs of Fig. 9, for two different sets of samples, illustrate the type of result obtained. In

both cases, the first derivatives of the spectra exhibit regions of wide fluctuations, with no detectable structure, and regions of almost complete coalescence of the curves, for example in the vicinity of the two absorbance peaks at about 1,470 and 1,900 nm, associated with the presence of water (insets in Fig. 9). In neither situation (of apparently random noise or coalescence) is there any trend associated with the trace metal content of the samples, nor is there any other local feature of the first derivatives of the spectra that is directly correlated with trace metal content, regardless of how this parameter is quantified.

Fig. 8 Relationship between reflectance and wavelength in the visible/near-infrared for representative Elba soil samples



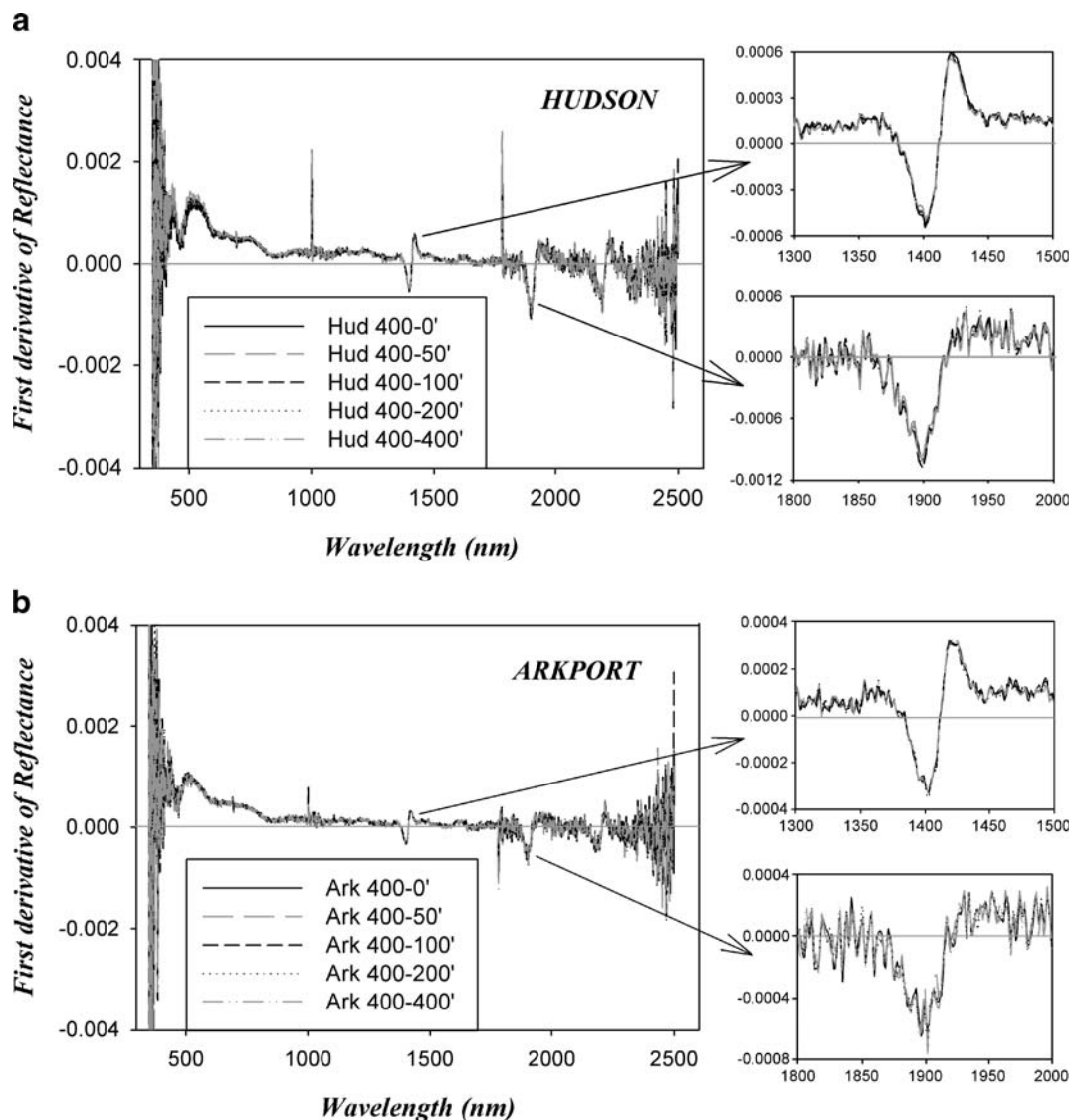


Fig. 9 a Left: graph of the first derivative of the reflectance visible/near-infrared spectra of the Hudson soil samples whose original spectra are plotted in Fig. 4b. Right: magnifications of two regions of the graph, showing quasi-perfect coalescence of

the different spectra. **b** Left: graph of the first derivative of the reflectance visible/near-infrared spectra of the Arkport soil samples whose original spectra are plotted in Fig. 5a. Right: magnifications of two regions of the graph

4 Conclusions and Practical Consequences

The experimental results described in this article provide conclusive evidence that the trace metal content of the three soils considered, a silt loam, a sandy loam, and a metalliferous peat, does not lead to singular or diagnostic features in any specific region of the NIR spectrum, as would be revealed for example in graphs of the first derivative of the reflectance. This rules out the possibility for trace

metal content to be considered a “primary” parameter for NIRS, as defined in the “Introduction”. Even though spectra obtained with samples differing in their trace metal content are in some cases significantly distinct from each other, the ordering of the spectra never varies monotonically with trace metal content in any recognizable pattern. Therefore, trace metal content is not a “secondary” parameter for NIRS either. Evidence suggests that, following the “surrogate calibration” hypothesis of Shenk et al.

(1992), trace metal content is a tertiary parameter. In some specific circumstances, it may be that the amount of trace metals contained in a given soil, or given soils in a well-circumscribed geographic region, may be statistically correlated with the oxide or organic matter content of the soil(s). However, since NIR sensors are not sensitive to trace metals, one should not expect in general that individual NIR measurements will provide a reliable estimate of trace metal content. At this point, it is unclear whether a similar conclusion would apply to other soil compositional parameters, like the concentrations of nitrogen, calcium, magnesium, or potassium.

The “tertiary” nature of trace metal content in soils presents one advantage, which may prove significant in the future. With societal concern about global warming increasing rapidly, and in particular with heightened attention focused on the potential feedback of soil carbon losses on global climate change (Baveye 2007), a need should arise in the near future to closely monitor soil carbon stocks at local and regional scales. NIRS is a likely candidate for this type of monitoring, given the strong effect of soil organic matter on reflectance in the near infrared, and the fact that NIR measurements could be easily scalable from virtually point measurements to satellite-based measurements at a large spatial scale (Wu et al. 2009a, b). In that respect, the results obtained here indicate that NIR measurements of soil carbon will not suffer from interference due to the presence in some soils of high levels of trace metals, either naturally or because of extensive pollution. This clears at least one hurdle for the field application of NIRS.

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