

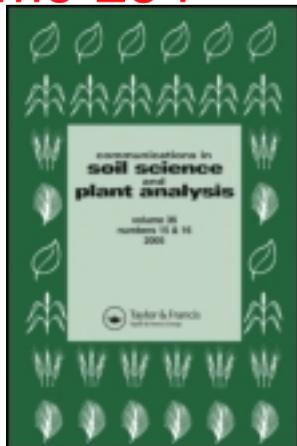
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### Hyperspectral Visible and Near-Infrared Determination of Copper Concentration in Agricultural Polluted Soils

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# Hyperspectral Visible and Near-Infrared Determination of Copper Concentration in Agricultural Polluted Soils

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*The objective of this research was to develop a hyperspectral imaging system for estimating copper concentration in soils as an alternative to standard chemical analyses and to evaluate the analytical accuracy of the system using the visible–near-infrared and near-infrared regions. Hyperspectral imaging is a complex technology providing elevated information content. This work was carried out on air-dried <2-mm soil fraction contaminated by adding 20 mL of copper sulfate at concentrations ranging from 0 to 1000 mg of copper per kg of soil. The samples were scanned in random order and with orientation using visible–near-infrared and near-infrared spectrophotometers. A range of partial least squares regression models derived from the spectral arrays were tested on their ability to predict copper concentration. Significant correlations between predicted and known chemical concentrations were achieved with a correlation coefficient of 0.93 for the visible–near-infrared and 0.77 for the near infrared.*

**Keywords** Agricultural polluted soil, copper, hyperspectral imaging, partial least squares, vineyard

## Introduction

Copper (Cu) is a frequent soil contaminant because of its wide use in agriculture (Alva, Huang, and Paramasivam 2000) and industry and high concentration in mine spoils (Arias et al. 1998). Although it is an essential element, high Cu concentration is potentially toxic to microorganisms, inhibits soil enzyme activity (Bäath 1989; McGrath, Zhao, and Lombi 2002; Sauvé 2006), and is phytotoxic and negatively correlated with plant growth parameters (Alva, Huang, and Paramasivam 2000; Ali et al. 2004; Bes and Mench 2008).

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The pollution of agricultural soil by Cu commonly occurs through the addition of contaminated waste matter, mineral fertilizers, and some pesticides. Generally, these compounds have been used to control fungal diseases as mildew, leaf spots, and blights in orchards, vineyards, and vegetable crops (Dell'Amico et al. 2008). Moreover, elevated levels of Cu in European agricultural soils result from applications of manure or sewage sludge. European Community regulations (EEC 1986) limit soil Cu to 50 mg kg<sup>-1</sup> where sewage sludge is to be spread. Copper originating from the intensive application of Cu-based fungicides belongs to the most important contaminants of vineyard soils as its concentrations exceed European legislative limits in the majority of these (Komárek et al. 2010).

The Italian Association between Public Agrochemical Laboratories (SILPA) was started in 1994 to collect soils samples in vineyards and determine if Cu is linked by superficial layers or is partially leached through deeper horizons. A decreasing gradient of Cu was found passing from superficial to deeper layers (Deluisa et al. 1996). Generally, the toxicity of Cu depends also on the depth of the root system (Magalães, Sequeira, and Lucas 1985). Because copper bioavailability is influenced not only by soil physical and chemical properties (Boon et al. 1998; Wenger and Gupta 1998; Alva, Huang, and Paramasivam 2000) but also by environmental factors such as climate, biological population, and source of contaminants (Yaron, Calvet, and Prost 1996; McLaughlin et al. 2000), correlation between total and bioavailable Cu cannot be predicted accurately (Pietrzak and McPhail 2004). As reported by Pietrzak and McPhail (2004), in recent decades a great number of sequential extraction techniques, such as fractionation and portioning, have been developed to study the physical–chemical forms in which Cu exists in soils. Moreover, agricultural and environmental planning requires data on soil properties for activities such as nutrient (Islam et al. 2003), carbon management (Garten and Wulschleger 1999), and land-use change management (Zornoza et al. 2008).

The spatial and temporal resolutions of soil sampling to acquire these data are limited by the cost and time required for traditional soil analysis. Practical methods that can rapidly estimate soil properties are needed to improve quantitative assessments of land-management problems (Shepherd and Walsh 2002) and to make precision soil management feasible (Viscarra Rossel and McBratney 1998a). Recent developments in imaging spectrophotometry that digitally captures and processes reflectance spectra to quantify soil properties are now desirable developments from spectroscopic techniques [e.g., mass spectroscopy (MS), nuclear magnetic resonance (NMR), visible (VIS), near-infrared (NIR), and mid-infrared (MIR) spectroscopy] as they offer alternatives to improve or replace conventional laboratory methods of soil analysis (Janik, Merry, and Skjemstad 1998). A great number of these techniques are nondestructive, preserve the integrity of the soil system, and provide larger amounts of inexpensive spatial data (Viscarra Rossel et al. 2006). The most recent advances in quantifying soil properties have focused on using narrow waveband VIS-NIR sensing (Viscarra Rossel et al. 2009), while the state of the art in optical sensing for this type of problem has started to encompass hyperspectral sensing (Ben-Dor, Irons, and Epema 1999).

Hyperspectral imaging is a complex technology that provides elevated information content while being rapid, nondestructive, and cost-effective. Hyperspectral sensors collect information as sets of “images.” Each image represents a range of the electromagnetic spectrum and is referred to as spectral band. These images are then combined to yield a three-dimensional hyperspectral cube for processing and analysis. The technique integrates conventional imaging and spectroscopy to obtain both spatial and spectral information from an object within a large field of view (FOV). Nowadays hyperspectral remote sensing is a good technology for characterizing soil properties (Lagacherie et al. 2008; Gomez,

Viscarra Rossel, and McBratney 2008) but proximal imaging applications are still underdeveloped. Among the hyperspectral techniques thus far examined in the laboratory, VIS-NIR and NIR have been shown to have potential as rapid, nondestructive approaches for analysis of several soil properties, including water, carbon, and macronutrient contents. One of the first applications using NIR was developed to estimate soil fertility in terms of nitrogen (N), phosphorus (P), and potassium (K) content (Gillon, Houssard, and Joffre 1999).

There is a particular interest in complementing current methodologies employed in soil surveying using proximal sensing as an input for predictive soil mapping. Although proximal sensing techniques tend to provide less accurate measurements than conventional laboratory analysis, hyperspectral imaging facilitates the collection of larger amounts of data using cheaper and less time-consuming methods and has the potential to reduce any accuracy deficit. Developments should enable proximal soil sensors to improve the efficiency of soil data collection and provide more information on soil spatial variation than is achieved by conventional surveying where relatively few very accurate measurements are performed (Viscarra Rossel and McBratney 1998b).

The objective of this research was to develop a hyperspectral imaging system for estimating Cu concentration in agricultural polluted soils ( $>50 \text{ mg kg}^{-1} \text{ Cu}$ ) as an alternative to the standard chemical analyses and to evaluate the analytical accuracy of the system using the VIS and NIR regions.

## Materials and Methods

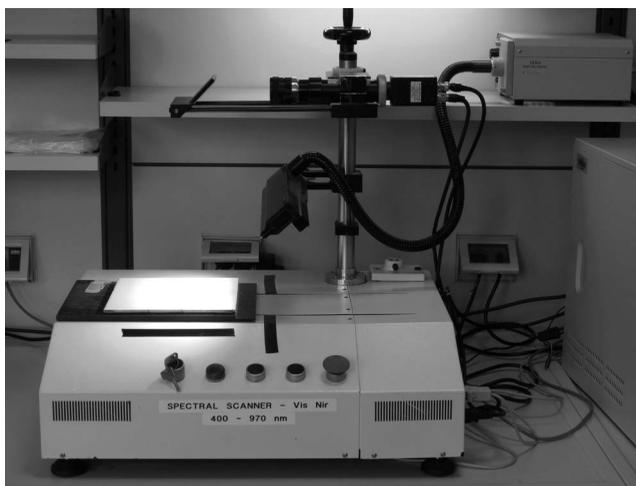
### *Soil Preparation*

For this study, we used an agricultural soil from the experimental farm of the University of Tuscia, located in Viterbo (central Italy). It is a conventionally managed soil in a randomized block design with three replicated plots of  $108 \text{ m}^2$ . The soil is clay loam and classified as Typic Xerofluvent (Lagomarsino et al. 2009). After removal of the litter layer, three soil cores from each block were taken inside each plot at 20 cm deep and then pooled together. Soil was pretreated by air drying, disaggregating, sieving to  $<2 \text{ mm}$ , and crushing with a planetary ball mill (RETSCH PM 100, RETSCH GmbH, Haan, Germany). The homogenized soil was then divided into 20 accurately weighed samples of approximately similar weights. The samples were then contaminated with Cu by adding 20 mL of copper sulfate solution ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) at concentrations ranging from 0 (control) to 1000 mg of Cu per kg of soil. All samples were oven dried at  $65^\circ \text{C}$  for 48 h to reduce moisture content to around 6% prior to spectrophotometric analysis.

### *Spectrophotometer Analysis*

Each of the 20 Cu-contaminated samples was poured into three borosilicate optical-glass Petri dishes (Duraplan) to a depth of 1 cm. All 60 Petri dishes were placed on a black background, and the images were acquired for the hyperspectral analysis. The acquisitions were repeated after 10 days and after 20 days. For each hyperspectral image, an operator selected two regions of interest (ROIs) to measure the mean VIS-NIR and NIR spectral reflectance. A total of 360 spectral measurements formed the dataset for subsequent analysis.

The imaging systems with VIS-NIR and NIR spectrophotometers (Figure 1) were composed of four parts: (1) a sample transportation plate (spectral scanner DV, Padua, Italy) (common to both systems); (2) a collimated illumination device (Fiber-lite, Dolan-Jenner, Mass., USA) with a 150-W halogen lamp and an illumination opening in the optical fiber measuring 200 mm long by 2 mm wide, positioned at  $45^\circ$  to the



**Figure 1.** Spectral images acquisition system.  $67 \times 50$  mm ( $300 \times 300$  DPI).

transportation plate for minimum light divergence (common to both systems); (3) an imaging spectrographs (VIS-NIR: ImSpec V10; NIR: ImSpec N17, Specim Ltd, Oulu, Finland) coupled with a standard C-mount zoom lens; and (4) digital camera [VIS-NIR: Teli charge-coupled device (CCD) monochrome camera, Toshiba-Teli CS8310BC; NIR: Pixelvision SU128 InGaAs IR camera]. The imaging spectrometers were used to acquire images ranging from 400 to 970 nm and from 1000 to 1700 nm. The two spectrographs are based on a patented prism-grating-prism (PGP) construction (a holographic transmission grating). The incoming line image (frame) was projected and dispersed onto the two-dimensional (2D) CCD. Each frame contained the line pixels in one dimension (spatial axis) and the spectral pixels in the other dimension (spectral axis), providing full spectral information for each line pixel. The reconstruction of the entire hyperspectral image of the sample was performed by scanning the sample line by line as the transportation plate moved it through the field of view. The resolution of the line image was 700 pixels by 10 bits for the VIS-NIR and 128 pixels by 12 bits for NIR. The system was operated in a dark laboratory to minimize interference from ambient light. All spectral values were expressed in terms of relative reflectance ( $R$ ), following Eq. (1):

$$R = \frac{r_s - r_b}{r_w - r_b} \quad (1)$$

where  $R$  is the relative reflectance of the sample at a given wavelength;  $r_s$  is the absolute signal value (radiance) measured for the sample at the wavelength;  $r_b$  is absolute signal value (radiance) measured at each wavelength for the black background (noise); and  $r_w$  is absolute signal value (radiance) measured at the wavelength for a standard white background (100% of reflectance). The hyperspectral images of the soil samples were analyzed using Spectral Scanner, v. 1.4.1 (DV Optics, Padua, Italy).

### **Chemometric Analysis**

Mean reflectance for each polluted soil sample was related to Cu concentration by partial least squares regressions (PLS). PLS is a soft-modelling method (Wold, Sjostrom, and

Eriksson 2001) for constructing predictive models when the factors are many and highly collinear (Menesatti et al. 2010). The predictive ability of the model is partially dependent on the number of the latent vectors (LVs) used and was assessed by the statistical parameters root mean square error (RMSE), standard error of prevision (SEP), and correlation coefficient ( $r$ ) between observed and predicted values and by calculating the bias.

Finally, we recorded the ratio of percentage deviation (RPD), which is the ratio of the standard deviation of the laboratory measured (reference) data to the RMSE (Williams 1987). It is the factor by which the prediction accuracy has been increased compared with using the mean of the original data.

Generally, a good predictive model should have high values for  $r$  and low values for RMSE and SEP. The model chosen was for the number of LVs that yielded the greatest  $r$ , minimum SEP for predicted and known Cu concentrations, and maximum RPD. We classified RPD values as follows: RPD values  $<1.0$  indicate very poor model and/or predictions and their use is not recommended; RPD values between 1.0 and 1.4 indicate poor model and/or predictions where only high and low values are distinguishable; RPD values between 1.4 and 1.8 indicate fair model and/or predictions that may be used for assessment and correlation; RPD values between 1.8 and 2.0 indicate good model and/or predictions where quantitative predictions are possible; RPD values between 2.0 and 2.5 indicate very good, quantitative model and/or predictions; and RPD values  $>2.5$  indicate excellent model and/or predictions (Viscarra Rossel et al. 2007).

The procedure for preparing the data for PLS analysis includes the following steps: (1) extraction of a subset of the raw spectra data, to be used as X-block variables; (2) X-block variables selection; (3) creation of concentrations values dataset to be used as reference or response variable (Y variable); (4) data fusion of the two datasets (Y and X-block) in one analysis dataset (AS); (5) SPXY (Harrop Galvao et al. 2005) separation of the AS into two subsets, one (MS) for the model (70% of AS) and one (TS) for the external validation test (30% of AS); (6) application of different preprocessing algorithms to X-block and Y; (7) application of chemometric technique (PLS): modeling and testing; and (8) calculation of efficiency parameter of prediction (RMSE, SEP  $r$ , and RPD both for model and test subset).

To divide the dataset into MS and TS subsets, for multivariate PLS analysis, the SPXY method (Harrop Galvao et al. 2005) was used. This method employs a partitioning algorithm that takes into account the variability in both X and Y spaces. To obtain the best prediction test, different X and Y preprocessing techniques were applied (Table 1).

## Results

The VIS-NIR- and NIR-derived models that yielded maximum  $r$  and RPD (calculated to RMSE of test subset) and minimum SEP for prediction of Cu concentration indicated good predictive models could be constructed. For VIS-NIR  $r = 0.9180$  in validation and calibration phase and  $r = 0.9319$  for independent test was achieved using 11 LV and resulting in a RPD = 2.7554 (Table 2, Figure 2). The model had low error value, s SEP = 108.35 and RMSE = 107.90, when validated. For the X-block abs were required preprocesses. For NIR,  $r = 0.7635$  after validation and calibration and  $r = 0.7662$  for independent test indicated a less accurate model with a RPD = 1.5385 (Table 2, Figure 3). For the X block, mean center followed by mean center weighting were required preprocesses, whereas for the Y block, autoscale was used. The SEP and RMSE values were greater than those observed for VIS-NIR models.

**Table 1**  
List of the different X and Y preprocessing techniques applied in the analysis

Label	Description
None	No preprocessing
Log 1/R	Transformation of reflectance in absorbance following log(1/R) formula
Diff1	Differences between adjacent variables (approximate derivatives)
Log10	Log 10
Logdecay	Log decay scaling
Baseline	Baseline (weighted least squares)
Abs	Takes the absolute value of the data
Autoscale	Centers columns to zero mean and scales to unit variance
Detrend	Remove a linear trend
GLS weighting	Generalized least squares weighting
Groupscale	Group/block scaling
Mean center	Center columns to have zero mean
Msc (mean)	Multiplicative scatter correction with offset, the mean is the reference spectrum
Median center	Center columns to have zero median
Normalize	Normalization of the rows
Osc	Orthogonal signal correction
Sg	Savitsky–Golay smoothing and derivatives
Snv	Standard normal deviate
Centering	Multiway center
Scaling	Multiway scale
Sqmns	Scale each variable by the square root of its mean

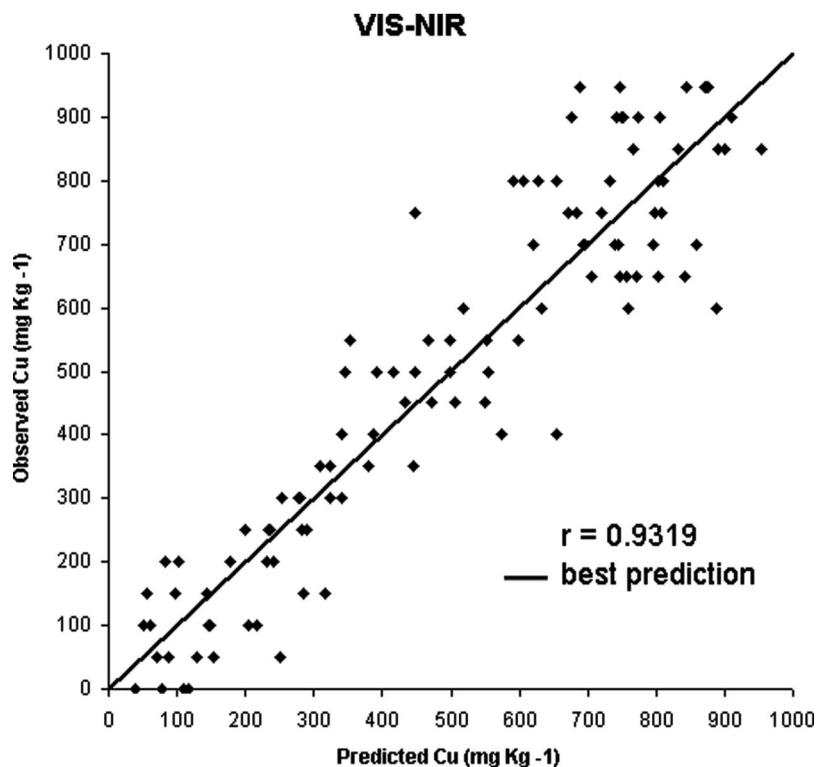
## Discussion

Soil is a complex, dynamic, living, natural entity and has complex interactions among physical, chemical, and biological factors (Doran and Safley 1997). Copper is strongly held by the soil, which means low leaching, especially with a dependence upon pH. These applications may lead to gradual accumulation of Cu in the soil and thereby increase Cu toxicity toward crops and beneficial microorganisms. Soil quality criteria and legislation on Cu levels in soils generally rely on data for total Cu content based on chemical analysis. Copper-based fungicides have been intensively used in Europe since the end of the 19th century to control vine fungal diseases, such as downy mildew caused by *Plasmopara viticola* (Komárek et al. 2010). In this experiment the soil and environmental conditions were controlled with extensive pretreatment. In fact, soil samples were finely fragmented to the size of mash to avoid gradients in the surface scan. Soil samples were brought to constant moisture. Indeed, water molecule presents, in the IR region, the resonance frequencies due to the presence of molecular functional group O-H. Under these conditions, the VIS-NIR hyperspectral imaging system offered better prediction of Cu concentration than the NIR system. Although both spectrophotometers, coupled with PLS data analysis, permitted rapid estimation of Cu concentration, the VIS-NIR was preferable. The extensive pretreatment required raises the question of whether the system would

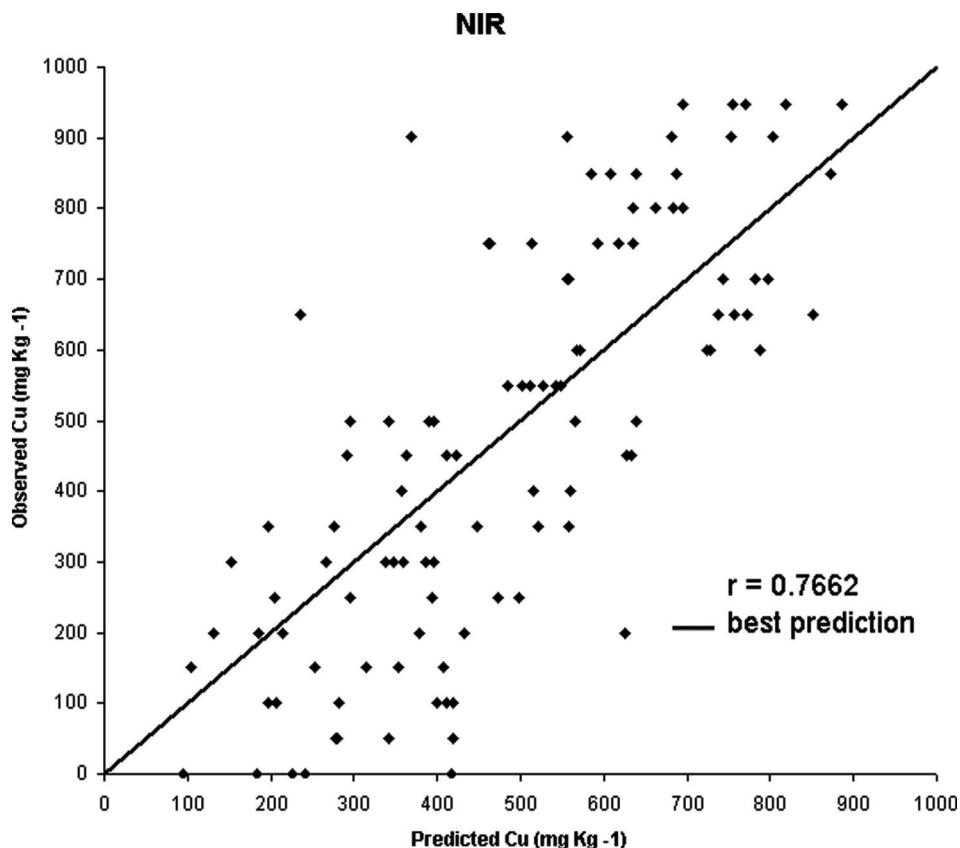
**Table 2**

Results of Partial Least Squares (PLS) multivariate analysis predicting the copper concentration in soil samples from spectral reflectance analysis. In the table are reported: number of Latent Vectors (LV), correlation coefficient ( $r$ ), Ratio of Percentage Deviation (RPD), Standard Error of Prediction (SEP) and Root Mean Squares Error (RMSE)

Parameters	VIS-NIR	NIR
<b>MODEL (70%)</b>		
N° LV	11	8
First pre-processing X-Block		mean center
Second pre-processing X-Block	abs	
Pre-processing Y-Block		autoscale
$r$ (observed vs predicted)	0.9180	0.7635
RPD	2.5218	1.5484
SEP	112.54	187.45
RMSE	112.31	187.08
<b>TEST (30%)</b>		
$r$ (observed vs predicted)	0.9319	0.7662
RPD	2.7554	1.5385
SEP	108.35	184.43
RMSE	107.90	184.41



**Figure 2.** Correlation between measured and predicted values of copper in the test-set observed for the visible-near infrared (VIS-NIR) spectral analysis (i.e., 30% of whole sample dataset).



**Figure 3.** Correlation between measured and predicted values of copper in the test-set observed for the near infrared (NIR) spectral analysis (i.e., 30% of whole sample dataset).

be suitable for precision agriculture because reducing pretreatment would surely reduce analytical accuracy (Alchanatis, Schmilovitch, and Meron 2005). However, acquiring more detailed information capturing spatial and temporal differences is clearly possible and should be cost-effective when compared to standard chemical analysis. The results indicate that VIS-NIR hyperspectral imaging has the potential to be developed, through appropriate engineering design, into a tool for optimized soil and land management, perhaps in conjunction with plant-sensing systems as developed by Menesatti et al. (2010).

Also variations due to moisture content, stones, soil peds, and heterogeneous distribution of soil material was eliminated by sample pretreatment, a necessary first step in system development (Bricklemyer and Brown 2010), the results indicate that the methodology has potential, given that the same spectra have the potential to be used to predict these soil characteristics (Bonifazzi, Menesatti, and Millozza 2004; Bonifazi et al. 2005), and thus there is scope to establish low-cost proximal hyperspectral imaging systems for precision agriculture, reclamation, and similar land and soil management. This is particularly important because aerial and satellite remote sensing, which provide an excellent means of determining variability of soil properties at the landscape scale, is limited by cloud cover and the low spatial resolution. A field-based proximal hyperspectral imaging system would overcome these issues and represents an exciting new frontier for soil research. Even if such systems are less accurate than conventional soil analysis techniques, proximal sensors will

facilitate the collection of larger amounts of spatial and temporal data because they are less costly, require less time (Viscarra Rossel and McBratney 1998b), and can build data set of multiple properties with the same sample support that will facilitate understanding of soil system processes.

## Conclusions

The objective of this research was to develop a hyperspectral proximal imaging system for sensing of Cu in agricultural polluted soils (concentrations  $>50 \text{ mg kg}^{-1} \text{ Cu}$ ). It was found that the VIS-NIR detector provided data that could produce the most accurate PLS prediction model for pretreated soils. The initial application of the system will be to investigate heavy-metal speciation and interactions with other soil properties to address practical problems for soil remediation, soil survey, and precision agriculture sampling. The benefit of the system will be reduced analysis costs, thus permitting increased spatial and temporal resolution for measurement of soil properties.

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