



# Prediction of low heavy metal concentrations in agricultural soils using visible and near-infrared reflectance spectroscopy

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## ABSTRACT

In order to monitor the accumulation of heavy metals effectively and avoid the damage to the health of agricultural soils, a promising approach is to predict low concentrations of heavy metals in soils using visible and near-infrared (VNIR) reflectance spectroscopy coupled with calibration techniques. This study aimed to (i) compare the performance of a combination of partial least squares regression with genetic algorithm (GA-PLSR) against a general PLSR for predicting low concentrations of four heavy metals (i.e., As, Pb, Zn and Cu) in agricultural soils; (ii) explore the transferability of GA-PLSR models defined on one subset of land-use types to the other types; and (iii) to investigate the predictive mechanism for the prediction of the metals. One hundred soil samples were collected in the field locating at Yixing in China, and VNIR reflectance (350–2500 nm) spectra were measured in a laboratory. With the entire soil samples, GA-PLSR and PLSR models were calibrated for the four heavy metals using a leave-one-out cross-validation procedure. The GA-PLSR models achieved better cross-validated accuracies than the PLSR models. For the transferability of GA-PLSR models, the soil samples were divided into three pairs of training sets and test sets from different land-use types. Three GA-PLSR models defined on the training sets had good transferability to the test sets, but nine GA-PLSR models were not successful. As for the predictive mechanism, besides the widely-used correlation analysis between OM and the metals, the relationship between the content of OM and the prediction accuracy of the metals was investigated and the similarity of the important wavelengths for OM and the metals was compared. The three methods verified that OM had a significant correlation with the predictions of the spectrally-featureless metals (Pb, Zn and Cu) from VNIR reflectance. We conclude that GA-PLSR modeling has a better capability for the prediction of the low heavy metal concentrations from VNIR reflectance, and it has a potential of transferability between different land-use types, and its accuracy is fundamentally influenced by OM.

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## 1. Introduction

In China, the human activities, such as mining, transportation, sewage disposal and fertilizing, have been posing an ongoing threat to the soil health over the last two decades (Wei and Yang, 2010). Moreover, the consumption of metal-polluted crops (e.g., rice, corn and soybean) grown in agricultural soils greatly raises the potential risks of food security and human health (Zhuang et al., 2009). Therefore, the determination of heavy metal concentrations of agricultural soils is necessary to monitor the health of agricultural soils and further to take preventative measures to avoid soil contamination.

Conventionally, the spatial distribution of heavy metal concentrations in soil is investigated based on numerous soil samples and laboratory analysis, which is time-consuming with high expense and low efficiency (Jarmer et al., 2008; Kemper and Sommer, 2002; Kooistra et al., 2003; Mouazen et al., 2007; Ren et al., 2009). Due to its rapidness,

inexpensiveness and non-destruction, visible and near-infrared (VNIR) reflectance spectroscopy coupled with calibration techniques has been developed to predict various soil properties, such as moisture (Gill et al., 2006), organic matter (Kooistra et al., 2001), clay (Gomez et al., 2008a), Fe (Ren et al., 2009) and heavy metals (Wu et al., 2005). Among the calibration techniques, partial least squares regression (PLSR) is considered as a common standard tool (Viscarra Rossel et al., 2006), and principle component regression (PCR) (Chang et al., 2001), stepwise multiple linear regression (SMLR) (Kemper and Sommer, 2002), back propagation neural network (BPNN) (Mouazen et al., 2010) and support vector regression (SVR) (Gill et al., 2006) were also employed by many studies. In order to simplify the calibration models and improve the prediction accuracy, PLSR has been combined with wavelength selection methods such as genetic algorithm (GA-PLSR) (Vohland et al., 2011) for predicting soil organic carbon and with interval partial least squares algorithm (iPLSR) (Inoue et al., 2012) for predicting nitrogen content in rice, but such approach has not yet been studied in the prediction of soil heavy metal concentrations according to our reviews.

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Hitherto the prediction of heavy metals has been focused on soils polluted by medium and high concentrations of heavy metals, for example, soils collected from sediment (Choe et al., 2008; Malley and Williams, 1997; Moros et al., 2009), alluvial (Clevers et al., 2004; Kooistra et al., 2001, 2004; Vohland et al., 2009; Wu et al., 2007), mining (Kemper and Sommer, 2002; Ren et al., 2009; Siebielec et al., 2004), urban (Pandit et al., 2010) and suburban (Wu et al., 2005) areas. Little attention has been devoted to predict low heavy metal concentrations of agricultural soils. Such prediction, however, is indispensable for monitoring soil health since a minor increase of heavy metal concentration may lead to large pollution levels (Pandit et al., 2010). In addition, most of the previous studies were carried out with soil samples from a homogeneous land-use type such as grassland (Vohland et al., 2009) and paddy field (Wu et al., 2007), without much consideration of soil samples from different land-use types.

Heavy metals in soil are deemed spectrally featureless, and most of them cannot be detected with VNIR reflectance spectroscopy at concentrations  $\leq 1000 \text{ mg kg}^{-1}$  (Wu et al., 2007). Therefore, it is not straightforward to derive heavy metal concentrations from VNIR reflectance of soils. Some studies have declared that there were significant correlations between heavy metals and spectrally-active properties of soils, such as organic matter (Kooistra et al., 2001; Malley and Williams, 1997; Moros et al., 2009; Vohland et al., 2009), clay (Kooistra et al., 2001) and Fe (Ren et al., 2009; Wu et al., 2005, 2007). Thus, such properties might play a bridge role in the mechanism of the prediction for soil heavy metal concentrations from VNIR reflectance. Various studies have explored the predictive mechanism and proclaimed that it was diverse with different soil conditions and properties (Malley and Williams, 1997; Wu et al., 2005).

Using VNIR reflectance acquired in laboratory, this study (i) applied the GA-PLSR modeling to predict low concentrations of heavy metals (i.e., As, Pb, Zn and Cu) in agricultural soils and compared its performance against general PLSR approach; (ii) explored the transferability of GA-PLSR models between different land-use types without extra calibrations; and (iii) investigated the predictive mechanism for the assessment of the metals in soils with three methods from different views.

## 2. Materials and methods

### 2.1. Study area

The study area is located at Yixing (Fig. 1), in the south of Jiangsu Province, China. It has distinctive seasons with an annual temperature of  $15.7 \text{ }^\circ\text{C}$  and a mean annual precipitation of 1177 mm (Zhang et al., 2005). According to the USDA Soil Taxonomy, the inceptisol dominates the study area. Yixing is a typical agricultural region, cropland distributing in the low-lying area, woodland and tea plantation spreading in the southern hills and low mountains, cereal dominating in the northern and western area, and vegetables (e.g., gingeli and soybean) growing in the eastern area.

### 2.2. Field sampling and pre-processing

A total of 30 sampling sites ( $30 \times 30 \text{ m}$ ) (Fig. 1) were set during August 11–14, 2010 in agricultural areas, which covered nine land-use types including gingeli (*Sesamum indicum* L.) cropland, corn (*Zea mays* L.) field, soybean (*Glycine max* Merr.) cropland, paddy (*Oryza sativa* L.) field, tea (*Camellia sinensis* L.) plantation, shrubland (*Llex Cornuta* Lindl.), arbor (*Cinnamomum camphora* Presl.) woodland, grassland (*Setaria viridis* Beauv.) and bare land. At each site, the surface soil samples (0–10 cm) were collected at three or four sampling points. The location of each sampling point was acquired using a Global Positioning System (GPS–Garmin Map 60cs) with an accuracy of about  $\pm 5 \text{ m}$ . As a result, a total of 100 soil samples were collected, and each sample was kept in a labeled sample bag.

All the soil samples were air-dried at room temperature for three days to standardize the moisture level, and the small stones and plant residues were removed. The 100 soil samples were ground with an agate mortar and passed through a 20-mesh sieve (0.84 mm) in order to minimize the impacts of particle-size on soil spectral reflectance (Chang et al., 2001; Kooistra et al., 2001). Afterwards, each soil sample was split into two sub-samples, one for laboratory spectral measurement and another one for chemical analysis of soil properties after passing through a 100-mesh sieve (0.15 mm).

### 2.3. Chemical analysis of soil properties

The pH, content of organic matter (OM), and concentrations of heavy metals including arsenic (As), plumbum (Pb), zinc (Zn) and copper (Cu) were measured with about 50 g soils. The pH was measured with potentiometry method, and the OM content was determined using potassium dichromate volumetric method (Jackson, 1960). Before the heavy metal concentrations measured, the soil samples were pre-processed by electric heating board acid ( $\text{HCL-HNO}_3\text{-HClO}_4$ ) digestion. The Pb, Zn and Cu concentrations were measured with an atomic absorption flame spectrometer (AAS), and the As concentration was measured using an atomic fluorescence spectrophotometry. In order to minimize the experimental errors, the national geochemical standard soil samples were used in the chemical analysis of the heavy metal concentrations (Wu et al., 2008).

### 2.4. Spectral measurement of soil samples

The reflectance spectra of the soil samples were measured in a laboratory using an ASD FieldSpec® 3 portable spectroradiometer (Analytical Spectral Devices, Inc., USA), which covers a spectral range of 350–2500 nm and offers data collection in 10 scans per second. The spectral measurements were made in a dark room in order to control the illumination conditions and reduce the effects of stray light. The following five steps were carried out to ensure the measurement accuracy: (i) for each sample, about 50 g soils were homogenized and smoothed on a glass utensil (2 cm height by 10 cm in diameter) to make the diffuse reflection maximized and to increase signal-to-noise ratio (Mouazen et al., 2010); (ii) a 50 W halogen lamp (Analytical Spectral Devices, Inc., USA) pointing at an angle of  $15^\circ$  to the vertical was mounted on a tripod about 40 cm above the nadir to ensure the uniform distribution of incident light; (iii) the fiber optic with a  $25^\circ$  field-of-view, was positioned in a pistol and mounted on a tripod 15 cm above the center of the observed sample, to reduce the impacts of background scattering on the soil reflectance spectra (Ren et al., 2009); (iv) a calibrated white Spectralon panel was systematically measured under the same conditions before the spectral measurement; and (v) 10 successive measurements were performed for each sample, and the measured values were averaged as the final spectrum.

### 2.5. Spectral pre-processing

Due to the large instrument noises, the spectral bands (350–399 nm and 2451–2500 nm) were first removed from the initial reflectance spectra of the soil samples to improve the signal-to-noise ratio. Afterwards, the remaining reflectance spectra were transformed into the absorbance ( $\log_{10} 1/R$ , R is reflectance) in order to reduce the nonlinearities and scattering effects (Gomez et al., 2008a; Kemper and Sommer, 2002). The spectra were then subjected to the Savitzky–Golay smoothing method with a second order polynomial fit and a window size of 7 data points. This method can reduce the impacts of random noise on the robustness of calibration models (Gomez et al., 2008a; Wu et al., 2005). All the transformations were implemented using MatLab software version 7.11.0 (The MathWorks, Inc., USA).

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