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Predicting cadmium concentration in soils using laboratory and field reflectance spectroscopy

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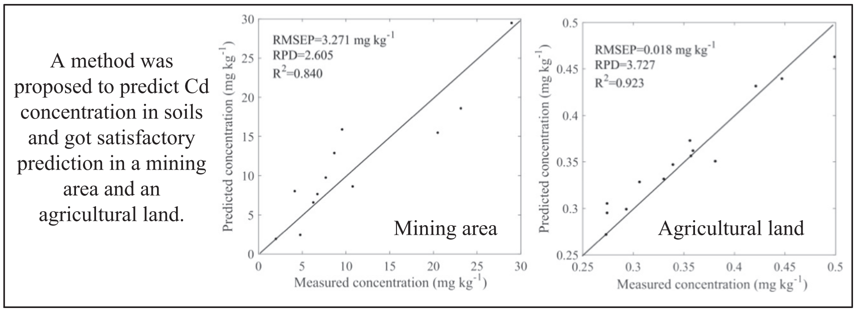
HIGHLIGHTS

- A method was proposed to predict Cd concentration in soils.
- The method achieved the prediction in different study areas.
- The method has the potential to be applied to field conditions.
- Distribution of Cd concentration for soil samples has impact on the prediction.

GRAPHICAL ABSTRACT



A method was proposed to predict Cd concentration in soils and got satisfactory prediction in a mining area and an agricultural land.

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ABSTRACT

Visible and near-infrared spectroscopy (VNIRS, 350–2500 nm) is a promising alternative to rapidly investigate soil contamination by heavy metals. To explore the possibility of predicting heavy metal concentration in soils using laboratory and field reflectance spectroscopy and examine transferability of the prediction method, 46 soil samples from a mining area, 42 soil samples from an agricultural land, and the corresponding two sets of field soil spectra were collected. Cadmium (Cd) was taken as an example in this study. The collected soil samples were air-dried, ground, sieved, and then used for laboratory spectral measurement and chemical analysis. Soil reflectance spectroscopy associated with organic matter was extracted from the VNIRS and used to predict Cd concentration based on strong sorption and retention of Cd on soil organic matter. Genetic algorithm (GA) was adopted for band selection, and the selected bands were used to calibrate the prediction model with partial least squares regression (PLSR). Compared with the prediction using entire VNIR region, the ratio of prediction to deviation (RPD) and the coefficient of determination (R^2) were improved from 1.473 and 0.508 to 2.997 and 0.881 for laboratory spectra and 1.437 and 0.484 to 1.992 and 0.731 for field spectra by using spectral bands associated with organic matter in the mining area. The RPD and R^2 values were improved from 1.919 and 0.707 to 3.727 and 0.923 for laboratory spectra and 1.057 and 0.036 to 1.747 and 0.646 for field spectra by the prediction method in the agricultural land. The improvement was further revealed by prediction of Cd concentration with a selected subset of soil samples from the mining area. The results suggest that predicting Cd concentration in soils with GA-PLSR using reflectance spectroscopy associated with organic matter is feasible and the prediction method could have the potential to be applied to field conditions.

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1. Introduction

Soil serves many essential functions in natural environment and satisfies basic needs of human society. Soil contamination by heavy metals has evolved into an environmental problem. The situation is more severe in regions with rapid urbanization and industrialization in the last several decades (Wong et al., 2002). The dominant sources of heavy metal pollution to agricultural soils are swage irrigation, fertilizer and pesticide, and mining activities (Luo et al., 2012; Wei and Yang, 2010). Heavy metal contamination in agricultural soils may increase these contaminant elements uptake by crops, which further increases human health risk through food chains (Cao et al., 2010; Khan et al., 2008). Heavy metals are notable for their tendency to be accumulated in selected tissues of the human body, and cadmium (Cd) is toxic even at low concentrations (Khlifi and Hamza-Chaffai, 2010).

The conventional method to investigate soil contamination by heavy metals is based on soil sampling in field and subsequent chemical analysis for heavy metal concentration in laboratory. The alternatives to measure heavy metal concentration in soil samples are atomic absorption spectrometry (AAS), inductively coupled plasma-mass spectrometer (ICP-MS), ICP optical emission spectroscopy (ICP-OES), and X-ray fluorescence (XRF). Reflectance spectroscopy of soil is a cumulative property derived from inherent spectral behavior of soil physical and chemical properties (Stoner and Baumgardner, 1981). Spectroscopic technique has several advantages over the conventional method, such as rapidity and relatively low cost (Kooistra et al., 2001; Viscarra Rossel et al., 2006). Furthermore, soil reflectance spectra can be measured in field and on airborne and spaceborne platforms which may provide information over large scales and describe the dynamic evolution of soil contamination.

Transition elements, such as Ni, Cu, and Cr, with an unfilled d shell can exhibit absorption features in the visible and near-infrared (VNIR, 350–2500 nm) region according to crystal field theory (Burns, 1993). However, heavy metals cannot be detected with reflectance spectroscopy in the VNIR region at relatively low concentrations in soil, regardless of the absorption features (Wu et al., 2007). Therefore, direct quantitative prediction of heavy metal concentration in soil using VNIR spectroscopy is not possible (Rathod et al., 2013). The risk of heavy metal contamination in soil depends on the concentration of pollutants in soil solution, which in return relies on the sorption and desorption equilibria that rule the partition of heavy metal between soil solution and soil solids, especially soil colloids (Covelo et al., 2007a). The most important colloids involved in heavy metal sorption are clays, metal oxides, hydroxides, and organic matter (Bradl, 2004). Absorption features in soil reflectance spectrum over the VNIR region are primarily associated with soil spectrally active constituents including iron oxides, clay minerals, water content, and organic matter, due to the vibration, bend, and stretch of chemical bonds (Viscarra Rossel and Behrens, 2010). Therefore, prediction of heavy metal concentration in soil using reflectance spectroscopy is achieved indirectly via the relations between heavy metal and soil spectrally active constituents including organic matter, clay minerals, and metal oxides (Kooistra et al., 2001; Rathod et al., 2013).

The potential of spectroscopic technique in prediction of heavy metal concentration in soil is widely recognized (Kemper and Sommer, 2002; Kooistra et al., 2001; Malley and Williams, 1997; Sun and Zhang, 2017; Wu et al., 2005). Considering future application of reflectance spectroscopy in soil science, predicting soil contaminant elements using field spectra (FS) and hyperspectral remote sensing images is the trend of the development. Reliability of predictions of soil contaminant elements using reflectance spectroscopy is also essential to investigate soil contamination. Therefore, transferability of the prediction method is another practical interest of the investigation. The transferability refers to the ability to predict soil contaminant elements under laboratory and field conditions and in different areas. However, most existing studies are carried out in one study area and using laboratory spectra (LS) of soil samples alone, which also makes it hard to study the transferability of the prediction method. Soil spectrally active constituents, such as organic matter and clay minerals, are predicted using FS measured with portable spectrometers (Kooistra et al., 2003; Nocita et al., 2011; Viscarra Rossel et al., 2009). The prediction of soil spectrally active constituents in field lays the foundation to predict heavy metal concentration in soil using FS, which further brings the possibility to examine the transferability of the prediction method.

Predictions of Cd concentration in soils are conducted using VNIR spectroscopy (Chen et al., 2015; Gholizadeh et al., 2015; Xia et al., 2007), without considering the detailed sorption and desorption of Cd on soil spectrally active constituents. Sorption of heavy metals on soil constituents is influenced by a variety of parameters, the most important ones being pH, type of heavy metal, heavy metal competition, and soil composition (Bradl, 2004). Soil reflectance spectroscopy associated with the spectrally active constituents that have strong sorption for zinc was used to predict zinc concentration in soil under laboratory condition (Sun and Zhang, 2017), which provides an alternative to predict contaminant elements in soil using reflectance spectroscopy. Studies on competitive sorption and desorption of heavy metals in soils indicate that the soils with strong sorption for Cd and high capacity to retain Cd exhibit high organic matter contents (Covelo et al., 2007b; Vega et al., 2006). Thus, based on the sorption and retention of organic matter for Cd, spectral bands associated with organic matter were used to predict Cd concentration in soils.

To explore the possibility of predicting heavy metal concentration in soils using laboratory and field reflectance spectroscopy and examine the transferability of the prediction method, two sets of LS of soil samples from a mining area and an agricultural land and the corresponding two sets of FS were used. Cd was taken as an example in this study. Spectral bands associated with organic matter were used to predict Cd concentration in soils. The four sets of reflectance spectra were used to explore the possibility of predicting Cd concentration in soils using spectral bands associated with organic matter. Soil spectra from the two study areas were used to examine the transferability of the prediction method in different areas, and the two sets of FS were used to examine the transferability of the prediction method from laboratory to field conditions.

2. Materials and methods

2.1. Study areas and soil samples

The mining area to collect soil samples and measure FS was in the vicinity of Shuikoushan lead/zinc mine in Hengyang City, Hunan Province, and southern China. A previous study on soil heavy metal pollution in Shuikoushan lead/zinc mine shows that there were serious degrees of Cd, Pb, and Hg pollution (Li et al., 2012). The agricultural land was in Baoding City, Hebei Province, and northern China. Climate type is subtropical monsoon climate in Hengyang City and warm temperate continental monsoon climate in Baoding City. The main terrain in the vicinity of the lead/zinc mine is mountains and hills, whereas plain is the main terrain in the agricultural land. The two study areas are shown in Fig. 1(a).

In Hengyang, FS were measured in the vicinity of Shuikoushan lead/zinc mine, and the corresponding topsoil samples at a depth of 0–20 cm were collected at the locations where the FS were measured, The FS measurement was conducted in November 2016 since the bare fields, needed for soil spectral measurement, are available in winter. A spade and polyethylene bags were used to collect soil samples in the mining areas. Forty-six topsoil samples and field soil spectra were collected in the area of 112°35′24″ E to 112°36′37″ E and 26°32′37″ N to 26°34′12″ N at altitudes below 200 m, as shown in Fig. 1(b). Soil sampling was carried out along roads, due to the main terrain in the vicinity of the lead/zinc mine are mountains and hills.