



Review

Visible and near-infrared reflectance spectroscopy—An alternative for monitoring soil contamination by heavy metals

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HIGHLIGHTS

- Visible and near-infrared reflectance spectroscopy can monitor soil heavy metals.
- Summary on mechanisms for estimating heavy metal concentrations.
- Discussions on three types of spectra and their roles in monitoring heavy metals.
- Comprehensive review on methods for monitoring heavy metals.
- Discussions on challenges in mapping soil contaminations with heavy metals.

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ABSTRACT

Soil contamination by heavy metals is an increasingly important problem worldwide. Quick and reliable access to heavy metal concentration data is crucial for soil monitoring and remediation. Visible and near-infrared reflectance spectroscopy, which is known as a noninvasive, cost-effective, and environmentally friendly technique, has potential for the simultaneous estimation of the various heavy metal concentrations in soil. Moreover, it provides a valid alternative method for the estimation of heavy metal concentrations over large areas and long periods of time. This paper reviews the state of the art and presents the mechanisms, data, and methods for the estimation of heavy metal concentrations by the use of visible and near-infrared reflectance spectroscopy. The challenges facing the application of hyperspectral images in mapping soil contamination over large areas are also discussed.

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1. Introduction

Soil is a dynamic, open, and complex system occurring in the upper few meters of the earth's surface, at the interface of atmosphere, biosphere, hydrosphere, and geosphere [1]. A major function of soil is to provide fundamental natural resources for the survival of plants, animals, and the human race [2]. The functions of soil depend on the balances of its structure and composition, as well as the chemical, biological, and physical properties [3].

These balances are, however, being disrupted by highly accumulated heavy metals in soils [4], due to anthropogenic activities, such as industrial pollutants, pesticides, livestock wastewater, mine drainage, and petroleum contamination [5,6]. The chemical, biological, and physical unbalance caused by soil contamination by heavy metals may be detrimental to plant, animal, and human health. For example, the symptoms of reduced root growth, reduced seed sprouting, and seedling stunting, necrosis, and chlorosis appear in susceptible plants growing in soils contaminated with heavy metals [7,8]. Agricultural crops (fruits, grains, and vegetables) for livestock or human consumption, growing on contaminated soil, can potentially uptake and accumulate heavy metals in their edible plant parts, and may be hazardous to animal and human health through the food chains [5,9,10].

A reliable and environmentally friendly method is therefore needed to rapidly detect and survey the spatial distribution of soil heavy metals, to diagnose suspected contaminated areas as well as control the rehabilitation processes [11]. The conventional method of obtaining the spatial distribution of heavy metals is based on regular field samplings and subsequent chemical analyses in the laboratory (e.g. wet chemistry), followed by geo-statistical interpolation [12,13]. However, this method may be costly and time-consuming as a result of the intensive soil samplings in the field and the analyses in the laboratory. Moreover, such investigations can only provide limited information at specific locations and moments in time, and they cannot describe the spatial and temporal dynamics of heavy metal concentrations over large areas [14].

Visible and near-infrared reflectance spectroscopy (VNIRS, 350–2500 nm) provides a valid alternative to the conventional method for the estimation of heavy metal concentrations in soils, and it applies the spectral information of soils to estimate the soil properties (including heavy metal concentrations). Recent studies have suggested that VNIRS can provide estimations of the soil physical, chemical, and biological properties [15,16]. Compared with the conventional analytical methods, the practical advantages of the VNIRS technique include: (i) the technique is non-destructive and cost-effective; (ii) no or less hazardous chemical reagents are required; (iii) the measurement is fast and repeatable; (iv) several soil properties can be estimated from a single scan; (v) the technique can be used both in the laboratory and in situ; and (vi) this technique has better spatial and temporal continuities [15,17].

The first study of the accurate estimation of soil heavy metal concentrations by the use of VNIRS was published in 1997 [18]; however, the application of this technique only really began to take off much more recently [19–35]. These recent studies have explored the mechanism and have perfected the technical approaches (see Fig. 1) in the field of using VNIRS to estimate soil heavy metal concentrations.

In this paper we: (i) review the mechanisms, data, and methods for the estimation of soil heavy metal concentrations with VNIRS;

(ii) discuss the usefulness and challenges of hyperspectral images for mapping heavy metal contamination over large areas; and (iii) describe the pre-processing methods, spectral indices, variable selection methods, modeling strategies, and calibration methods. The purpose of this review is to promote the research and application of VNIRS in the monitoring of soil contamination by heavy metals.

2. Mechanisms for the estimation of heavy metal concentrations in soils by the use of visible and near-infrared reflectance spectroscopy

The absorptions of soils over the visible/near-infrared spectral regions (350–2500 nm) are primarily associated with Fe-oxides, clay minerals, water, and organic matter, as a consequence of the vibrational energy transitions of these dominant molecular bonds [36]. Most Fe-oxides in soils, e.g. goethite (α -FeOOH), have absorptions over the visible (350–780 nm) and short-wave near-infrared (780–1100 nm) spectral regions [37]. Clay minerals hold spectral features in the long-wave near-infrared (1100–2500 nm) regions, due to OH, H₂O, and CO₃ overtones and combination vibrations [38]. Water has strong absorption features over visible/near-infrared regions, most visibly near 1400 and 1900 nm, while there are weaker overtone bands elsewhere [36]. Soil organic matter has distinct absorption features over the visible/near-infrared regions, due to the various chemical bonds such as C–H, C–C, C=C, C–N, and O–H [39].

Some transition elements (such as Ni, Cu, Co, and Cr) can also exhibit absorption features in the visible/near-infrared regions under two particular conditions: (i) the elements are present at very high concentrations (>4000 mg kg⁻¹); and (ii) they have an unfilled *d* shell [30]. The reason for this is that when the atom of a transition element is located in a crystal field, the energy levels of the *d* orbitals will split, that is, an electron moves from a lower level to a higher one. Thus, the electron transition results in the electromagnetic energy being absorbed [38]. Wu et al. [30] noted that Cr and Cu show spectral features (610 and 830 nm) at concentrations >4000 mg kg⁻¹. Thus, when the heavy metals hold absorption features, they can be estimated based on their intimate and direct relationships with the spectral features [19].

However, such high soil contamination may only occur in mining or industrial areas. In most areas, the heavy metal concentrations in soils are usually found at trace or ultra-trace level. When heavy metals are present in only small amounts in the soil, they do not have spectral features in the visible/near-infrared regions, which means that it is difficult to directly estimate the heavy metal concentrations in the soil by the use of the soil spectral features [40].

Although soil heavy metals with low or moderate concentrations are spectrally featureless, they can be easily bound to Fe-oxides, clays, and organic matter [30]. Metal cations (M²⁺) adsorbed onto such hydroxylated surface sites (ROH, in which R can be Al, Fe, Mn, Si, etc. upon mineral surfaces) are generally described as follows: ROH + M²⁺ = RO – M⁺ + H⁺; consequently, an increase in the cations of heavy metals results in a decrease in ROH and an increase in RO (e.g. Fe-oxides) on the surfaces of the clay and oxide minerals [19,40]. Moreover, heavy metals are bound to soil organic matter due to metal complexation (Fig. 2, [41]), and the depletion of soil organic matter (e.g. the decomposition of soil organic

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