Proximal Spectral Sensing to Monitor Phytoremediation of Metal-Contaminated Soils

Paresh H. Rathod, David G. Rossiter, Marleen F. Noomen & Freek D. van der Meer


To link to this article: http://dx.doi.org/10.1080/15226514.2012.702805

Accepted author version posted online: 22 Jun 2012.

Submit your article to this journal

Article views: 352

View related articles

Citing articles: 9 View citing articles

Full Terms & Conditions of access and use can be found at http://www.tandfonline.com/action/journalInformation?journalCode=bijp20
REVIEW ARTICLE
PROXIMAL SPECTRAL SENSING TO MONITOR PHYTOREMEDIATION OF METAL-CONTAMINATED SOILS

Paresh H. Rathod, David G. Rossiter, Marleen F. Noomen, and Freek D. van der Meer

Department of Earth Systems Analysis, Faculty of Geo-information Science and Earth Observation, University of Twente, Enschede, The Netherlands

Assessment of soil contamination and its long-term monitoring are necessary to evaluate the effectiveness of phytoremediation systems. Spectral sensing-based monitoring methods promise obvious benefits compared to field-based methods: lower cost, faster data acquisition and better spatio-temporal monitoring. This paper reviews the theoretical basis whereby proximal spectral sensing of soil and vegetation could be used to monitor phytoremediation of metal-contaminated soils, and the eventual upscaling to imaging sensing. Both laboratory and field spectroscopy have been applied to sense heavy metals in soils indirectly via their intercorrelations with soil constituents, and also through metal-induced vegetation stress. In soil, most predictions are based on intercorrelations of metals with spectrally-active soil constituents viz., Fe-oxides, organic carbon, and clays. Spectral variations in metal-stressed plants is particularly associated with changes in chlorophyll, other pigments, and cell structure, all of which can be investigated by vegetation indices and red edge position shifts. Key shortcomings in obtaining satisfactory calibration for monitoring the metals in soils or metal-related plant stress include: reduced prediction accuracy compared to chemical methods, complexity of spectra, no unique spectral features associated with metal-related plant stresses, and transfer of calibrations from laboratory to field to regional scale. Nonetheless, spectral sensing promises to be a time saving, non-destructive and cost-effective option for long-term monitoring especially over large phytoremediation areas, and it is well-suited to phytoremediation networks where monitoring is an integral part.

KEY WORDS: soil contamination, heavy metals, phytoremediation, infrared spectroscopy, remote sensing

INTRODUCTION

The term “phytoremediation” refers to a non-destructive method to remove contaminants such as heavy metals from soils by means of vegetation (Salt, Smith, and Raskin 1998). This approach, covering both phytoextraction and phytostabilization, has gained popularity compared to soil cleaning for both financial and environmental reasons. Phytoremediation,
like any remedial system, requires monitoring to determine progress towards its objectives (ITRC 2009). This is especially true for phytoextraction system, since it would take decades to decontaminate a site, and also for the phytostabilization system, wherein contaminants are left in place, hence long-term monitoring is essential to make sure that stabilizing conditions are maintained in the future (USEPA 2000). Monitoring implies an extensive and repeated measurement, so that measurement techniques must be fast, inexpensive, and sensitive enough to distinguish real change in status from system noise.

**Current Practice in Phytoremediation Monitoring**

The US-DOE (2000) has categorized phytoremediation monitoring into (i) performance monitoring, i.e., determining the effectiveness of phytoremediation process to meet standard regulatory limits; (ii) risk monitoring, i.e., assuring that bioaccumulation of metals in plant or metal stabilization in soil root zone does not cause human health or ecological risk; and (iii) optimization monitoring, i.e., managing agronomic practices for optimal plant growth rate to facilitate the optimal metal removal from site (i.e., biomass yields \( \times \) plant metal concentration), and for optimal root growth to phytostabilize the metals in the root zone. Performance and risk monitoring are often done by measuring changes in mass balance of the target contaminant or its degradation products in the soil-plant system. All types of monitoring can also be done by measuring plant growth parameters and stress response. Both soil and plant status can be measures to assess the phytoremediation system. Soil variables to be measured include (i) physico-chemical status and contaminant levels and (ii) speciation, bioavailability and spatial variability of contaminants. Plant variables include (i) plant health status, as an indicator of metal-induced stress, (ii) plant tissue composition, e.g., metal contents in leaves, shoot and roots, (iii) transpiration rate, and (vi) plant coverage and root density.

Many standard monitoring methods require destructive soil and plant sampling for chemical analyses in the laboratory to determine metal content. Field methods for assessing plant stress may use sap flow loggers to measure plant water use, photosynthetically active radiation sensors, dendrometers for measuring plant growth, or leaf area and root measurement systems. These methods are expensive and hence unfeasible for monitoring large areas. This motivates the search for fast, inexpensive techniques that can be applied to many samples and repetitive measurements. An obvious candidate is remote sensing, which covers large areas at low cost and high temporal resolution (Dematte, Fiorio, and Ben-Dor 2009; Nanni and Dematte 2006). Remote sensing is routinely used to assess agricultural conditions, and can also be used at phytoremediation sites (Burckhard 1998, 1999), although plant growth is affected by much more than any contamination. Furthermore, remotely-sensed data can easily be integrated into Geographic Information System (GIS) for analyses such as spatial autocorrelation or trend analysis to produce maps of phytoremediation sites.

**Potential of Remote Sensing for Monitoring Phytoremediation**

Remote sensing refers to any technique that senses without touching the target, either close (laboratory), medium (field), or far (air or space). A wide variety of sensors are available at all scales with countless applications (Borengasser, Hungate, and Watkins 2007; Navalgund, Jayaraman, and Roy 2007). Measurements by sensors must be calibrated with direct measurements of the property of interest. A further step is to determine the physical basis for any observed relation. This can be **direct**, i.e., the target property affects
the sensor, or indirect, i.e., some other part the of system affects the sensors and this part is affected by the target property. In context of phytoremediation of metal-contaminated soils we can distinguish (i) direct measurements of targets, for example heavy metals in soils; (ii) indirect measurements via other soil properties; (iii) direct measurements of targets in plants; and (iv) indirect measurements via plant properties, e.g., metal-induced stress response. Of the many available remote sensing systems, visible and near-infrared (Vis-NIR; 350–1100 nm), shortwave-infrared (SWIR; 1100–2500 nm) and mid-infrared (MIR; 2500–25000 nm) reflectance spectroscopy, have been most used to assess soil properties (Cécillon et al. 2009; Du and Zhou 2009; Stenberg et al. 2010) and plant conditions (Font, del Río-Celestino, and de Haro-Bailón 2007).

It is useful to distinguish proximal (also called near) sensing from far remote sensing. Proximal sensing is close enough to the target (either in field or laboratory) that the sensor records a single spectrum of the target, generally considered as single “pure” object (Viscarra Rossel, McBratney, and Minasny 2010). Common illumination is tungsten halogen-bulb radiation (in the laboratory) and direct solar radiation (in the field). Common instruments used in the field or laboratory to measure the visible infrared (Vis-IR) spectra are Analytical Spectral Devices Inc. FieldSpec portable spectroradiometers, Spectra Vista Corporation’s GER series spectroradiometers, etc. Far remote sensing for constituents or status generally uses hyperspectral images, also termed imaging spectroscopy, where the image sensor collects data from airborne or satellite platforms with an area-array detector which integrates over a larger area. The aim of this paper is to review applications of proximal spectral sensing for monitoring soil metal contamination and relevant plant health status in order to evaluate its suitability as technique for monitoring phytoremediation sites. The sections “Near/Proximal Spectral Sensing for Assessing Metal Contamination in Soils” and “Proximal Spectral Sensing for Monitoring Vegetation in Phytoremediation Systems” summarize the infrared spectroscopic studies, respectively on monitoring soil metal contamination and changes in plant spectral properties due to phyto-accumulation of metals or toxic effects of elevated concentrations of metals in the root zone. The paper ends with challenges and ideas of possible up-scaling of proximal sensing techniques to hyperspectral imaging spectroscopy for phytoremediation monitoring.

NEAR/PROXIMAL SPECTRAL SENSING FOR ASSESSING METAL CONTAMINATION IN SOILS

Proximal soil sensing has gained much attention among soil scientist for measuring a wide range of soil constituents, notably organic carbon, plant nutrients and soil minerals, as well as soil functions such as workability (Viscarra Rossel et al. 2010). This technique is able to collect in-situ spectral data in the Vis-IR regions from close by, or within the soils using hand-held and/or field-based sensors. These sensors are of active or passive; invasive (direct sensor-to-soil contact) or non-invasive (measuring soil above the surface). However, there is not much literature available on proximal sensing of heavy metals, most likely because they are difficult to directly sense with these systems (see below).

Infrared spectroscopy is sensitive to both organic and inorganic constituents of soil and is based on vibrations of the bonds within molecules, when stimulated with Vis-NIR radiation. Visible radiation (350–780 nm) is primarily associated with iron-containing minerals, e.g., hematite and goethite (Sherman and Waite 1985), and with organic matter (Daniel et al. 2004). Near- and shortwave-infrared radiation (780–2500 nm) is mostly absorbed by water, soil organic matter (Song and He 2005), and by ions of transition metals (Fe, Ni, Cr,
Co, Cu) due to electronic processes (Holze 2004; Hunt 1977). Infrared spectroscopy combined with statistical data-reduction and regression techniques (Xu et al. 2008), has been used for soil characterization and quantitative prediction of various physico-chemical constituents of soil, for examples Fe-oxides (Nanni and Dematte 2006; Scheinost et al. 1998), organic matter, organic and inorganic carbon (Morgan et al. 2009; Reeves III 2010), and clays (Van Der Meer 1999; Waiser et al. 2007). Moreover, several soil environmental concerns, such as salinity (Fariñteh et al. 2008) and hydrocarbon contamination (Chakraborty and Weindorf 2010; Van der Meer et al. 2002) have also been investigated using infrared spectroscopy. The feasibility of Vis-IR spectroscopy for monitoring metal-contaminated soils has been of research interest since it was first reported by Malley and Williams (1997). An important distinction is between direct methods, where metal contamination affects the spectrum directly, and indirect methods, where metals either affect some other soil constituent that affects the spectrum, or where metals are correlated with some other constituents. We consider these methods in turn.

**Direct Prediction of Heavy Metals in Soil**

Direct quantitative prediction of heavy metals using soil Vis-IR spectroscopy is, in general, not possible since most metallic ions are spectrally featureless in Vis-IR regions. However, transition elements such as Ni, Cu, Co, and Cr with an unfilled ‘d’ shell, can exhibit absorption features due to crystal field effects (Burns 1993; Clark 1999). For example, Wu et al. (2007) modeled absorption feature of transition metals (Ni, Cr, and Cu) using reflectance spectra of artificially contaminated soil samples. Metals could not be detected directly at concentration <1000 mg kg\(^{-1}\), but Cr and Cu exhibited absorption features (610 and 830 nm) at concentrations >4000 mg kg\(^{-1}\). Such high soil contamination occurs only near some mining or industrial areas. On contaminated agricultural soils having moderate to low, diffuse contamination, direct prediction of heavy metals with their absorption features seems impossible. Since many phytoremediation sites are of this type (e.g., contaminated floodplains), indirect methods must be used.

**Indirect Prediction of Heavy Metals in Soil**

The sorption of metals in soils is mainly due to oxides of Fe and Al, clay minerals and organic matter. Therefore, indirect prediction of metallic ions via their intercorrelations with these spectrally active soil constituents has been well investigated. A problem with this approach is determining what proportion of these natural constituents has sorbed metal cations. In general this is solved by knowing that a site is contaminated, from a field study or historical knowledge, and then assessing the level of contaminant by the correlated constituent. Using this indirect approach in assessing metals in phytoremediation system has the additional difficulty that the concentration of predictor constituents is not expected to vary as a result of metal being removed or stabilized from the system by plants; if it does, the confounding effect makes statistical interpretation very difficult. The basic principle involves the metal cation (M\(^{2+}\)) binding onto the hydroxylated sites (ROH; where R = Al, Fe, Mn, Si; ROH + M\(^{2+}\) = RO-M\(^{+}\) + H\(^{+}\)) on a surface, such as clays and metal oxides. In heavily contaminated soils, the extent of ROH sites may decrease, with a consequent increase in RO, and these changes may cause variation in soil reflectance spectral features. Various prediction mechanisms have been proposed based on such metal-binding reactions and associations of the metal with spectrally active soil constituents. The most common
Predictions Based on Iron Oxides and Clays

Most Fe-oxide in soils and sediments, e.g., goethite ($\alpha$-FeOOH), exhibit absorption bands in the Vis-NIR (Torrent and Barrón 2002), while clay minerals have absorption features in the SWIR and MIR regions due to OH, H2O, and CO$_2$ overtones and combination vibrations (Clark 1999). Variation in spectral absorption features near 500 nm and 2200 nm are associated with FeO and hydroxyl lattice on mineral surface, respectively (Ben-Dor, Irons, and Epema 1999).

Kemper and Sommer (2002) showed that Vis-NIR wavelengths used for predicting metals in soil polluted by a mining accident could be attributed to the absorption features of Fe-oxides and clay minerals. This is as expected, since soil samples were taken from floodplains of the Agrio and Guadiamar rivers (Spain), which were contaminated by pyritic sludge due to the Aznalcóllar Mine accident. MLR and ANN models were successful ($R^2 > 0.80$) in matching predicted and chemically-analyzed concentrations for As, Pb, Hg, and Sb, whereas predictions of Cd, Zn, and Cu were poor. This can be attributed to their different geo-chemical behaviour in soils, e.g., solubility and precipitation. Contrary to the above findings, Xia et al. (2007) found a significant exponential relationship between Cd concentration in sediment of the Changjiang (Yangtze) river in China and spectral proxies of Fe-oxides (first derivatives of absorption at 560–760 nm), clay minerals (first derivatives at 1410, 1910, 2300 nm) and organic matter (400–530 nm). In their study, about 70% of total Cd was presented in exchangeable and reducible forms, associated with Fe- and Mn-oxides and clay minerals thereby allowing their predictions by soil reflectance.

Choe et al. (2008) correlated the metal concentrations in gold mining areas (SE Spain; concentration of Pb, Zn, As ranged from 96–18811, 61–728, and 62–826 mg kg$^{-1}$, respectively) to the variation in spectral absorption features of the hydroxyl lattice on surface of clays and oxides due to metal complexation. Results showed significant correlations between Pb and the absorption ratio of 610 to 500 nm, Zn and absorption area at 2200 nm, and As and the asymmetry of absorption at 2200 nm. Stepwise linear multiple regression using all three spectral features was much stronger ($R^2 = 0.84$), and it showed a weak relationship for Zn and Pb. However, with a forward stepwise multiple linear regression model, superior predictions for Zn, Pb, and As were reported with $R^2 = 0.59, 0.61,$ and 0.87, respectively. In another study, authors reported similar results for As, Cu, and Pb concentration in areas around an Au-Ag mine in Republic of Korea (Choe et al. 2009). Both studies as well as the study by Kemper and Sommer (2002) were done on soils from mining regions, where heavy metal contamination is very high, and metals were of highly correlated to each other and to the absorption features of Fe and Fe-oxides.

Similarly, for metal-contaminated agricultural soils in near Nanjing (China), Wu et al. (2005a) showed that the most important wavelengths for metal prediction were attributed to absorption features of Fe-oxides and clays at 520, 900, and 2000–2200 nm, respectively related to the goethite, Fe$^{3+}$ or Fe$^{2+}$ and clay absorption. However, PLS regression coefficients in later two regions were lower, indicating a weak absorption capability of Fe-oxides
and clay minerals in other forms than goethite. A satisfactory prediction was obtained, with correlation coefficients of predicted vs. measured above 0.87 for Ni and Cr, and varying from 0.65–0.81 for Cu, Hg, Pb, Zn and As. In another study on assessing Hg concentration in soils of the same region, Wu et al. (2005b) found that the wavelengths 496 and 2210 nm used for Hg prediction were attributed to absorption features of goethite and clay minerals, respectively. They worked out the prediction capability of reflectance spectra to classify Hg contamination classes, and found that classification accuracy for low contamination was satisfactory; however for the highly contaminated classes, it was not. Therefore, they suggested considering the various soil Hg chemical forms in model calibrations to improve prediction accuracy. Continuing the above studies, Wu et al. (2007) showed that the major prediction mechanism of certain metals was based on their correlation with total Fe, i.e., both active and residual Fe. They supported this conclusion by combing statistical methods and chemical sequential extraction, wherein inclusion in PLSR models of residual fractions of metals strengthened the prediction. The results showed the highest prediction accuracy for Ni, Cr, Co, and the lowest for Cd. The poorer prediction of Cd was explained by its higher exchangeable and lower residual fractions. It shows that the correlated constituent alone is not sufficient to predict the metal with high accuracy. This however requires a detailed chemical analysis to get best calibrative models. It is also an argument that the residual fraction has no direct environmental impact because it is too strongly fixed to soil. Recent works of Ji et al. (2010), Ren et al. (2009), and Wu et al. (2011) demonstrated the potential of Vis-IR spectroscopy for monitoring of heavy metal (Ni, Cr, Cu, Co) in agricultural soils by spectral features via Fe-based indirect prediction. However, predictions for Cd were poor, which agrees with other researchers’ findings (Kemper and Sommer 2002; Wu et al. 2007).

**Predictions Based on Organic Matter or Organic Carbon**

In contrast to above results, many studies conclude that metal sorption by soil organic matter (SOM), often reported as soil organic carbon (SOC) is the major mechanism to predict heavy metal by Vis-IR spectroscopy. An association of metals with soil SOM is well described (Kabata-Pendias and Pendias 2001). SOM has distinct spectral fingerprints in the Vis-IR regions due to various chemical bonds such as C–H, C–C, C≡C, C–N, and O–H (He et al. 2009; Ludwig and Khanna 2001). Again, the question is how the researcher can determine whether the detected SOM is contaminated or not. As with the association with inorganic constituents, studies are mostly of known contaminated sites, and have been used to assess contaminated levels at one point in time, not for monitoring. This is the same for other indirect approaches using clays or Fe-oxides (previous section).

Malley and Williams (1997) were the first to predict heavy metal concentrations in freshwater sediments by infrared spectroscopy (1000–2500 nm) on the basis of their association with OM. They obtained good predictive relations between NIR-predicted and chemically-analyzed metal concentration: $R^2 > 0.90$ for Cu, Zn, Mn; 0.80–0.90 for Pb, Ni, Fe; 0.61 for Cd. The poorer prediction for Cd was attributed to its association with inorganic soil constituents and its shorter residence time in the sediments, since it had been experimentally elevated several years before sampling. Similarly, Kooistra et al. (2001) used absorption features of OM (2000–2500 nm) in PLSR models to assess Cd and Zn contaminated areas in the floodplains of river Rhine (Netherlands). Moros et al. (2008; 2009) also used a similar wavelength range, in their case 2241–2598 nm, in PLSR models for screening several metals in estuarine sediments. For instance, PLSR models
well predicted the contents of As, Pb, and Cd, while Co and Ni were poorly predicted due to their inorganic forms in the sediments. Vohland et al. (2009) showed that a spectroscopic assessment of trace metals in German floodplain soil by means of active SOC as major predictor is feasible, however, the PLSR accuracies for Zn, Pb, Cu prediction were low ($R^2 = 0.56–0.71$). Similarly, the spectral region of 400–530 nm, absorption at 630 nm, and absorption ratio of 624/564 nm were found to be dominant spectral proxies of OM/SOC, respectively for prediction of total Cd in river sediments (Xia et al. 2007), for Cd in agricultural soils in the Changjiang river delta (Ji et al. 2010), and Pb, Cu, Zn in soils (Liu et al. 2011b). Recently, Zheng, Zhou, and Wu (2011) found that prediction of As in soil having lower OM content was better ($R^2 = 0.69$) than that in soils with higher OM. Pandit, Filippelli, and Li (2010) observed that SOM masks spectral signatures, so that most significantly correlated spectral bands, i.e., 800 and 1300 nm to soil Pb did not result in highly accurate predictions.

Predictions using Mid-Infrared Spectra

It has been found that NIR-based calibrations underestimated certain inorganic forms of heavy metal e.g., dust-borne heavy metals in heavily polluted arable soil and in forest soil organic layers close to industrial emissions (Chodak, Nikli, and Beese 2007; Siebielec et al. 2004). Instead, mid-infrared reflectance spectroscopy has been reported more promising (Janik, Merry, and Skjemstad 1998), since the MIR regions contain more wavelengths associated with the vibrations of fundamental organic bonds (e.g., C−H, O−H, C=O, C−O−C, N−H, etc.) and also to the inorganic components e.g., phosphate and carbonate in the soils (Siebielec et al. 2004). In that study, prediction of Cd, Cu, Ni, and Zn based on MIR-calibrations gave better results, with $R^2 = 0.94, 0.80, 0.99,$ and 0.96, respectively. Dupuy and Douay (2001) showed that MIR spectral bands centered at 5848 nm (1710 cm$^{-1}$) and 5917–5988 nm (1690–1670 cm$^{-1}$) vary with Pb concentration, which seems to be preferentially complexed by functional groups such as phenolic hydroxyls or carboxylic groups present in organic matter (Logan et al. 1997). MIR spectroscopy substantially outperformed NIR for prediction of metal contents in ex-situ soils (Wu, Wu, and Ma 2010), where a PLSR calibration model for 8 elements had satisfactory $R^2$ values (Ni $>$ 0.80 $>$ Cr, Cu, Zn, Pb, Hg $>$ 0.60 $>$ As, Cd) when applied to validation set. However, Bray, Rossel, and McBratney (2009) and Moros et al. (2009) preferred reflectance spectroscopy in Vis-IR over MIR, since it may be used in-situ for real-time diagnostic screening.

Challenges to Indirect Prediction Models

As discussed above, metals can indirectly be assessed by soil reflectance via surrogate calibration using regression modeling, which largely involves the metal’s correlation with certain soil constituents. Variation in results obtained in the reported studies, as summarized in Table 1, is possibly due to many factors including soil sampling, chemical analytical procedure, selection of spectral features, regression methods, and sample size. Key shortcomings in estimating soil metals by spectral sensing in comparison with classic chemical methods are the reduced accuracy of the prediction, and the difficulty of in-situ subsurface sensing, and the dependence of model calibrations on the quality of the chemical reference data. Most studies discussed above were done in the laboratory with small to medium sized sample sets (Table 1), where conditions are more controlled than in the field. Even so, prediction accuracy of lab-based calibration may be influenced by analytical or subsampling
Table 1  Summary of indirect predictions of heavy metal through soil reflectance spectra

<table>
<thead>
<tr>
<th>Heavy Metals*</th>
<th>Concentration range in soils (mg kg(^{-1}))</th>
<th>Regression statistics (technique)</th>
<th>Type of spectra or absorption features used</th>
<th>Sample size (#); Sampling site</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>–</td>
<td>(R^2 = 0.92) (PLSR)</td>
<td>Reflectance spectra at 1100–2498 nm</td>
<td>169; River sediments</td>
<td>Malley and Williams (1997)</td>
</tr>
<tr>
<td>Zn</td>
<td>–</td>
<td>(R^2 = 0.92) (PLSR)</td>
<td>VNIR soil reflectance spectra</td>
<td>69; Floodplain soils</td>
<td>Kooistra <em>et al.</em> (2001)</td>
</tr>
<tr>
<td>Hg</td>
<td>0.01–0.29</td>
<td>(R^2 = 0.96) (MLR), 0.93 (ANN)</td>
<td>2nd Derivatives of 700–1400 nm</td>
<td>214; Mining</td>
<td>Kemper and Sommer (2002)</td>
</tr>
<tr>
<td>Pb</td>
<td>8–221</td>
<td>(R^2 = 0.95) (MLR), 0.94 (ANN)</td>
<td>All predictions using mid-infrared spectra; Mean and variance, MSC</td>
<td>70; Agril. soils</td>
<td>Siebielec <em>et al.</em> (2004)</td>
</tr>
<tr>
<td>Ni</td>
<td>13.3 (mean)</td>
<td>(R^2 = 0.99) (PLSR)</td>
<td>Reduced spectra at 128 nm interval</td>
<td>120; Suburban soils</td>
<td>Wu <em>et al.</em> (2005a)</td>
</tr>
<tr>
<td>Zn</td>
<td>14–4500</td>
<td>(R^2 = 0.96) (PLSR)</td>
<td>1st Derivatives spectra at 1000–2500 nm</td>
<td>105; Agril. soils, delta</td>
<td>Wu <em>et al.</em> (2005b)</td>
</tr>
<tr>
<td>Pb</td>
<td>18–6530</td>
<td>(R^2 = 0.94) (PLSR)</td>
<td>1st Derivatives reflectance spectra</td>
<td>61; Agril. soils, delta</td>
<td>Wu <em>et al.</em> (2007)</td>
</tr>
<tr>
<td>Ni</td>
<td>10.6–57.5</td>
<td>(R^2 = 0.93) (PLSR)</td>
<td>Normalized reflectance at 578 nm</td>
<td>69; River sediments</td>
<td>Xia <em>et al.</em> (2007)</td>
</tr>
<tr>
<td>Hg</td>
<td>0.04–1.26</td>
<td>(R = 0.84) (PCR)</td>
<td>Adsorption area at 2200 nm; Log</td>
<td>49; Au-Ag mining</td>
<td>Choe <em>et al.</em> (2008)</td>
</tr>
<tr>
<td>Cr</td>
<td>60.8–104.0</td>
<td>(R^2 = 0.85) (PLSR)</td>
<td>Ratio of 1344/778 nm, 610/500 nm</td>
<td>22; Au-Ag mining</td>
<td>Choe <em>et al.</em> (2009)</td>
</tr>
<tr>
<td>Cd</td>
<td>0.17–1.57</td>
<td>(R = 0.76) (Univariate regression)</td>
<td>Normalized reflectance at 578 nm</td>
<td>117; River sediments</td>
<td>Moros <em>et al.</em> (2009)</td>
</tr>
<tr>
<td>As</td>
<td>62.3–826.9</td>
<td>(R^2 = 0.84) (SMLR), 0.87 (EMLR)</td>
<td>Adsorption area at 2200 nm; Log</td>
<td>49; Au-Ag mining</td>
<td>Choe <em>et al.</em> (2008)</td>
</tr>
<tr>
<td>Cu</td>
<td>21.9–252.6</td>
<td>(R^2 = 0.72) (SMLR), 0.81 (EMLR)</td>
<td>Ratio of 1344/778 nm, 610/500 nm</td>
<td>22; Au-Ag mining</td>
<td>Choe <em>et al.</em> (2009)</td>
</tr>
<tr>
<td>As</td>
<td>0.6–220</td>
<td>(R = 0.91) (PLSR)</td>
<td>NIR region 1067–2598 nm; MSC</td>
<td>33; Agril. soils at mines</td>
<td>Ren <em>et al.</em> (2009)</td>
</tr>
<tr>
<td>Pb</td>
<td>150–600</td>
<td>(\text{Accuracy} = 75.9%) (OLR)</td>
<td>Reflectance spectra at 2500–25000 nm</td>
<td>489; Urban soils</td>
<td>Bray <em>et al.</em> (2010)</td>
</tr>
<tr>
<td>Zn</td>
<td>40–1322</td>
<td>(R^2 = 0.84) (PLSR)</td>
<td>MSC reflectance spectra</td>
<td>109; Floodplain soils</td>
<td>Vohland <em>et al.</em> (2009)</td>
</tr>
<tr>
<td>Cr</td>
<td>31.0–108.9</td>
<td>(R = 0.76) (Univariate regression)</td>
<td>Reflectance at 2376 nm</td>
<td>122; Agril. soils, delta</td>
<td>Ji <em>et al.</em> (2010)</td>
</tr>
</tbody>
</table>

(Continued on next page)
Table 1 Summary of indirect predictions of heavy metal through soil reflectance spectra (Continued)

<table>
<thead>
<tr>
<th>Heavy Metals*</th>
<th>Concentration range in soils (mg kg$^{-1}$)</th>
<th>Regression statistics (technique)</th>
<th>Type of spectra or absorption features used</th>
<th>Sample size (#); Sampling site</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>187–412</td>
<td>$R^2 = 0.69$ (Linear regression)</td>
<td>Reflectance at 800 nm</td>
<td>8; Along military park</td>
<td>Pandit et al. (2010)</td>
</tr>
<tr>
<td>Cu</td>
<td>1.6–332.1</td>
<td>$R = 0.89$ (Linear regression)</td>
<td>1st Derivatives spectral ratio of 624/564</td>
<td>30; Floodplain soils</td>
<td>Liu et al. (2011b)</td>
</tr>
<tr>
<td>Pb</td>
<td></td>
<td>$R = 0.81$ (Linear regression)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr, Ni</td>
<td>$R^2 = 0.93, 0.91$ (MARS)</td>
<td>S-G smoothed reflectance spectra</td>
<td>120; Agril. soils</td>
<td>Wu et al. (2011)</td>
<td></td>
</tr>
</tbody>
</table>

*details are of those metals, for which prediction/calibration statistics were higher. For further information refer given references.

(abbreviation/symbol: $R^2 =$ coefficient of determination, $R =$ correlation coefficient, MLR = multiple linear regression, EMLR = Enter MLR, ANN = artificial neural networks, PLRS = partial least square regression, PCR = principal component regression, MARS = multiplicative adaptive regression splines, OLR = ordinal logistic regression, MSC = multiplicative scatter correction, S-G = Savitzky-Golay)

errors. Additionally, use of different spectrometers might lead to variations in results due to instrumental variation, and this needs to be corrected by spectral standardization using common internal standards (e.g., clean sand) and protocols to correct the spectra (Pimstein, Ben-Dor, and Notesco 2011). Further study is needed to comparison the errors of chemical analysis and spectral sensing. In-situ spectral measurements also suffer from complications due to, e.g., soil roughness, soil moisture, sun zenith, low signal-to-noise, and vegetative cover. However, these shortcomings do not imply that model calibrations from one soil dataset would be irrelevant to another. A comparative study is needed to validate a calibration model (e.g., developed using soil data set from a naturally multi-metal contaminated site such as a river floodplain) using an independent soil dataset. It is feasible to apply such locally-calibrated models to larger regions having broad range of metal content and similar soil types for preliminary monitoring of contaminants (Wu et al. 2011). Many scientists advocate a soil spectral library concept (Cécillon et al. 2009; Du and Zhou 2009; Slonecker et al. 2010) that might be useful for this purpose.

Reliable and robust indirect prediction is challenging as soil predictive properties, especially SOM, SOC, clay contents, Fe-oxides, and other hydroxides varied distinctly from one study to another. This is not surprising, since naturally metal-contaminated sites, such as abandoned mines, have extreme variations in all these properties which alter the soil reflectance. But it may be not the same for agricultural or anthropogenic metal contamination, as Pandit et al. (2010) have shown that little SOM is needed to retain soil Pb, and consequently an increase in SOM would not retain any more Pb. Interactions between soil constituents and metal sorption are largely controlled by soil pH, ionic strength, ligand ions, nature and species of metallic ions present, etc. (Naidu, Sumner, and Harter 1998). A clear relationship between soil texture and accuracy of predictions was observed by Siebielec et al. (2004) for all studied metals except Fe. Predictions of metals were inaccurate in soils having clay content less than 70–80 g kg$^{-1}$. Organic matter itself changes in quality as it decomposes and passes through various humus forms; this strongly
influences soil reflectance (Ben-Dor and Banin 1995). Moreover, complexation of metals to organic fractions is variable and depends on size fractions (Ducaroir and Lamy 1995; Parat et al. 2002). A metal binding to OM is usually attributed to humic substances enriched with functional groups, such as carboxyl and hydroxyl, which serve as electron donors; accordingly, variations in soil spectral feature will occur due to humus type, irrespective of metal complexation. In soil with multi-metal contaminations, it is possible that while SOM has little relation to one metal, it does affect other metals as reported by Pandit, Filippelli and Li (2010) in case of Pb deposition in soil. However, these authors succeed in predicting soil Pb by PLSR modeling ($R^2 = 0.95$) using a full Vis-IR spectrum data. The sorption of metals by Fe-oxides depends on soil pH and presence of humic substances, and accordingly the order of binding of metals onto the surface differs with these (Kabata-Pendias and Pendias 2001). Soil constituents associated with metals do not change their concentration due to phytoremediation, but their geo-chemical behaviour or associations might change with the progress of phytoremediation, particularly when soil amendments or chelating agents are used to enhance metal extraction or stabilization, and this should be addressed appropriately when interpreting indirect models.

PROXIMAL SPECTRAL SENSING FOR MONITORING VEGETATION IN PHYTOREMEDIATION SYSTEMS

For successful phytoremediation, another key consideration is that the system must function for decades to meet an acceptable limit of contaminants in soils, i.e., the chemically reactive pool of metals. Hence, the survivability and growth rate of plants, exposed to metal load, needs to be monitored closely and periodically. To this respect, monitoring of variations in plant spectral characteristics in Vis-IR regions due to direct effects of metal phytoextraction and/or indirect toxic effects of metal in soil rhizosphere, as in the case of phytodegradation and phytostabilization, could provide a measure of plant health status before any stress-related damage is visible. Spectral characteristics of leaf are mainly governed by its cellular structure, water content, biochemical composition, and pigments content (Guyot, Baret, and Jacquemoud 1992). Excessive concentrations of heavy metals (both essential and non-essential elements) in soils and their plant uptake adversely affect plant growth causing metabolic disturbance (Maksymiec 2007; Prasad 2004) and/or ultra-structural changes in tissues (Kabata-Pendias and Pendias 2001) that distinctly influence the spectral characteristic of the plant (Figure 1). In general, metal-induced stress causes a decrease in chlorophyll content (Zengin and Munzuroglu 2005) and changes in leaf internal structure (Slaton, Raymond, and Smith 2001); these directly or indirectly alter the reflectance of Vis-IR radiation, (Horler, Barber, and Barringer 1980; Milton et al. 1989; Schwaller, Schnetzer, and Marshall 1983).

In recent years, several papers have explored the concept of vegetation stress as bio-indicators of soil contamination using Vis-IR reflectance spectroscopy. For example, Noomen et al. (2008) studied spectral changes in leaves of maize and wheat plants as a result of soil contamination with hydrocarbons; Font et al. (2004, 2002, 2005) monitored heavy metals in plant samples of Indian mustard, amaranth and rice; Woodhouse et al. (1994) detected Zn and Cu-induced stress in wheat and lettuce, and Rosso et al. (2005) showed that visible reflectance of pickleweed leaves closely followed the changes in pigment concentration due to Cd treatments. Burckhard (1998, 1999) and Su et al. (2007) advocated that Vis-IR spectroscopy can also be deployed at phytoremediation sites for monitoring plant physiological status and metal bio-accumulation. For many years, spectral sensing of
vegetation in Vis-IR regions has been utilized in identification or classification of metal-contaminated soils (Kooistra et al. 2003, 2004) using a variety of vegetation spectral indices including the red edge. This has also great potential in monitoring phytoremediation, such as monitoring the variation in relative concentration of metals in soil and stress effects in plants attributed to effects of phytoextraction or phytostabilization of metals.

**Red Edge Position Relevant to Metal and Metal-induced Stress**

The typical reflectance spectrum of healthy vegetation is characterized by an absorption of blue and red light caused by chlorophyll, respectively at around 450 and 680 nm, and a rapid rise to a spectral peak around 780 nm due to reflection of NIR radiation by internal leaf mesophyll tissues (Figure 1). The red edge position (REP), i.e., the wavelength at maximum slope of the reflection curve between red (670–680 nm) and NIR (760–780 nm), has been studied as an indication of plant chlorophyll status. Many definitions and techniques are available in literature for computing the REP (Cho and Skidmore 2006; Dawson and Curran 1998; Guyot and Baret 1988; Pu et al. 2003). ‘Red shift’ and ‘blue shift’ are two important features of the REP for spectral analysis (Horler, Dockray, and Barber 1983). A red shift is a shift of the REP towards longer wavelengths, and is generally thought to be caused by an increase in chlorophyll concentration. A blue shift is a shift towards shorter wavelengths around 680 nm, and is associated with a decrease in chlorophyll content. This has been observed in several studies on spectral changes due to high soil metal contamination (Cheng, Tang, and Wu 2008; Collins et al. 1983; Götze et al. 2010; Slonecker et al. 2010). For metal-contaminated floodplains (concentrations of Pb, Cd, Zn, and Cu 70–490, 6.6–7.3, 170–1450, 30–130 mg kg$^{-1}$ respectively) of river Waal (one branch of the Rhine) in the Netherlands, Clevers et al. (2004) observed a significant negative correlation between the REP of reflectance of grass species (*Poa annua* and *Lolium perene*) and Pb in soils ($R^2 = 0.64$). These findings were further confirmed by Kooistra et al. (2004), who found significant $R^2$ values (0.43–0.61 for Zn, Cd, Cu, Pb) between the REP of grass species and measured metals in soils in floodplain along the same river.
Dunagan, Gilmore, and Varekamp (2007) found a blue shift in spectra of field mustard grown in Hg-spiked and contaminated soils during early and pre-mature growth stages, and this was consistent with reduction in chlorophyll content due to Hg toxicity. Similar results of blue shift for cabbage leaf spectra have been reported by Cheng et al. (2008) and Liu et al. (2008) respectively with an increased Zn and Cu pollution in soil ($R^2 \geq 0.95$). Studies by Ren et al. (2010, 2008) proved that the REP shift has potential for estimation of Pb concentration in rice plant at early tillering stage. In these studies, REP of rice crop exposed to 2.5 mg kg$^{-1}$ of Pb shifted towards shorter wavelength by 22 nm on 30th day after sowing. Yang et al. (2008) also noted 19 nm blue shift of REP in spectrum of Chinese sumac plant in a Cu mining area, compared with plant spectra from non-mining area. However, this blue shift is also associated with stresses due to nutrient deficiencies, which implies that a shift of the REP alone does not characterize metal-specific plant stresses. This demands a search for combined changes in spectral parameters that are unique to each kind of metal-related plant stress.

### Vegetation Indices Relevant to Metals and Metal-induced Stress

Vegetation indices are mathematical calculations, generally ratios or linear combinations, of two or more spectral wavelengths to amplify vegetation spectral signals by minimizing background effects. Well-studied indices to discriminate stressed plants are the Normalized Difference Vegetation Index (NDVI) and the Ratio Vegetation Index (RVI). A high value of such indices indicates high chlorophyll content and healthy plant status (Schowengerdt 2007). Ren et al. (2010) observed a significant correlation between metals concentration in paddy leaves and NDVI values with coefficient values $r = -0.76, -0.68, -0.76$, respectively for Cu and NDVI$_{(660,870)}$; Zn and NDVI$_{(510,870)}$; Pb and NDVI$_{(510,810)}$. Gallagher et al. (2008) also demonstrated that NDVI and red/green wavelength ratio indices can be useful in detecting metal-induced stress in hardwood assemblages ($Betula populifolia$) on urban brownfields. For field mustard grown in Hg-spiked soils, Dunagan et al. (2007) reported significantly lower RVI ($R_{750/700}$) and NDVI $[R_{750} - R_{690}]/(R_{750} + R_{690})$ values than control plants at early to mid-growth stages. Yang et al. (2008) studied several indices of spectral data of three plants (Chinese sumac, sweet wormwood herb and sword fern) of copper and tin mining areas. For all studied plants, the index $R_{725/675}$ was highly correlated to Cu, Mn, Pb and Zn concentrations in soil. However, Schuerger et al. (2003) concluded that NDVI and RVI ($R_{750/700}$) could not differentiate between plant stress induced either by deficient or toxic (25, 50, and 100 mg L$^{-1}$) levels of zinc.

Kooistra et al. (2003) showed that reflectance of ryegrass ($Lolium perenne$) can be used to predict elevated Zn contamination levels in the soil of floodplain of rivers Rhine and Meuse (Netherlands) using several vegetation indices (Table 2) and regression models, wherein a simple linear regression model using index MSAVI2 performed best as compared to multivariate PLSR model. In another study, Kooistra et al. (2004) obtained satisfactory relationships between concentrations of Ni, Cd, Cu, Zn, and Pb in river floodplain and spectral reflectance of grass species ($Poa annua$ and $Lolium perenne$) in the 400–1350 nm range with $R^2$ from 0.50 to 0.73 for DVI (Difference Vegetation Index) using PLSR models. However, the obtained relationship was species dependent; the authors found low $R^2$ ($0.17$–$0.22$) and high cross-validation errors for herbaceous vegetation ($Urtica dioica$, $Cirsium arvensis$, and $Rumex acetosa$). This is probably due to differences in morphology, metal tolerance of plants and time of data collection (Bork, West, and Price 1999). Furthermore, studies of Götze et al. (2010) and Panigada et al. (2010) shown that pigment
Table 2: Vegetation indices* studied for heavy metals induced plant stress

<table>
<thead>
<tr>
<th>Vegetation Indices</th>
<th>Equation (R denotes reflectance; NIR = Near-infrared)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Difference Vegetation Index (DVI)</td>
<td>((RNIR - R_{red}))</td>
<td></td>
</tr>
<tr>
<td>Ratio Vegetation Index (RVI)</td>
<td>(\frac{RNIR}{R_{red}})</td>
<td></td>
</tr>
<tr>
<td>Ratio Difference Vegetation Index (RDVI)</td>
<td>(\frac{RNIR - R_{red}}{(R_{red})^{1/2}})</td>
<td></td>
</tr>
<tr>
<td>Soil Adjusted Vegetation Index (SAVI)</td>
<td>((RNIR - R_{red}) (1 + L) (RNIR + R_{red} + L)) (L = 0.5)</td>
<td></td>
</tr>
<tr>
<td>Modified SAVI second (MSAVI2)</td>
<td>(2 \times RNIR + 1 - [(2 \times RNIR + 1)^2 - 8 (RNIR - R_{red})^{1/2}])</td>
<td></td>
</tr>
<tr>
<td>Infrared Percentage Vegetation Index (IPVI)</td>
<td>(\frac{RNIR}{(RNIR + R_{red})})</td>
<td></td>
</tr>
<tr>
<td>Modified Simple Ratio (MSR)</td>
<td>([(RNIR + R_{red}) - 1] / [(RNIR + R_{red}) + 1]^{1/2})</td>
<td>Liu et al. (2010a)</td>
</tr>
<tr>
<td>NDVI</td>
<td>((R_{800} - R_{670}) / (R_{800} + R_{670})) (R_{670} = 670) nm, (R_{800} = 800) nm</td>
<td>Liu et al. (2010a)</td>
</tr>
<tr>
<td>Optimized SAVI (OSAVI)</td>
<td>([1 + 0.5] \times (R_{800} - R_{670}) / (R_{800} + R_{670} + 0.5))</td>
<td>Liu et al. (2010b)</td>
</tr>
<tr>
<td>Modified Chlorophyll Absorption Ratio Index (MCARI)</td>
<td>([R_{700} - R_{670}] - 0.2 \times (R_{700} - R_{670}) / (R_{670}))</td>
<td>Liu et al. (2010b)</td>
</tr>
<tr>
<td>Modified Triangle Vegetation Index (MTVI)</td>
<td>(1.5 \times [1.2 \times (R_{572} - R_{550}) - 2.1 \times (R_{570} - R_{550})])</td>
<td>Panigada et al. (2010)</td>
</tr>
<tr>
<td>Photochemical Reflectance Index (PRI)</td>
<td>((R_{534} - R_{570}) / (R_{534} + R_{570})) (R_{570} = 570) nm, (R_{534} = 534) nm</td>
<td>Peñuelas and Filella (1998)</td>
</tr>
<tr>
<td>Chlorophyll Index (CI)</td>
<td>((R_{750} - R_{705}) / (R_{750} - R_{705})) (R_{705} = 705) nm</td>
<td></td>
</tr>
<tr>
<td>Normalized Pigment</td>
<td>((R_{680} - R_{480}) / (R_{680} - R_{480})) (R_{480} = 480) nm</td>
<td></td>
</tr>
<tr>
<td>Chlorophyll Index (NPCI)</td>
<td>((R_{680} - R_{480}) / (R_{680} - R_{480})) (R_{480} = 480) nm</td>
<td></td>
</tr>
</tbody>
</table>

*Refer article of Zarco-Tejada, Berjón, and Miller (2004) for further details of modified vegetation indices.

indices such as NPCI and PRI (Table 2) were highly correlated to metal related plant stress, and this could be due to influenced plant metabolism by metal stress (Curran, Dungan, and Peterson 2001). Liu et al. (2010b) developed regression models using continuum removal normalized band depth values at wavelengths 537, 667, 747 nm to estimate metals in grass via changes in chlorophyll concentrations. Estimated Cu and Pb were significantly correlated to the measured values \((r = 0.89\) and \(0.87\), respectively). Recently, Liu et al. (2010a, 2011a) concluded that spectral indices sensitive to chlorophyll (e.g., NDVI, MTVI, MCARI, OSAVI; Table 2) using a back propagation and dynamic neural network model were accurate in predicting heavy metals in paddy.

It is evident that most studied vegetation indices use spectral wavelengths in vicinity of the red edge region, which is sensitive to changes in chlorophyll and other pigments. However, it was pointed out by several researchers (Carter 1993; Chapin III 1991; Schuerger et al. 2003; Sridhar et al. 2007a, 2007b) that red edge-based indices cannot differentiate the changes due to metal accumulation or toxicity from other stresses, since loss of chlorophyll is a general symptom of many biological and physiological stresses in plants. In other words, these indices characterize stressed plants irrespective of specific metal stress. Instead, the infrared regions have been considered in several studies for metal detection, since this region
is particularly influenced by structural variations in leaf internal architecture. Excessive metal accumulation is known to affect leaf internal structure, cell structure, and chloroplast ultrastructure. For example, changes in leaf structure of Indian mustard due to Zn, Cd phytoextraction (Sridhar et al. 2005) and decreases number of mesophyll cells in several plant species have been observed due to metal toxicity (Chmielewska and Chwil 2005; Küpper et al. 2000).

With this perspective, in studies on phytoextraction of Cd, Zn (by barley, *Hordeum vulgare* L.) and As, Cr (by Chinese brake fern, *Pteris vittata* L.), Sridhar et al. (2007a, 2007b) considered wavelength range 800–1300 nm for spectral analysis, as this region is sensitive to leaf structural changes due to phyto-accumulation of metals. They found that a ratio index \( R_{1108/10} \) was sensitive to foliar structural changes in metal accumulators. The ratio index significantly correlated (*p < 0.05, **p < 0.01) with Cr content in shoot (*r* = 0.59*) and roots (*r* = 0.84**); so did NDVI values with Cr shoot (*r* = 0.53*) and roots (*r* = 0.77**). By contrast, NDVI showed better correlation with As content in shoot and roots compared to ratio index, but could not distinguish Cr-treated plants from As-treated and control plants, as the ratio index did. However, the ratio index was not sensitive to Cd and As in leaves, which was attributed to the fewer leaf structural changes in Cd- and As-treated plants. These results are in good agreement with study of Bandaru et al. (2010), wherein changes in spinach leaf reflectance around 1048, 1098, and 1080 nm were strongly correlated with leaf As concentration and structural parameters *viz.*, leaf thickness, mean ratio of palisade mesophyll to spongy mesophyll, mean leaf air space ratio, and mean mesophyll surface area. Regression analysis using optimum NIR bands and its ratio index (*i.e.*, \( R_{1048/1021} \)) show great potential for predicting As in spinach leaf, with \( R^2 = 0.69 \) and 0.59, respectively. For predicting As in two *Pteris* fern species, Slonecker et al. (2009) used NIR and SWIR wavelengths 998, 1448, 1644, 2184 nm and 956, 1174, 1888, 2140, 2331 nm respectively for *Pteris multifida* and *Pteris cretica mayii*. Wavelengths at 1448, 2140, and 2331 were likely to be related with leaf chemistry and chemical absorption *i.e.* lignin and cellulose. A first derivative model for both ferns showed the best \( R^2, 0.59 \) and 0.75 respectively. Götze et al. (2010) also showed that band depth of continuum removal at 1730 nm (CR1730; which is thought to be sensitive to lignin or protein production as influenced by metal accumulation, is a potential indicator for metal stress detection. These results imply that combinations of the red edge index and spectral ratio indices in the infrared region are more feasible for monitoring physiological status of plants during the process of phytoremediation(Sridhar et al. 2007a, 2007b).

**CHALLENGES AND FUTURE PROSPECTS**

Although the potential of proximal spectral sensing techniques for assessing properties of soils and plants are recognized, these techniques have not been applied in practice for monitoring soil remediation programs, for several reasons. First, the direct quantification of metals in soil is not possible since most metallic ions, except that of transition elements at very high concentrations, are spectrally inactive within Vis-IR regions. Second, spectral characteristics of metal-contaminated soil have been mainly studied in the laboratory or field with studies of limited scope, so no general prediction mechanisms can be obtained. The main difficulties in producing satisfactory predictions for metals in soil, as discussed in section named “Challenges to Indirect Prediction Model,” are the compositional diversity of soils and the presence of various metallic ions-soil constituent complexes in soil. Third,
the potential of imaging spectroscopy, i.e., remotely sensed data from either airborne or satellite platforms, for monitoring of full-scale phytoremediation site is yet to be studied. For the emerging field of phytoremediation, imaging spectroscopy promises great value over proximal sensing since, if successful, it could assess metal-contaminated sites before (providing a spatial overview of metal contamination), during (for optimization and performance monitoring of phytoremediation via assessing plant status), and after (for risk monitoring) the establishment of a phytoremediation system. There are several airborne hyperspectral sensors that could be used for monitoring plants and soils, such as the Airborne Visible InfraRed Imaging Spectrometer (AVIRIS), the Compact High Resolution Imaging Spectrometer (CHRIS), the HyMap series of airborne hyperspectral scanners, and the Hyperion space-borne imager. Absorption features of Fe-oxides, which are associated with metals, are broad and thus can be determined with multiple bands using above sensors (Wu et al. 2011). On the other hand, imaging spectroscopy is complicated due to factors not relevant for proximal sensors, including mixed pixels, lower spectral resolution, low signal-to-noise ratio, and atmospheric attenuation. Despite these problems, several studies have shown that imaging spectroscopy can be a promising tool for assessing metal-contaminated soils – both directly (Chevrel et al. 2003; Choe et al. 2008; Kemper and Sommer 2003; Lehmann and Gläßer 2005; Wu et al. 2011), and indirectly through monitoring stressed vegetation (Boluda et al. 1993; Lehmann and Gläßer 2005; Lyalko et al. 1996; Reusen et al. 2003; Shafri, Salleh, and Ghiyamat 2006; Splajt, Ferrer, and Frostick 2003; Zhang 2010). European MINEO “Monitoring and assessing the environmental Impact of mining in Europe using advanced Earth Observation Techniques” projects (http://www2.brgm.fr/mineo/) have employed remotely-sensed data to assist with the monitoring of mine waste areas.

Fourth, most remote sensing methods for vegetation monitoring are only capable of monitoring relatively severe plant stress (US-DOE, 2000). In particular, quantification of metal-induced plant stress with spectral sensing has not yet been studied. As the aim of phytoremediation is metal removal or stabilization, it is important to study the changes in plant spectral properties in relation to changes in metal concentration in soil due to the remediation process. There are many other techniques available for detecting early signs of natural as well metal-related stress, for instance chlorophyll fluorescence spectroscopy or imaging (Colls and Hall 2004; Zarco-Tejada et al. 2009) and thermal infra-red reflectance/emission spectroscopy to monitor plant surface temperature (Suresh et al. 1989); these can deliver complementary information. In general, most effects of metal-induced stress (specifically toxicity) on plant physiology resembles plant-stress caused by others stressors. Further research is therefore needed to distinguish metal-induced stress from natural stress and to delineate species-specific spectral responses of metal-stress. This should be done considering the sources and nature of metal contamination in each specific phytoremediation project. However, the phytoremediation clean-up approach offers a good match with studying field deployment of remote sensing techniques, as phytoremediation involves the use of homogeneous plant species, and thus complications due to signatures from multiple-species are eliminated.

CONCLUSION

This review paper has shown that remote sensing techniques, particularly proximal spectral sensing at laboratory and field scales, are a promising and inexpensive alternative for assessing metal contamination in field soils. Indirect spectroscopic assessment of
heavy metals in contaminated soil is possible on the basis of metals’ intercorrelations with spectrally active soil constituents. As an interrelationship exists between soils, vegetation and metal contamination, there is a potential of spectral sensing for optimizing phytoremediation systems through timely and repeated plant health monitoring. However, field sampling and laboratory measurements, mostly chemical analyses of plants and soil, are still mandatory for model calibration and validation. Field-based proximal spectral sensing has proved to be promising for monitoring phytoremediation process; the application of far remote sensing is a challenging research area.

REFERENCES


Zhang B. Hyperspectral remote sensing of vegetation growing condition and regional environment. 2nd Workshop on hyperspectral image and signal processing: Evolution in remote Sensing (WHISPERS); 14–16 June 2010; Reykjavik, Iceland: IEEE. p. 1–4.