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*Chapter 9*

# THE USE OF REMOTE SENSING TO LOCATE HEAVY METAL AS SOURCE OF POLLUTION

## I. Melendez-Pastor, J. Navarro-Pedreño[*], I. Gómez, and M.B. Almendro-Candel

Department of Agrochemistry and Environment. Universidad Miguel Hernández de Elche. Avenida de la Universidad, Edificio Alcudia, 03202, Elche, Spain

## ABSTRACT

The use of remote sensing techniques to detect sources of pollution is a good tool to prevent possible environmental affections. In the case of heavy metals, the pollution coming from wrong agricultural practices are not able to be detected by remote sensing before the addition of pollutants. However, natural source of heavy metals, for instance, the presence of minerals in the soil surface may be important as a prevention technique to avoid heavy metal pollution. If the source of heavy metal is detected by remote sensing, the practices applied to the soil can be done according to those pollutants and avoiding the mobilization and transfer of heavy metal to other environmental compartments.

A review of the role of remote sensing in soil heavy metals detection is presented. Principles of spectroscopy and basic mapping techniques applied in soil mapping are included. Finally, illustrative examples of studies that applied remote sensing techniques for mapping heavy metals in soil surface in Mediterranean environments were compiled. Remote sensing is revealed as a successful tool for mapping background levels of soil heavy metals and accurate delineation of polluted areas.

## INTRODUCTION

The term pollution refers to the introduction by the man into de environment of chemicals or energy forms liable to endanger human health, harm to living resources and ecological systems, damage to the structures or amenity of interference with legitimate uses of the

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[*] Author to whom correspondence should be addressed: E-mail: jonavar@umh.es
Tel. +34966658417; Fax. +34966658340

environment (Holdgate 1979). Soil -the unconsolidated mineral or organic matter on the surface of the Earth that has been subjected to and show effects of genetic and environmental factors of: climate (including water and temperature effects), and macro- and microorganisms, conditioned by relief, acting on parent material over a period of time (SSSA 2008)– is vital to support the environment and our societies but, as a non-renewable resource (Larson & Pierce 1991), must be carefully preserved to avoid its degradation. The global and continuous increase of population, urbanization and industrialization has induced pollution of soils threatening human and ecosystems health (Kaya 2006).

## HEAVY METALS IN SOIL

Heavy metals are contaminants capable of induce environmental and health problems in soils, water, atmosphere and living organisms (Navarro-Pedreño et al. 2008). The term heavy metals is applied for metallic elements which have densities $>5.0$ Mg m$^{-3}$, including Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, and Zn (SSSA 2008). Some metalloids like As are considered in heavy metals studies by its toxicity. Some of these elements are essential for plant nutrition, becoming a problem when the concentration is high enough to induce toxicity. Heavy metals are naturally present in soils depending on the type and chemistry of the parent material, or are artificially introduced into de soil system by anthropogenic activities (Mirsal 2004). Major source of heavy metals in soil are: 1) geochemical origin; 2) human activities like mining and smelting, agriculture materials (fertilizers, pesticides, sewage sludge, etc), fossil fuel combustion, metallurgical and chemical industries, sports and military ammunition, and 3) atmospheric deposition (Alloway 1995). Continuous monitoring of soil pollution by heavy metals is needed to ensure the sustainability of ecosystems (Kaya 2006).

## THE ROLE OF REMOTE SENSING IN SOIL SCIENCES

The acquisition of soil information for large areas and for repeated time periods has been a major challenge for soil scientist. In coordination with field soil surveys and physical-chemical analytical methods that are costly and time consuming, lower cost methods and tools for soil mapping over large areas are needed. In the early 70s, digital soil mapping (Webster & Burrough 1972a, b) began a new era in soil mapping and had a continuous development by the improvement of the information and remote-sensing technologies, computing, statistics and modeling, spatial information and global positioning systems, measurement systems (such as infrared spectroscopy), and in more recent times, online access to information (Sanchez et al. 2009).

Remote sensing is defined as the science an art of obtaining information about an object, area, or phenomenon through the analysis of data acquired by a device that is not in contact with the object, area or phenomena under investigation (Lillesand et al. 2003). Remote sensing is based on the analysis of the interaction between a flux of electromagnetic radiation and the object or phenomena under investigation. Remote sensors are carried onto aerial or satellite platforms which offer the capability of rapid and synoptically monitoring of large areas (Andrew & Ustin 2008). Remote sensors can be used to frequently revisit a study area

providing data to monitor a phenomena or process. In particular, remote sensing is useful for surveying natural resources and monitoring the environment (e.g. urban growth, rainforest deforestation, floods mapping, etc.), especially when fast and repeated observations are required (López-Pamo et al. 1999).

The process of soil information acquisition by remote sensing is complex and requires a great knowledge of the interaction between the radiation and the soil. In this sense, researchers infer the three dimensional properties of soils by the convergence of two possible forms of evidence (Frazier 2006): 1) direct evidences of soil properties by their spectral characteristics and patterns of distributions, and 2) indirect evidences derived from observations of geomorphology, vegetation types and physiological status, and human induced land covers. With these basic premises, a wide range of remote sensing applications in Soil Sciences has been developed supporting the usefulness of remote sensing in soil studies. Examples of remote sensing applications in soil sciences are: the mapping of soil classes (Kariuki et al. 2003, Debella-Gilo & Etzelmüller 2009), soil salinity detection (Taylor et al. 1996, Metternicht 2001, Dehaan & Taylor 2003, Farifteh et al. 2007, Schmid et al. 2009, Melendez-Pastor et al. 2010), soil moisture mapping (Ferrer et al. 2003, Merlin et al. 2008, Barrett et al. 2009), the detection of soil nutrients (Rivero et al. 2009, Sridhar et al. 2009), and many others.

## SPECTROSCOPY OF MINERALS AND ROCKS

Due to remote sensing is relatively a new science based in the analysis of the electromagnetic radiation with the object under investigation, remote sensing has employed the scientific background of other science disciplines -like physics and chemistry- that previously analyzed this topic. In this sense, spectroscopy, defined as the study of the interaction between the electromagnetic radiations with the matter as a function of wavelength, plays a prominent role in remote sensing. A basis statement that supports the ability of remote sensing to study an object or phenomena is that each material is identifiable by a characteristic spectral signature that contains information about its chemical composition and physical structure. Thus it is not possible to generate extensive catalogs of material-specific spectra known as spectral libraries (Clark et al. 2007, Baldridge et al. 2009).

Basically, two physical processes are employed in remote sensing to acquire information about a target material: 1) a remote sensor detects a portion of the incident electromagnetic radiation (in the visible and near-infrared (VNIR) spectral regions) after it has interacted with a material (reflection or scattering); and 2) a remote sensor detects the efficiency at emitting thermal radiation (emission) by the target material (Rees 2001). The first process requires the action of an illumination source (i.e. the Sun or an active sensor), while the second one is based in the recording of the radiation emitted by any material with a temperature above 0K (absolute zero). After remote sensors record the electromagnetic radiation flux emitted or reflected by the target, and the data is transferred to receiving station (or stored in the instruments onboard and airplane), the information is digitally available for remote sensing data processing. Later, the analysis of reflectance spectra provides a rapid and inexpensive technique for determining the mineralogy and chemical composition of samples (Van Der Meer 2002).

The analysis of spectral signatures is wavelength-dependent since chemical species exhibit characteristic absorption features for certain spectral regions. The information provided by spectral signatures in the visible and near-infrared (from 400 to 2500 nm) results from absorptions of energy due to two types of processes (Burns 1970, Hunt 1977, Clark 1999, Van Der Meer 2002): 1) Electronic transitions; they are due to isolated atoms and ions have discrete energy states and when absorb or emit photons of an specific wavelength takes place a change from one energy state to another. Usually, when a photon is absorbed it is not emitted with the same wavelength. In solids, electrons can be shared between individual atoms and their energy level may become smeared over a range of values dented as energy bands. This kind of process is associated with transition metal ions such as Fe, Ti, Cr, etc. 2) Vibrational processes; the apparently random motions of any vibrating system are made up from a restricted number of simple motions called normal or fundamental modes. If a fundamental mode is excited an overtone occurs, producing a band at (or near) twice of the fundamental frequency. Vibrational absorptions are seen in the infrared spectrum only if the molecule responsible shows a dipole moment (it is said to be infrared active). Electronic transitions exhibit broader absorption features than due to vibrational processes. Figure 1 is used to locate and identify the origin of a large quantity of electronic and vibrational features in VNIR spectra of minerals. Four types of electronic processes (i.e. crystal field effects, charge transfer, color centers and conduction bands) are identifiable in the figure and properly discusses in Hunt (1977). It's remarkable the fact that many absorption bands for the two iron oxidation-states ($Fe^{2+}$ and $Fe^{3+}$) in several mineral species are showed. VNIR multispectral and hyperspectral sensors are the most commonly employed remote sensor for mineral mapping (Rowan et al. 1977, López-Pamo et al. 1999, Kruse et al. 2003, Rowan et al. 2003).
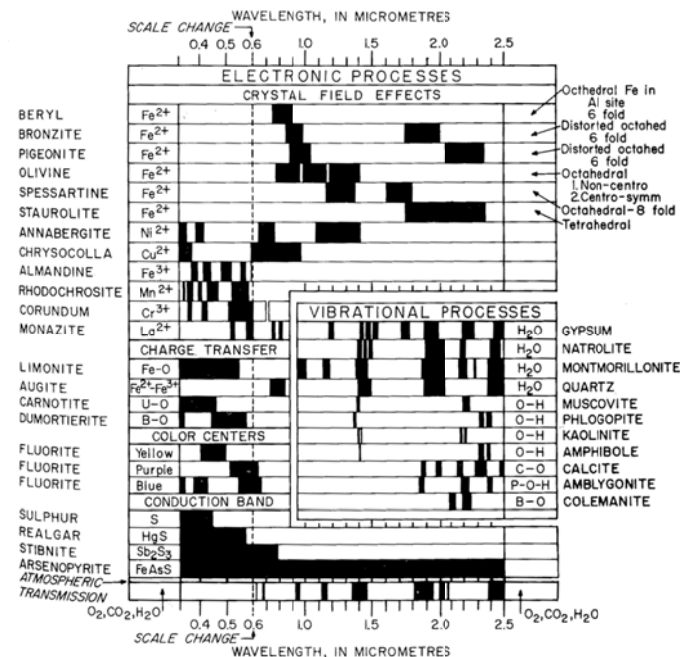


Figure 1. Spectral signature diagram. Black bars indicate the widths of absorption bands. From Hunt 1977.

Remote thermal sensors are also very useful in Soil Sciences. The emissivity of a material in the thermal (3 to 15 μm) region determines the quantity of radiation emitted at a given temperature and is negatively related to the reflectivity at the same wavelength, with high emissivities for most materials with the exception of metals and some minerals (Rees 2001). Thermal remote sensing has been employed for mapping evaporite minerals (Crowley 1993; Crowley & Hook 1996) and hydrothermally altered rocks (Vaughan et al. 2005).

For microwave (frequencies between 0.3 and 300 GHz) regions, the amount of thermal radiation is also determined by the emissivity of the materials for such wavelengths but the microwave observations are made with different observation angles respect to the normal and polarization types which largely the emissivity (Rees 2001). Microwave sensors are useful for soil moisture mapping (Ferrer et al. 2003, Merlin et al. 2008, Barrett et al. 2009). In addition, ground penetrating radar (GPR) can be employed to locate buried waste and for measurement of organic pollutants in ground water, like the presence of hydrocarbon films by measuring the degree of depression of the capillary zone (Mirsal 2004).

Finally, some relatively new applications employs gamma-ray sensor in soil research. The gamma-ray response recorded by the sensor (usually onboard an airplane) denotes the mineralogy and geochemistry of the parent mineral and the derived alteration and weathering products, including residual and transported clays, sands and silts (Martelet et al. 2006). Measurements are usually taken in the spectral windows for 40K, 238U and 232Th. In soil science studies, gamma-ray sensors has been employed in several applications like soil type mapping (Cook et al. 1996) or the analysis of mineralization styles (Shives et al. 2000).

# MAPPING TECHNIQUES

The basic underlying purpose of remote sensing is the extraction of thematic information by transforming data into information (Jensen 2004). In this sense, many multipurpose digital image processing techniques has been developed and tested in varied applications. In soil mineralogy mapping, digital image processing techniques employ the knowledge acquired by the spectrometric analysis of mineral and rocks spectra to develop mathematical methods capable to enhance and quantify the presence of mineral specie. Image transformations and imaging spectroscopy are two of the most employed digital image processing techniques for mineral mapping.

## Image Transformations

An image transformation is an operation that re-express the information content of an image or an image set, including arithmetic operations (although they are not strictly transforms), empirically based image transforms (e.g. tasselled cap transform, perpendicular vegetation index), principal components analysis, the hue-saturation-intensity (HSI) transform, or harmonic analysis transforms like the Fourier or Wavelet transforms (Mather 2004).

Many spectral ratios have been employed in mineral mapping to enhance the spectral contrast of specific absorption features. A selection of spectral indexes employed in mineral

mapping is showed in Table 1. The brightness index (BI) quantifies the average reflectance magnitude as is calculated as a Euclidian distance in a space of $n$ spectral dimension, considering soil reflectivity in the visible region (Mathieu *et al.* 1998). The coloration index (CI) developed by Escafadal and Huete (1991) reduces the influence of soil color on the sensitivity of some vegetation indices and related by Madeira et al. (1997) to absorption of iron oxides like goethite and hematite. The redness index (RI) calculated from Helmholtz chromatic co-ordinates (lambda d, Pe, Y) and correlated to hematite content (Madeira et al. 1997). Rowan and Mars (2003) mapped granitoids and gneisses with intense $Fe^{3+}$ absorption bands with a simple ratio between red and green spectral bands ($Fe^{3+}$ ratio). Special attention requires the relative absorption-band depth (RBD concept (Crowley *et al.* 1989) which is a three-point ratio formulation for mapping Al-O-H, Mg-O-H and $CO_3^{2-}$ absorption intensities. The general formulation of the RBD ratio is the following:

$$RBD = \frac{band\ 1 + band\ 2}{band\ 3}$$

The numerator corresponds to the sum of the 'shoulders' of the absorption band while the denominator corresponds with the band of the absorption feature minimum. RBD's success lies in the removal of the continuum to enhance the intensity of the absorption feature (Crowley *et al.* 1989). Rowan and Mars (2003) employed three different version of the RBD spectral index to map limestone, dolomite and muscovite with a multispectral sensor.

The Crosta technique (Crosta and Moore 1989) is a feature oriented principal component selection. Through the analysis of the eigenvector values it allows the identification of the principal components that contain spectral information about specific minerals, as well as the contribution of each of the original bands to the components in relation to the spectral response of the materials of interest (Ranjbar et al. 2004). The technique can be applied on four and six selected bands of Landsat Thematic Mapper (TM) and Landsat Enhanced Thematic Mapper Plus (ETM+) data to map iron oxides, hydroxyl minerals, the presence of hydrothermally altered rocks and the main structural features that can be related with ore deposition, for exploration of porphyry copper mineralization or clay alterations (Crosta & Moore 1990, Ruiz-Armenta & Prol-Ledesma 1998, Ranjbar et al. 2004, Mohammadzadeh & Babaee 2006, Aydal et al. 2007).

In a similar approach, Yamaguchi and Naito (2003) employed an orthogonal transformation of the five ASTER multispectral sensor bands in the short wave infrared region (SWIR, from 1600 to 2430 nm) to represent specific spectral patterns, proposing five spectral indices, from lower to higher orders: the brightness index, the alunite index, the kaolinite index, the calcite index and the montmorillonite index. They calculated a set of coefficients to be multiplied by the corresponding band reflectance. The final value of the indexes results from the summation of all band-specific products.

**Table 1. Spectral indices for mineral mapping. The numeric values of wavelength correspond with the midpoint of the full width and half maximum (FWHM) of the original sensor bands**

| Index | General formulation | References |
|---|---|---|
| Brightness Index | $$BI = \frac{\rho_{BLUE}{}^2 + \rho_{GREEN}{}^2 + \rho_{RED}{}^2}{3}$$ | Mathieu et al. 1998 |
| Coloration index (CI) | $$CI = \frac{\rho_{RED} - \rho_{GREEN}}{\rho_{RED} + \rho_{GREEN}}$$ | Escafadal & Huete 1991 Madeira et al. 1997 |
| Redness index (RI) | $$RI = \frac{\rho_{RED}{}^2}{\rho_{BLUE} \cdot \rho_{GREEN}}$$ | Madeira et al. 1997 |
| $Fe^{3+}$ | $$Fe^{3+} ratio = \frac{\rho_{RED}}{\rho_{GREEN}}$$ | Rowan & Mars 2003 |
| Ca-$CO_3$ (limestone) | $$RBD_{limestone} = \frac{\rho_{2260nm} + \rho_{2395nm}}{\rho_{2330nm}}$$ | Rowan & Mars 2003 |
| Ca, Mg-$CO_3$ (dolomite) | $$RBD_{dolomite} = \frac{\rho_{2205nm} + \rho_{2330nm}}{\rho_{2260nm}}$$ | Rowan & Mars 2003 |
| Muscovite | $$RBD_{muscovite} = \frac{\rho_{2165nm} + \rho_{2260nm}}{\rho_{2205nm}}$$ | Rowan & Mars 2003 |
| Brightness Index | $Y_i = 0.446X_{1i} + 0.449X_{2i} + 0.453X_{3i} + 0.447X_{4i} + 0.441X_{5i}$ | Yamaguchi & Naito 2003 |

**Table 1 (Continued)**

| Alunite Index | $Y_i = -0.694X_{1i} - 0.219X_{2i} + 0.562X_{3i} + 0.389X_{4i} - 0.048X_{5i}$ | Yamaguchi & Naito 2003 |
|---|---|---|
| Kaolinite Index | $Y_i = 0.012X_{1i} - 0.763X_{2i} + 0.505X_{3i} + 0.372X_{4i} - 0.124X_{5i}$ | Yamaguchi & Naito 2003 |
| Calcite Index | $Y_i = 0.156X_{1i} + 0.522X_{2i} - 0.388X_{3i} - 0.647X_{4i} + 0.365X_{5i}$ | Yamaguchi & Naito 2003 |
| Montmorillonite Index | $Y_i = 0.696X_{1i} + 0.069X_{2i} - 0.364X_{3i} + 0.185X_{4i} - 0.589X_{5i}$ | Yamaguchi & Naito 2003 |

## Imaging Spectroscopy

Imaging spectroscopy deals with the mapping of specific ground materials by detecting specific chemical bonds, and analyzing reflectance/absorbance features in hyperspectral (or multispectral) images (Clark 1999; Clark et al. 2003). Methods on imaging spectroscopy were first developed when the first hyperspectral remote sensors were constructed in the early 80's. Nowadays, imaging spectroscopy is a field of great interest in remote sensing with applications in soil mineral mapping (Clark et al. 2003, Kruse et al. 2003, Bartholomeus et al. 2007) and vegetation studies (Okin et al. 2001, Kokaly et al. 2003, Andrew & Ustin 2008).

Imaging spectroscopy is based in the analysis of absorptions in a spectrum whereas absorption features have two components: the continuum and individual features. The continuum is the "background absorption" onto which other absorption features are superimposed (Figure 2) and may be due to the wing of a larger absorption feature (Clark & Roush 1984, Clark 1999). The apparent depth or strength of an absorption feature relative to the continuum is dependent on the intrinsic absorption strength, the grain size and abundance of the material as well as the abundance, absorbing nature, and grain sizes of the other materials mixed with the sample (Clark & Roush 1984). The depth of an absorption band (D) is usually defined relative to the continuum with the following expression (Clark & Roush 1984, Clark 1999, Clark et al. 2003):

$$D = 1 - \frac{R_b}{R_c}$$

where $R_b$ is the reflectance at the band bottom and $R_c$ is the reflectance of the continuum at the same wavelength as $R_b$.
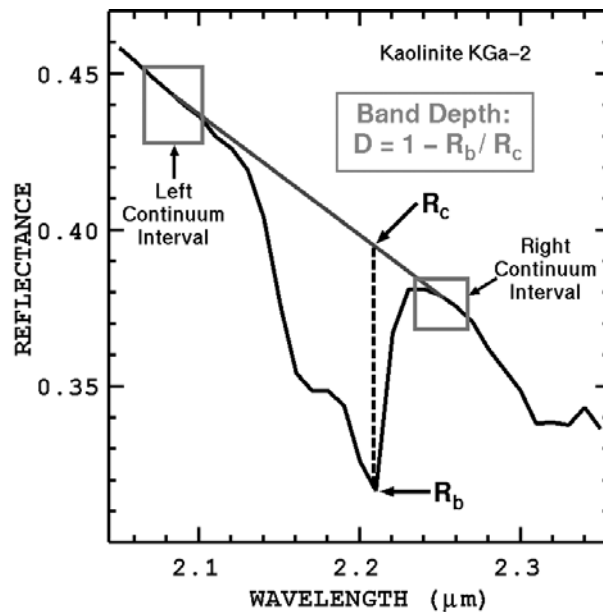


Figure 2. Characteristics of an absorption feature. From Clark et al. 2003.

The continuum should be removed by division, whether you are working in reflectance or emittance, and by subtraction when working with absorption coefficients. The continuum-removal process isolates spectral features and puts them on a level playing field so they may be intercompared (Clark 1999).

Many algorithms are available and have been developed to extract information from hyperspectral (and multispectral) data by using the high spectral dimensionality of those datasets. Van der Meer *et al.* (2002) reviewed a large set of analytical techniques for imaging spectrometry studies, including: binary encoding (Goetz et al. 1985), waveform characterization (Okada & Iwashita 1992), spectral feature fitting (SFF) also known as the TETRACORDER algorithm (Crowley et al. 1989, Clark et al. 2003), spectral angle mapper (SAM) (Kruse et al. 1990), spectral unmixing (Adams & Adams 1984, Adams et al. 1986), iterative spectral unmixing (ISU) (Van der Meer 1999), multiple endmember spectral mixture analysis (MESMA) (Roberts *et al.* 1998), constrained energy minimization (CEM) (Farrand & Harsanyi 1997), foreground-background analysis (FBA) (Smith et al. 1994), cross correlogram spectral matching (CCSM) (Van der Meer & Bakker 1997), geophysical inversion (Van der Meer 2000), and supervised and unsupervised statistical classification methods (e.g. minimum Euclidean distance, maximum likelihood, etc.) frequently employed in land-cover mapping.

# EXAMPLES OF SOIL HEAVY METALS DETECTION WITH REMOTE SENSING

This section provides a compilation of various studies that employed remote sensing techniques (field or laboratory spectroscopy and aerial or satellite data) for mapping heavy metals (Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, and Zn) and metalloids (As, Sb) in soil. Table 2 shows the chemical elements assesses in the studies included in this compilation and the main characteristics of the mapping approaches.

Kemper and Somner (2003) employed a spectral mixture modeling approach combining field and airborne hyperspectral sensor in combination with soil samples. They mapped heavy metal sludge contamination (As, Cd, Cu, Hg, Pb, Sb, and Zn) after the mining accident in Aznalcóllar (southwest Spain). The variable multiple endmember spectral mixture analysis (VMESMA) tool was used aiming to estimate the quantities and distribution of the waste sludge material. They employed field observations and chemical measurements of samples taken in the area to assess the sludge abundances obtained by unmixing the hyperspectral spectral data.

Bartholomeus *et al.* (2007) quantified topsoil iron content with imaging spectroscopy techniques in south Spain. They combined laboratory, field and airborne hyperspectral sensors in combination with soil samples. They employed the redness index (RI) and the continuum-removal and band-depth (CR-BD) analysis to assess the correlations between the spectral data and iron content. A final map of iron content in partially vegetated (vegetation coverage was determined by spectral mixture analysis) areas was obtained with the established regression functions.

**Table 2. Main characteristics of the studies that employed remote sensing techniques for mapping heavy metals and metalloids in soils**

| Elements | References | Study areas | Sensors (1) | Spectral regions (2) | Mapping methods (3) |
|---|---|---|---|---|---|
| As | Kemper & Sommer 2003 | Southwest Spain | FAH | VNIR, SWIR | VMESMA |
| As | Choe et al. 2008 | Southeast Spain | FAH | VNIR, SWIR | Ratios, CR-BD, SAM |
| Cd | Kemper & Sommer 2003 | Southwest Spain | FAH | VNIR, SWIR | VMESMA |
| Cu | Kemper & Sommer 2003 | Southwest Spain | FAH | VNIR, SWIR | VMESMA |
| Cu | Choe et al. 2008 | Southeast Spain | FAH | VNIR, SWIR | Ratios, CR-BD, SAM |
| Fe | Kemper & Sommer 2003 | Southwest Spain | FAH | VNIR, SWIR | VMESMA |
| Fe | Bartholomeus et al. 2007 | South Spain | FAH | VNIR, SWIR | RI, CR-BD, SMA |
| Hg | Kemper & Sommer 2003 | Southwest Spain | FAH | VNIR, SWIR | VMESMA |
| Pb | Kemper & Sommer 2003 | Southwest Spain | FAH | VNIR, SWIR | VMESMA |
| Pb | Choe et al. 2008 | Southeast Spain | FAH | VNIR, SWIR | Ratios, CR-BD, SAM |
| Sb | Kemper & Sommer 2003 | Southwest Spain | FAH | VNIR, SWIR | VMESMA |
| Zn | Kemper & Sommer 2003 | Southwest Spain | FAH | VNIR, SWIR | VMESMA |
| Zn | Choe et al. 2008 | Southeast Spain | FAH | VNIR, SWIR | Ratios, CR-BD, SAM |

Notes:

1. FAH: field and airborne hyperspectral

2. V: visible, 400-700 nm; NIR: near-infrared, 700-1000nm; SWIR: short-wave infrared, 1000-2500nm (notation in Ben-Dor & Banin, 1994).

3. CR-BD (continuum-removal and band-depth analysis); VMESMA (variable multiple endmember spectral mixture analysis); RI (redness index); SMA (spectral mixture analysis); SAM (spectral angle mapper)

Choe *et al.* (2008) derived parameters (i.e. spectral ratios and continuum-removal and band-depth analysis) from spectral variations associated with heavy metals in soils of southeast Spain. They found significant correlations between ground-derived spectral parameters and heavy metal concentrations for with the depth of the absorption at 500 nm (Depth$_{550\ nm}$) for Pb and Zn, with the ratio of 610 to 500 nm (R$_{610,550\ nm}$) for Cu, Pb and Zn, with the depth of the absorption at 2200 nm (Depth$_{2200\ nm}$) for Zn and As, with the area of the absorption at 2200 nm (log(Area$_{2200\ nm}$)) for Cu, Pb, Zn and As, and with the asymmetry of the absorption feature at 2200 nm (Asym$_{2200\ nm}$) for As. They applied these parameters to a hyperspectral aerial image acquired with the HyMAP sensor. The pixels classified in the rule image of Depth$_{500\ nm}$, the ratio R$_{1344,778\ nm}$, and Area$_{2200\ nm}$ derived from a HyMAP image showed similar spatial patterns to the gradient maps of ground-derived spectral parameters.

# CONCLUSION

Heavy metals are pollutants of great importance for human health and ecosystems. The use of remote sensing techniques to determine the presence of these pollutants in soils is a good tool for this purpose. However, not too many research and studies are done. To know the level of heavy metal pollution in soils is vital for most of the human activities in the Earth surface, thus the improvement of remote sensing techniques to study soil pollution are needed.

The development of new sensors join to the improvement of the imaging analysis are the key factors to aid us to locate heavy metals in large areas and favors to take the best decisions for land management and pollution control.

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