

Recent applications of vibrational mid-Infrared (IR) spectroscopy for studying soil components: a review

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Abstract

The present review highlights the recent applications of mid-infrared spectroscopy and in particular of diffuse reflectance spectroscopy (DRIFT) and attenuated total reflectance (ATR) and processing methods (e.g., deconvolution, derivative and chemometrics) to rapidly provide valuable information on soil composition and organic geochemistry. Research has demonstrated that both DRIFT and ATR techniques can be considered useful tools for the analysis of a large number of soil samples, giving not only typical spectral patterns but permitting an accurate prediction of quantitative parameters such as, e.g., total carbon, total nitrogen, C/N ratio, lignin, dissolved OC, carbonyl-C, aromatic-C, O-alkyl-C, and alkyl-C contents. Based on literature results, infrared spectroscopy can be recognized as one of the most promising analytical techniques for investigating soil science.

Keywords: attenuated total reflection, chemometrics, diffuse reflectance infrared Fourier transform, humic substances, mid-infrared spectroscopy, soil minerals, soil organic matter

Introduction

The most direct way to study the vibrational states of a molecule is through mid-Infrared (MIR) spectroscopy. The MIR can identify the kind of molecular motions and bonds or functional groups present in the sample, since each frequency corresponds to a given amount of energy and a specific molecular motion (e.g. stretching, bending, etc.), so permitting to characterise complex systems as soil components. The spectrum obtained can be considered as a fingerprint of a specific compound in the examined system; in fact, the frequency of a functional group is quite specific and independent of a specific molecule. The intensity of each band is related to the change in the electrical dipole moment of the bond during the vibration, so the bonds with higher changes in the dipole moment (e.g., O-H, N-H, C=O, C-O) will give higher intensity bands relative to the other bonds (Griffiths and De Haseth, 2007). In addition, the intensity of a band is affected by the concentration of the functional group or its abundance in a mixture of compounds. In this way, MIR can be used as a quantitative technique, assuming that the dipole moment-related “response factor” is taken into account (Griffiths and De Haseth, 2007).

MIR spectroscopy has frequently been applied to investigate soil properties and soil organic matter (SOM) characteristics (Aguiar, et al., 2013; Bellon-Maurel and McBratney, 2011; Calderon, et al., 2011a, 2011b; Demyan, et al., 2012; Du and Zhou, 2009; Francioso, et al., 2009; Haberhauer and Gerzabek, 1999; Kaiser, et al., 2011). Currently, the combination of multivariate statistical methods used for the Fourier Transform IR (FTIR) spectra analysis has provided a powerful method for the discrimination and identification and/or quantification of single components in soils (Aguiar, et al., 2013; Bellon-Maurel and McBratney, 2011; Bornemann, et al., 2010; Calderon, et al., 2011a, 2011b; D'Acqui, et al., 2010; Fernandez-Getino, et al., 2013; Janik, et al., 2007a, 2007b; Ludwig, et al., 2008; Minasny, et al., 2008; Pirie, et al., 2005; Reeves III, 2010; Stumpe, et al., 2011; Tatzber, et al., 2010; Viscarra Rossel, et al., 2006; Yang, et al., 2012).

The representation of MIR spectra is not uniform in the literature. Usually, the absorption spectrum is presented as a transmittance ($T(\nu) = I(\nu) / I(\nu_0)$) or absorbance ($A(\nu) = -\log T(\nu)$) spectrum, where $I(\nu)$ is the spectrum (i.e. the dependence of intensity on frequency) of the sample and $I(\nu_0)$ is the spectrum of the background. Direct transmission is applicable only to samples that do not absorb all the incoming IR energy.

For most samples, such as soil or soil organic matter (SOM), it is necessary to prepare a pellet where the sample is mixed with alkali halides (NaCl, KCl, KI and KBr), non IR-absorbing materials. The pellet is prepared by grinding 1-2 mg of sample with about 200 mg of alkali halide in a mortar and by using a hydraulic press to create a thin disk. This technique yields a very clear signal, but requires a long preparation and few mg of sample for each pellet.

Diffuse reflectance infrared Fourier Transform (DRIFT)

This technique was introduced by Nguyen, et al. (1991) for studying soil chemical composition and was subsequently used to investigate SOM and the chemical composition of humic substances, as well as the effect of amendment practice on soil (Aguiar, et al., 2013; Calderon, et al., 2011a, 2011b; Demyan, et al., 2012; Ellerbrock, et al., 2009; Ferrari, et al., 2011; Janik, et al., 2007a; Kaiser, et al., 2007; Leue, et al., 2010; Ludwig, et al., 2008; Minasny, et al., 2008; Reeves III and Smith, 2009). It has also been applied to study many other agricultural related aspects such as the composition of different coal ranks (Chen, et al., 2012; Li, et al., 2010) and their soluble SOM fraction (Gezic, et al., 2012; Ghosh, et al., 2009), the chemistry of waste and compost materials (Huber-Humer, et al., 2011; Salati, et al., 2013; Smidt and Meissl, 2007), the decomposition processes of forest litter (Duboc, et al., 2012; Nault, et al., 2009; Osono, et al., 2011; Tatzber, et al., 2010), the chemical structure of pyrogenic organic matter (OM) (Francioso, et al., 2011; Nocentini, et al., 2010) and the behaviour of chemical compounds adsorbed on clays (Aochi and Farmer, 2011; Dorado, et al., 2010).

The principle of the technique is based on the scattering of the incident light in all directions when it is absorbed by powders and/or a rough surface. A part of the incident radiation is reflected at the solids surface to produce Fresnel reflectance (mirror-like), while another part goes through the sample, interacts with it and reemerges in many directions. Absorption and scattering of light in many directions by a sample is known as diffuse reflectance (Griffiths and Fuller, 1982).

The description of diffuse reflectance (R^∞) of an "infinitely thick" layer is represented in the Kubelka-Munk (K-M) equation (1):

$$f(R_{\infty}) = (1 - R_{\infty})^2 / (2R_{\infty}) = k / s \quad (1)$$

where R_{∞} is the absolute reflectance of the layer, s is a scattering coefficient, and k is the molar absorption coefficient. In practice, the diffuse reflectance of a sample is measured with respect to non-absorbing standards, such as KBr or KCl. Therefore, R_{∞} in equation (1) may be replaced by R'_{∞} where

$$R'_{\infty} = R'_{\infty}(\text{sample}) / R'_{\infty}(\text{standard}) \quad (2)$$

The Kubelka-Munk (KM) theory predicts a linear relationship between the molar absorption coefficient, k , and the peak value of $f(R_{\infty})$ for each band, provided s remains constant. Since s depends on the size and range of the particles, the K-M function can be used for accurate quantitative analysis. In the case of dilute samples in non-absorbing matrices, the absorption coefficient (k) is associated with sample absorptivity, a (at a given frequency) and concentration (c):

$$k = 2.303 \cdot a \cdot c \quad (3)$$

Therefore, substituting Eq. (2) into Eq (1) and the value of k , Eq. (4) can be obtained for the relative diffuse reflectance:

$$f(R_{\infty}) = (1 - R_{\infty})^2 / (2R_{\infty}) = 2.303 a \cdot (c / s) \quad (4)$$

Care must be taken in applying the K-M equation when R_{∞} is lower than about 30%, since when the sample concentration is high, deviations from linearity can occur. Moreover, this equation is valid if the Fresnel's reflectance is negligible and if the scattering coefficient remains constant as the concentration varies (Griffiths and Fuller, 1982). A high Fresnel's reflectance produces anomalous band dispersion for high absorptivity bands. In soil, this last effect, mainly related to soil structure, is particularly important because soil structure and particle size can vary greatly and can therefore affect the spectrum (Richter, et al., 2009). Fresnel's reflectance can be minimized or eliminated by grinding and diluting the sample with non-absorbing powder (KBr, KCl, Ge or Si). However, the use of alkali halides can cause interferences due to ion exchange between the sample and the KBr or to the adsorption of water onto the KBr. Stumpe, et al. (2011) analyzed the effects of 180 well-characterized soil samples that were ground for different times (0, 2 or 4 minutes) and then used for DRIFT measurements. The results indicated that spectral information were better achieved for lightly ground (2 minutes) soil samples compared with intensively ground (4 minutes) or unground samples. The grinding procedure did not affect the clay minerals spectra whilst the quartz and soil organic carbon (SOC) spectra were modified. The geometry of intact structural soil surfaces was also investigated by Leue, et al. (2010). They tried to develop an approach to correct for surface geometry effects. The objectives were to analyze the effects of particle size, porosity, and specific surface shapes on the DRIFT signal intensity. The spectra were obtained from differently textured quartz samples and from gypsum blocks with defined surface shapes as models for soil porous systems. The measured DRIFT signal intensity, as well as the resolution and the simulated reflectance, decreased with increasing particle size.

Attenuated total reflectance (ATR)

ATR is applied for the investigation of SOM (Artz, et al., 2008; Cecillon, et al., 2012; Delarue, et al., 2013; Gezic, et al., 2012; Li, et al., 2010; Neves-Fernandes, et al., 2010; Tremblay, et al., 2011; Vergnoux, et al., 2011) or when ions, like nitrate,

ammonium etc., are assayed in soil (Du and Zhou, 2009; Jahn, et al., 2006). This technique ensures a direct analysis of undiluted opaque samples in a highly reproducible way (Tremblay, et al., 2011), permitting band intensities to remain within a linear range. With this accessory, the IR radiation propagates through a crystal with a high refractive index, allowing the radiation to be reflected within the ATR element one or several times (Madejova, 2003; Sorak, et al., 2012). The sample is pressed into intimate contact with the top surface of the crystal (germanium, ZnSe and diamond). The IR radiation from the spectrometer enters the crystal, is then reflected through it and penetrates a finite amount "into" the sample, with each reflection along the top surface via the so-called "evanescent" wave (Linker, 2011). At the end of the crystal the beam is directed back into the normal path beam of the spectrometer. To obtain an internal reflectance, the incidence angle must be beyond the 'critical angle', which is a function of the real parts of the refractive indices of both the sample and the ATR crystal:

$$\theta_c = \sin^{-1}(n_1/n_0) \quad (5)$$

where n_1 is the refractive index of the sample and n_0 that of the crystal. The evanescent wave exponentially decays into the sample with the distance from the crystal surface, over a distance of the order of microns. The depth of the evanescent wave (d) penetration:

$$d = \frac{\lambda}{\left\{2\pi n_1 \left[\sin^2 \theta - (n_1/n_2)^2\right]^{1/2}\right\}} \quad (6)$$

is defined as the distance from the crystal-sample interface where the intensity of the evanescent wave decays to 37% of its original value and λ is the wavelength of the IR radiation. In the case of a ZnSe crystal ($n_0=2.4$), the penetration depth at 1000 cm^{-1} for a sample with a refractive index of 1.5 is estimated to be $2.0\ \mu\text{m}$ if the angle of incidence is 45° . In the same conditions, for a Ge crystal ($n_0=4.0$), the penetration depth is about $0.664\ \mu\text{m}$. The penetration depth and the total number of reflections along the crystal can be controlled either by varying the angle of incidence or by changing the crystal. The diamond ATR crystal is considered to be the best material to record spectra of hard samples since it cannot be scratched, which results in no performance degradation.

The choice of the method, transmission (e.g. KBr-pellet), DRIFT or ATR, depends on parameters such as the sample size, the information needed (bulk versus surface analysis) or the time required for the sample preparation. Currently, the improved design of DRIFT accessories has made this technique widely used for studying soil compounds (Aguiar, et al., 2013; Calderon, et al., 2011a, 2011b; Demyan, et al., 2012; Ellerbrock, et al., 2009; Francioso, et al., 2009; Leue, et al., 2010; Ludwig, et al., 2008; Minasny, et al., 2008); ATR is also now being widely used (Artz, et al., 2008; Gezic, et al., 2012; Neves-Fernandes, et al., 2010; Vergnoux, et al., 2011).

Data processing

The improved performances of FTIR spectrometers in terms of high signal-to-noise ratios, high data acquisition speed, specificity and reproducibility, make this technique an important tool for fast and cheap analyses of a large number of soil samples (Reeves III and Smith, 2009). In this context, mineral compounds and/or specific functional groups have been identified (Madejova, 2003; Tremblay, et al., 2011). However, the SOM or humic substances display a combination of complex

multi-component bands which overlap into a broad unresolved absorption. The individual component absorptions from condensed phase spectra hidden within a broad band cannot be resolved by increasing spectral resolution. The critical point is how to identify single functional group vibrations or the presence of well defined molecular structures. Normalization, baseline correction and smoothing are the first steps to process a spectrum (Demyan, et al., 2012; Du and Zhou, 2009; Fernandez-Getino, et al., 2013; Ludwig, et al., 2008; Tatzber, et al., 2010; Vegnoux, et al., 2011).

Spectral subtraction

Spectral subtraction is commonly used when a compound is present in a mixture. If the interaction between the components results in a change in the spectral properties of either one or both of the components, the changes can be observed in the difference spectra. Cox, et al. (2000) proposed the spectral subtraction for forensic analysis of SOM. In this method, soil is heated to combust the OM present in the soil and leaving the mineral component. By subtracting the FTIR spectrum recorded after combustion from that of untreated soil, it could be possible to acquire the so-called FTIR spectrum related to SOM present in soil (Figure 1). The method was considered simple and promising in routine analysis of SOM in different organo-mineral samples (Calderon, et al., 2011a, 2011 b; Kaiser, et al., 2011; Reeves, et al., 2005). On the other hand, the spectral subtraction is a subjective procedure because the best endpoint for the subtraction factor is arbitrarily determined. Spectral subtraction can also give spectral distortions, resulting in lower confidence for the user.

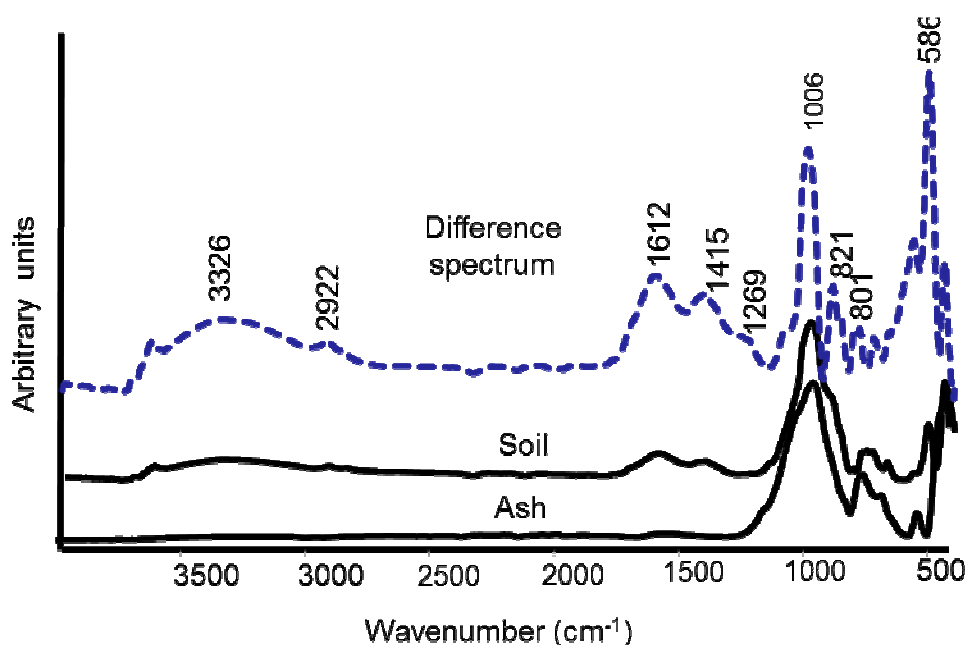


Figure 1 - Difference spectrum (top) of Italian soil produced by subtracting the ashed soil (bottom) from untreated soil (medium).

Spectral derivatives

Second derivative IR spectrum can obviously enhance the spectral resolution and amplify tiny differences in IR spectra. Many differences invisible in FTIR spectra such

as frequency position, information on the width and the maximum absorption intensity become clearer (Abdulla, et al., 2010; Griffiths and De Haseth, 2007). For example, the SOM spectra in the 1800-800 cm^{-1} region are very broad and exhibit many shoulders, indicating the presence of overlapping bands close in frequency (Figure 2). Therefore the structural information is hidden under these broad bands. Applying the second derivative to the SOM spectra, it is possible to obtain the resolution of each broad band into sharper downward pointing bands and the identification of the exact band frequency (Figure 2) with respect to the original spectra (Ferrari, et al., 2011). However, an accurate determination of the bandwidth from the maxima in the second derivative is complicated, due to the presence of neighbouring peaks. Despite this inaccuracy, the obtained parameters can be used as input parameters for a fitting procedure.

Curve fitting

The spectral analysis of SOM and humic substances frequently results in a poorly resolved spectrum, due to the existence of highly overlapped and hidden peaks. Therefore, it is not possible to assign specific peaks to the vibrations of specific functional groups. In such cases, the application of the original algorithm of non-linear peak fitting (Marquardt, 1963) can not only resolve the individual component bands, but may also make it possible to calculate the area under each of the individual bands (Griffiths and De Haseth, 2007). Therefore, curve-fitting analysis has become an important tool for qualitative and quantitative analysis of IR spectra. There are two essential input parameters for curve-fitting analysis: the number of component bands and their positions.

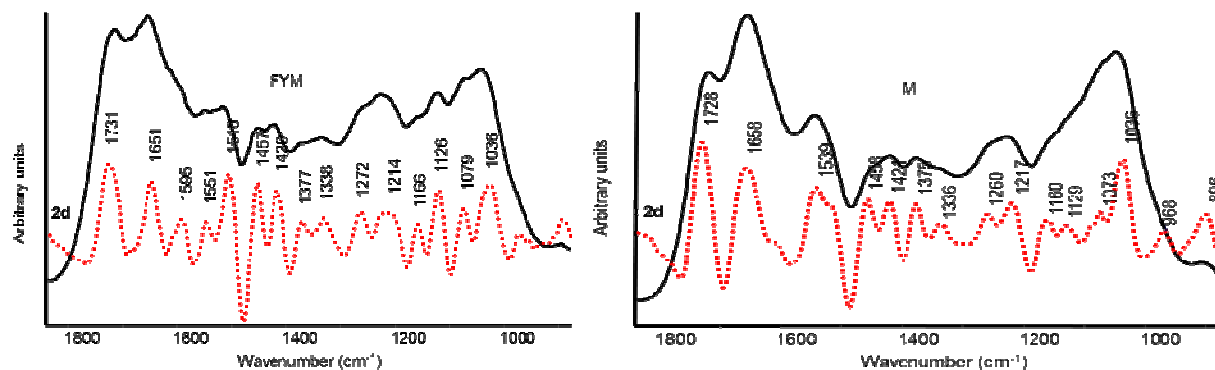


Figure 2 - DRIFT spectra of humic substances from a soil treated over 40 years with farmyard manure (FYM) and inorganic fertilizer (M) (Ferrari, et al., 2011). Spectra were processed with the second-order Savitzky-Golay method with 10 convolution points used to generate the second derivative of the spectra.

The focal point is to define the number of component bands really present in a broad band. It should be emphasized that to determine the number of component bands, one must be very careful to not over fit the absorbance by adding too many component bands; Fourier Self-Deconvolution (FSD) may be applied to determine the component bands and their positions with some curve-fitting software. FSD involves a certain degree of subjectivity because the operator must input two parameters: for example, the half-width at half-height and the resolution enhancement factor. Curves can also be decomposed into Gaussian, Voigt or Lorentzian functions. Three criteria are required to consider the curve-fitting

acceptable. First, the lowest RMS (root-mean-square) value obtainable has to be reached. Acceptable RMS values are usually of magnitude 10^{-5} for spectra with maximum absorbance values in the 0.05-0.09 range. Otherwise instead of the RMS, χ^2 can be evaluated to determine the best nonlinear fit, since it includes the effects of adding more parameters to the model. Second, the below and above fits should converge on the same model. Third, the second derivative of the composite sums should overlies the second derivative of the original spectra. Only when all three of the above criteria were met, was the curve-fitting result considered acceptable. An application of curve fitting was made for the direct analysis of charcoal fractions (Francioso, et al., 2012). The best goodness-of-fit, measured by the χ^2 parameter, was obtained with a pure Gaussian function (Figure 3). The study confirmed the importance of considering any hidden and overlapped peaks in the charcoal spectrum, in order to better quantify the changes caused by wildfire on SOM.

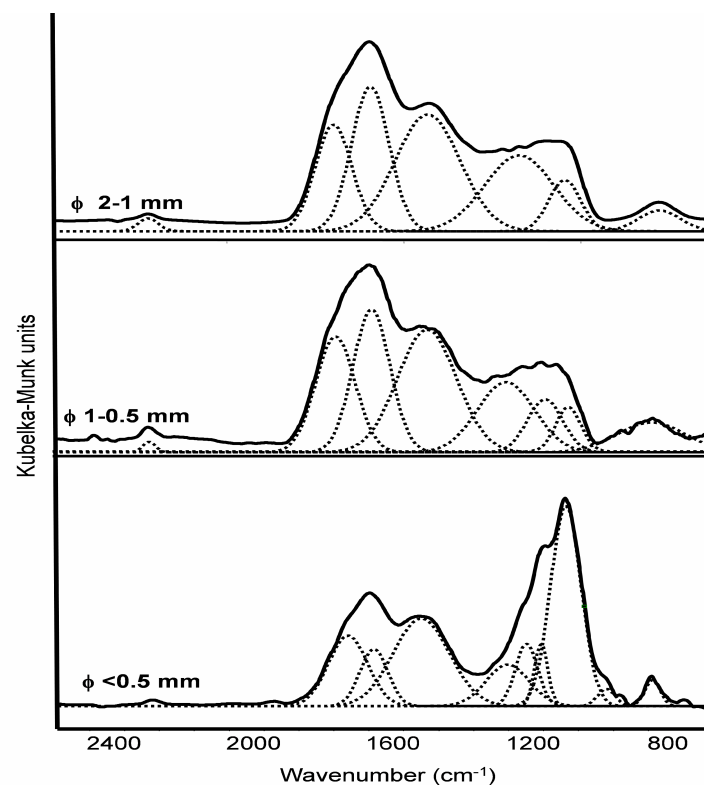


Figure 3 - DRIFT spectra of the charcoal from a burnt *Pinus pinea* forest collected 2 weeks after a severe wildfire and then it was separated in three size fractions (ϕ 2-1 mm, ϕ 1-0.5 mm and ϕ < 0.5 mm). Curve peak fitting was performed to fit the overlapping normal modes in the spectra (Francioso, et al., 2012).

Chemometric analysis

The chemometric techniques, such as partial least squares (PLS), principal components analysis (PCA) and artificial neural networks (ANN), have been applied when a large amount of data generated by FTIR spectrometers has to be processed to estimate the soil properties. PLS and PCA are the most popular procedures for quantitative determination or to predict one or several soil components (D'Acqui, et al., 2010; Reeves, et al., 2009; Viscarra Rossel, et al., 2006).

PCA and PLS serve two purposes in regression analysis. First, both techniques are used to convert a set of highly correlated variables to a set of independent variables by using linear transformations; second, both techniques are used for variable reduction. When a dependent variable for a regression is specified, the PLS technique is more efficient than the PCA for dimension reduction, due to the supervised nature of its algorithm. The Ratio of Performance to Deviation (RPD) is an important statistical parameter used to evaluate the calibration models. In agricultural application, $RPD > 3$ was considered acceptable and $RPD > 5$ excellent. However, there is no critical level of RPD for IR analysis in soil science, and acceptable values depend on the intended application of the predicted values. Three categories, based on RPD in the ranges > 2 , $1.4-2.0$, and < 1.4 , were used to indicate decreasing reliability of predicting (Chang, et al., 2001). Similar results of suitable limits for RPD were also described by Dunn, et al. (2002) and Pirie, et al. (2005). Strong correlations were found between FTIR spectra and soil parameters: C/N ratio, C and N content, lignin, HA, soil organic carbon (SOC), inorganic carbon, metals, pH, and others. In the last few years, many papers have dealt with the applications of PCA and PLS to the quantitative determination of the above-mentioned parameters on different soil layers and litter, as well as on particulate OM and on OM different fractions (Bornemann, et al., 2010; Calderon, et al., 2011a; D'Acqui, et al., 2010; Fernandez-Getino, et al., 2013; Ludwig, et al., 2008; Tatzber, et al., 2010). MIR spectroscopy predicted the C/N ratio well; the contents of C, N, and lignin, the production of dissolved OC, and the contents of carbonyl-C, aromatic C, O-alkyl -C, and alkyl-C were satisfactorily assessed. However, the N mineralization rate, and the alkyl-to-aromatic C ratio were predicted less satisfactorily (Ludwig, et al., 2008).

Soil mineral identification

FTIR spectroscopy was used to identify primary (quartz, feldspars) and secondary (silicates, clays, aluminosilicates) soil minerals (Janik, et al., 2007a; Madejova, 2003; Nguyen, et al., 1991; Viscarra-Rossel, et al., 2006). Table 1 reports the IR attributions and the integration limits used in some studies regarding the main bands of soil inorganic components. In particular the FTIR spectra of clay minerals made it possible to distinguish clay minerals from each other through the bands assigned to OH and Si-O groups (Bishop, et al., 2008; Madejova, 2003). Clays or aluminosilicates show two sharp peaks at 3695 and 3622 cm^{-1} due to OH stretching (Janik, et al., 2007b; Madejova, 2003; Nguyen, et al., 1991). A broad band near 3400 cm^{-1} is due to OH stretching (H bonded water); the position and intensity of this band is affected by various exchangeable cations. Its position decreases in the order $K^+ < Na^+ < Ca^{2+} < Mg^{2+}$, which is consistent with the increasing polarizing power (charge/radius) of the cation (Madejova, 2003). Also the band located at around 1630 cm^{-1} is widely accepted to be due to water associated with the clay. Spectra of several montmorillonite, nontronite, hectorite, and saponite clay films heated to 300°C exhibited a band at approximately 1400 cm^{-1} for all the clays except nontronite (Grim, et al., 1961). Vlaev, et al. (1989) specifically addressed the nature of absorption bands in the range $1640-1350\text{ cm}^{-1}$ for $\gamma\text{-Al}_2\text{O}_3$. On the basis of a chemisorption study, it was concluded that the band at $1640-1610\text{ cm}^{-1}$ was due to physically adsorbed water while the one at 1380 cm^{-1} was due to coordinatively bound water (Aochi, et al., 2011). Weak bands at about 1980 , 1870 and 1790 cm^{-1} are attributed to quartz overtone (Janik, et al., 2007b; Nguyen, et al., 1991). In addition, clay mineral spectra show an intense complex band at around 1048 cm^{-1} , related to the stretching vibrations of Si-O groups, while the bands at 525 and 468

cm^{-1} are due to Al-O-Si and Si-O-Si bending vibrations, respectively (Bishop, et al., 2008; Spence and Kelleher, 2012). The band at 622 cm^{-1} is assigned to coupled Al-O and Si-O out-of-plane vibrations. The presence of quartz mixtures is confirmed by a sharp band at 798 cm^{-1} with a shoulder near 779 cm^{-1} (Madejova, 2003).

Carbonate is a key component influencing both chemical and physical soil properties; it has been accurately estimated by using FTIR spectroscopy (Bruckman, et al., 2013; Grinard, et al., 2012; Tatzber, et al., 2007, 2010). Its spectrum is characterized by absorption bands near $3000\text{-}3700 \text{ cm}^{-1}$, due to hydrogen-bonded water and hydroxide ion; a weak band at around 2510 cm^{-1} , assigned to $\nu_s(\text{CO}_3^{2-}) + \nu_{as}(\text{CO}_3^{2-})$ combination band (Legodi, et al., 2001) and a strong band between 1430 and 1500 cm^{-1} , due to the CO_3^{2-} stretching vibration. At lower frequencies, the bands at around 712 cm^{-1} and 871 cm^{-1} result from in-plane and out-of-plane deformation vibrations of CO_3^{2-} , respectively.

Table 1. Assignments of the main bands observed in the MIR spectra of the inorganic components of soils according to ^a.

Peak (cm^{-1})	Integration limits/ cm^{-1}	Band assignments
3698	3719-3685	Si-O-H vibration of clays, kaolinite and Fe oxides Si-O-H vibration in clays, kaolinite, gibbsite and Fe
3622	3682-3577	oxides
~3460	3525-3460	O-H stretching of Gibbsite
~3430		O-H stretching of H-bonded water
2627		Aragonite (overtone/combination band)
2592		Calcite (overtone/combination band)
~2520	2562-2480	Carbonate (calcite or aragonite) (overtone/combination band)
~2000	2000-1790	Si-O vibration of quartz mineral (overtone/combination band)
1800		Calcite (overtone/combination band)
	1642-1569	OH bending of water
	1479-1408	Carbonates
	1293-1256	Bentonite
1238		Silicate
	1136-1070	O-Si-O stretching of silica, sulfates Si-OH of alumino-silicate lattice (kaolinite, illite, smectite)
	1056-945	smectite)
920		Al-OH deformation of kaolinite
	887-866	Carbonate
	820-752	Inorganic materials (clay and quartz minerals), carbonate, kaolinite
720		Calcite
700		Silica
650		Bentonite
520		Si-O-Al bending (octahedral Al)
470		Si-O-Si bending
	470-420	Kaolinite, illite, smectite

^a Calderon, et al. (2011b); Demyan, et al. (2012); Nguyen, et al. (1991); Tatzber, et al. (2010).

Particular attention has been devoted to the bands at 2506 cm^{-1} and 875 cm^{-1} because they are suitable for quantification purposes (Tatzber, et al., 2007). In particular, the band at 2506 cm^{-1} has been considered highly selective and gives a good linearity for carbonate calibration.

Soil organic matter characterization

The term soil organic matter encompasses all organic fractions present in soil, including plant residues in different decomposition stages, biomasses, dissolved organic matter and humic substances (HS) (Stevenson, 1994). Identification in SOM of specific mid-infrared peaks, which correspond to vibrations of certain functional groups such as carbohydrates, lignin, cellulose, fats and/or lipids and proteinaceous substances (Artz, et al., 2008), makes FTIR spectroscopy suitable to study the structural features and dynamics of SOM from different environments. Table 2 lists the main IR attributions and the integration limits used in some studies regarding the bands of SOM and HS. Generally, SOM spectra are characterized by broad and overlapping bands, so one must use caution when interpreting these spectra.

Bornemann, et al. (2010) summarized the literature for the structural assignments of several important bands of SOM: a broad band at about $3500\text{-}3300\text{ cm}^{-1}$ (OH stretch of different groups), a shoulder at around $3100\text{-}3040\text{ cm}^{-1}$ (NH_3^+ stretch and C=CH stretch vibrations), peaks at around 2960 and 2870 cm^{-1} and 2930 and 2940 cm^{-1} (CH_3 and CH_2 stretch of aliphatic chains, respectively) (Haberhauer and Gerzabek, 1999; Janik, et al., 2007a), a band at about $1720\text{-}1700\text{ cm}^{-1}$ (C=O stretch of carbonyl C) (Bardy, et al., 2008; Kaiser, et al., 2011; Sarkhot, et al., 2007), an intense band around $1650\text{-}1600\text{ cm}^{-1}$ (amide I, C=C stretch vibration; asymmetric -COO^- stretching) (Bardy, et al., 2008; Kaiser, et al., 2011; Verchot, et al., 2011), a medium peak around 1560 cm^{-1} (amide II, aromatic rings, carboxyl C) (Janik, et al., 2007a), a weak band at $1500\text{-}1510\text{ cm}^{-1}$ (aromatic C-H and C=C stretch); a weak peak around $1450\text{-}1370\text{ cm}^{-1}$ (CH_3 asymmetrical bending and CH_2 scissoring vibrations) (Haberhauer and Gerzabek, 1999; Verchot, et al., 2011), a variable intensity peak at about $1230\text{-}1250\text{ cm}^{-1}$ (amide III, C-O stretch of aromatic rings and carboxylic acids), a strong peak between $1100\text{-}1030\text{ cm}^{-1}$ and a minor absorption peak at 820 cm^{-1} (C-O stretch of cellulose and other β -anomers and β -glycosides) (Calderon, et al., 2011b; Kaiser, et al., 2011) and 870 cm^{-1} (aromatic C-H and C=C stretch) can be observed. A variety of methods for FTIR peak analysis have been used to investigate short and long-term application of organic and mineral fertilizers on SOM composition, compared with unfertilized ones. For example, Capriel, et al. (1997) determined the hydrophobicity index of SOM by using the area of the aliphatic C-H infrared band in the $3000\text{-}2800\text{ cm}^{-1}$ spectral region divided by organic C. The results showed that long term agricultural management influenced the amount of aliphatic C-H groups and implicitly the SOM hydrophobicity. A decrease of organic C due to management was accompanied by a decrease of hydrophobicity. Spaccini, et al. (2001) found that the aliphatic bands in the $2920\text{-}2860\text{ cm}^{-1}$ region can be used to study mineralization rates of corn residues in soil. Artz, et al. (2006) used the $1600/1030$ bands ratio (carboxylate/polysaccharide) as an index of decomposition in peat, suggesting that the band near 1630 cm^{-1} represents a relatively recalcitrant form of organic C, probably a combination of lignin and humic substances. Other authors (Ellerbrock, et al., 2005, 2009; Matějková and Šimon, 2012) proposed measuring the ratio of absorption bands related to relatively hydrophobic ($3000\text{-}2800\text{ cm}^{-1}$) and hydrophilic ($1740\text{-}1698$ and $1640\text{-}1600\text{ cm}^{-1}$) SOM functional groups. The hydrophobic/hydrophilic functional groups ratio was used to predict the

wettability or hydrophobicity of soils (Ellerbrock, et al., 2005). Grube, et al. (2006), used some band intensity ratios ($2925/1034\text{ cm}^{-1}$, $1384/2925$ and $1034/1384$) to follow SOM changes in composts over a short term (40 days).

Table 2. Assignments of the main bands observed in the MIR spectra of the organic components of soils according to ^a.

Peak (cm ⁻¹)	Integration limits/cm ⁻¹	Band assignments
	3440-3320	O–H and N–H stretching, H-bonded OH
	3107-3042	Aryl–H, R ₂ C=CH ₂ , R ₂ C=CHR
2930	3010-2800	Aliphatic CH stretching
1730–1700	1775-1711	C=O stretching
~1650	1691-1642	C=O stretching of amides (amide I), H-bonded conjugated ketones, carboxyls and quinones, lignine; C=N stretching
	1642-1569	Amide II of primary amides, aromatic C=C, C=O (quinones), carboxylates and amides, R–O–NO ₂
1530–1510	1544-1488	Aromatic C=C stretching, aromatic skeletal vibrations, aromatic skeletal (lignin), amide II
	1479-1444	CH and NH of amide II, aliphatic CH deformation
~1415	1444-1408	Benzoic acid, C–H deformation and C–O stretching of phenolic groups
1380	1403-1354	C–O of phenolic OH, COO ⁻ and O–H, CH ₃ bend, COCH ₃
	1342-1307	Sulfonamides, C–N (aromatic amines)
	1293-1256	Benzoic acids, C–O of aryl ethers, R–O–NO ₂ , P=O, C–O of phenols, C–O–C ether bond, amide III
~1230	1256-1198	C–O stretching and OH deformation of COOH, C–O of aryl ethers and phenols, acetates
1160	1185-1144	C–OH of aliphatic alcohols, carbohydrates
	1136-1070	C–O of various alcohol types, C–O of alkyl ethers, C–OH
	1056-945	C–O stretching (1080–1030, carbohydrate region of polysaccharides), RHC=CH ₂ , sulfones, P–O aryl, P–O alkyl, aromatic CH out-of-plane bending
	945-887	Benzoic acid, pyranose ring (carbohydrates), cellulose (ring breathing), RHC=CH ₂ , R ₂ C=CH ₂
870		Aromatic C–H and C=C
835		Lignin (Aromatic CH out of plane)
	820-752	R ₂ C=CHR, phenyls with three H adjacent
720		Long chain alkanes (CH ₂ wag)

^a Artz, et al. (2008); Barie, et al. (2012); Bornemann, et al. (2010); Du and Zhou (2009); Ferrari, et al. (2011); Tatzber, et al. (2010); Vergnoux, et al. (2011).

In another approach, a relative peak area has been used to study longer-term changes in HAs from soils under bare fallow over 36 years (Tatzber, et al., 2009), and also in bulk soils from a 140-year proglacial chronosequence (Egli, et al., 2010), which reflected changes in SOM quality as measured by independent methods. Demyan, et al. (2012), used the peak areas at 2930, 1620, 1530 and 1159 cm^{-1} selected in the typical range of organic functional groups. The peaks of SOM were proposed on the basis of the strength of the chemical bonds of the functional groups, such as aliphatic C-H being less stable than aromatic C=C bonds. All relative peak areas were significantly affected by fertilizer treatment, with a relative increase of the peak area at 2930 cm^{-1} in farmyard manure (FYM) compared with non-FYM treatments. The ratio of the relative peak areas at 1620 and 2930 cm^{-1} was shown to be a useful indicator of changes in stable and labile C in bulk soil samples; therefore, it can be taken as an indicator of SOM stability.

Humic substances characterization

Humic substances (HS) are natural organic components which are widely distributed in soils, river sediments and brown coals (Senesi and Loffredo, 2001; Stevenson, 1994). The variety of chemical and biological reactions involved in their genesis make HS very complex. Based on their solubility in aqueous solution, HS are operationally divided into three different fractions: (i) humic acid (HA), the fraction soluble at alkaline pH values; (ii) fulvic acid (FA), the fraction soluble at all pH values; and (iii) humin, the fraction insoluble at all pH values (Swift, 1996). The newest concept attributed to HS is an association of molecular structures (100-2000 Da) with macromolecular characteristics resulting from aggregates formed by hydrogen bonding, nonpolar interactions, and polyvalent cation interactions (Piccolo, et al., 2002; Simpson et al., 2002).

FTIR spectroscopy has been extensively used in the study of the composition, structure and functionalities of HS isolated from different ecosystems (Aguiar, et al., 2013; Baigorri, et al., 2009; D'Orazio and Senesi, 2009; Du and Zhou, 2009; Ferrari, et al., 2011; Francioso, et al., 2009; Senesi, et al., 2003; Stevenson, 1994; Tatzber, et al., 2008; Zhang, et al., 2011). Typical IR absorption of HS shows: a broad band at 3100-3600 cm^{-1} (H-bonded OH and NH groups), a slight shoulder at 3000-3100 cm^{-1} (aromatic C-H stretching), a band at 2800-3000 cm^{-1} (aliphatic C-H stretching), a broad band at 2600 cm^{-1} (hydrogen-bonded OH stretching of carboxyl and phenolic OH), a shoulder or a peak at 1725-1710 cm^{-1} (C=O stretching of COOH and ketones), a strong band at 1660-1630 cm^{-1} (C=O stretching of amide I, quinone and ketones), a band at 1630-1600 cm^{-1} (aromatic C=C stretching, $-\text{COO}^-$ asymmetric stretching), an absorption at 1540-1510 cm^{-1} (amide II, aromatic C=C stretching), a peak or a shoulder at 1490-1440 cm^{-1} (CH deformation of CH_2 and CH_3 , $-\text{COO}^-$ symmetric stretching), a band at 1450-1380 cm^{-1} (aliphatic CH deformation, $-\text{COO}^-$ symmetric stretching, OH deformation), a band at 1300-1200 cm^{-1} (C-O stretching of phenols and ethers, C-OH deformation) and a band at 1170-1030 cm^{-1} (C-O stretching of polysaccharide, C-O-C stretching in ethers, C-O of polyalcohol).

A major difference between FA and HA consists in a different content in functional groups and molecular weight size (Figure 4). FA are composed of molecules with low molecular-weight ranges with a higher number of functional groups, e.g. R-COOH and R-OH (Lumsdon and Fraser, 2005). On a mass basis, HA is less charged than FA, but HA shows more poliaromatic structure (Lumsdon and Fraser, 2005; Senesi and Loffredo, 2001). Some studies applied the FTIR spectroscopy to characterize functional groups (D'Orazio and Senesi, 2009; Francioso, et al., 2002) and biological

properties of different HA molecular weight fractions. The distribution of functional groups is also ascribable to the plant species and age, and the partial incorporation into rhizosphere HA of typical root exudates (D'Orazio and Senesi, 2009). Because of their variety of functional groups, humic substances are important reaction partners of metal ions for complexation and redox reaction (Stevenson, 1994). The major functional groups of HA and FA, which can interact with metal ions to form complexes with different stability and properties, are O-containing groups (carboxylic, phenolic, alcoholic, hydroxyl groups).

Results obtained by IR spectra have shown that carboxyl groups are the most important functional groups in HS, accounting for the majority of their charge, acidity, and metal and particle surface binding characteristics (Senesi and Loffredo, 2001; Stevenson, 1994). In HA spectra the carboxylate bands appear at $1624\text{-}1633\text{ cm}^{-1}$ and $1385\text{-}1383\text{ cm}^{-1}$, respectively, depending on pH. A number of studies have demonstrated that when carboxylic acids and their salts form complexes with metals, frequency shifting and changes in the shape of the stretching bands of -COO^- group occur (Nakamoto, 1997). The stability constant ($\log K$) for different metal-HA complexes is indicated in the following order of stability: $\text{Cu} > \text{Fe} > \text{Pb} > \text{Ni} > \text{Co} > \text{Ca} > \text{Cd} > \text{Zn} > \text{Mn} > \text{Mg}$ (Pandey, et al., 2000). From the frequency shift, $\Delta\nu = (\nu_{\text{as}} - \nu_{\text{s}})$, it is possible to identify the carboxylate-metal coordination mode by comparison with the corresponding salt (Nakamoto, 1997).

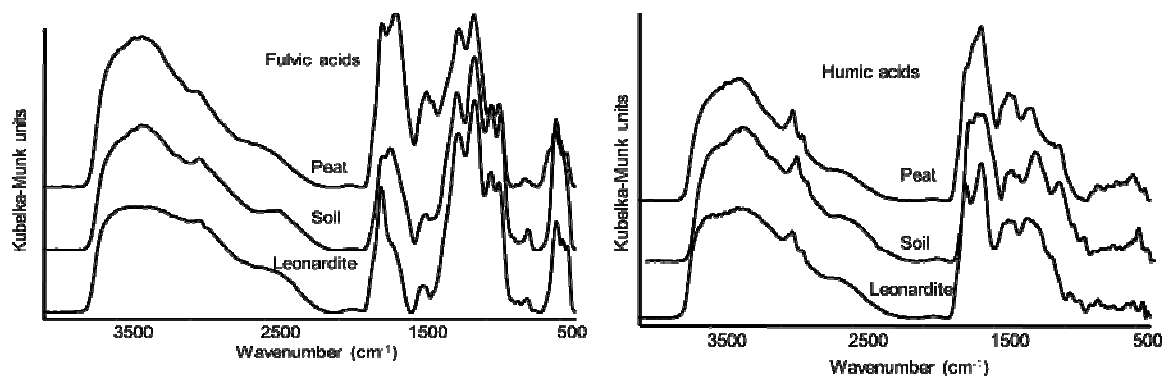


Figure 4 - FTIR spectra of fulvic and humic acids extracted from Italian soil, Irish peat and North Dakota Leonardite. The samples belong to the collection of the Department of Agricultural Sciences of Bologna University.

Guardato, et al. (2008) studied phosphate-metal-HA complexes involving Fe(III), Al(III), and Zn(II). Regarding Al-HA complexes, the results indicated that the metal complexation generated unidentate (pH 6) and bidentate-bridging (pH 4 and 8) interactions with the carboxylate group. The process of fixation of PO_4 did not induce remarkable changes in the complexation mode. In the case of Fe-HA complexes, the metal complexation was similar to that of Al-HA complexes at pH 8. At pH 6, however, the complexation mode was bidentate-bridging, and at pH 4 it was bidentate. In this case, however, PO_4 fixation induced a clear reduction in $\Delta\nu$ at all pH values. Sharma, et al. (2010) detected the HS complex formation with As and Fe, using FTIR. Several distinct peaks at 2916 , 1584 and 856 cm^{-1} were observed in comparison with the standard complexes of As, HS and Fe. The peak at 856 cm^{-1} in the spectrum obtained for the As-Fe-HS complex was probably due to the

asymmetric (As-O-Fe) vibration caused by As(V) binding to Fe-HS, suggesting that HS was also involved in the binding of As(V) to Fe. In the As-Fe-HS complex, the peak at 856 cm^{-1} was stronger than in the Fe-HS complex. This signal probably corresponds to the As-O stretching vibration, suggesting that the 856 cm^{-1} peak involved not only Fe-O vibrations but also the symmetric (As-O-Fe) vibration (Jing, et al., 2003; Reza, et al., 2012). The presence of other divalent and trivalent cations such as Ca^{2+} , $\text{Mn}^{2+/4+}$, Mg^{2+} , and Al^{3+} can favour the ternary complexes formation of As with other metal-HS complexes, as has been shown in previous studies (Bauer and Blodau, 2009; Wang and Mulligan, 2009). Alternately, As can bind to HS via the presence of carbonyl, phenol hydroxy, hydroxyl, methoxyl groups, and other functional groups on the benzene rings and the aliphatic side chains.

Jerzykiewicz (2013) studied the formation of HA and humin complexes with Hg(II). The FTIR spectra showed that the bands assigned to the stretching vibrations of C=O in the carboxylic groups (1720 cm^{-1}) and to the carboxylates (1650 cm^{-1}) reduced their intensity and were shifted $50\text{-}150\text{ cm}^{-1}$ toward lower wavenumbers, indicating the involvement of these groups in the coordination with Hg(II). Intensity modifications were also observed for bands at lower wave numbers: $1230\text{-}1260\text{ cm}^{-1}$ for HA and $1030\text{-}910\text{ cm}^{-1}$ for humin treated with Hg(II) ions. The latter band can be attributed to the stretching of C-O in the C-O-H groups, although closer structure assignments were difficult due to the mixing of different vibrational modes (Mohamed-Ziegler and Billes, 2002) and to the broadness of the bands.

Charred organic matter characterization

Forest fires are known to have an important impact on SOM dynamics, because a significant loss of organic matter may occur during burning. Depending on fire severity, the effects on the OM consist in slight distillation, charring, or complete oxidation. The fire effects, both in situ and in laboratory, led to an enrichment in aromaticity and a decrease in O-containing functional groups (Francioso, et al., 2011; Knicker, et al., 2005; Nocentini, et al., 2010; Vergnoux, et al., 2011). Although the identification of charcoal in soil is difficult, there is now evidence for the presence of charred material in soils through FTIR spectroscopy (Francioso, et al., 2011; Nocentini, et al., 2010; Vergnoux, et al., 2011).

FTIR spectra of charcoal in soil are dominated by a broad band between 3800 and 3000 cm^{-1} (O-H and/or N-H vibrational modes) with two shoulders at 2933 and 2850 cm^{-1} (C-H stretching, in alkyl groups such as CH_3 and CH_2 groups), as described in El-Hendawy (2006). Usually, also the band at 1715 cm^{-1} appears as a shoulder (CO stretching in COOH groups bound to aromatic rings, Nocentini et al. (2010)). Cheng, et al. (2006), used the peak heights ratio for carboxylic-to-aromatic C absorptions (1700 versus 1600 cm^{-1}) to investigate the oxidation of black carbon in soil. These authors found that the formation of carboxylic functional groups took place more in abiotic than in biotic environments. This was the reason for the enhanced CEC during oxidation in abiotic processes. Moreover, the strong bands at about 1600 and 1450 cm^{-1} (C=C or C=N stretching of polyaromatic rings) may be due to rearrangement and cyclization reactions of SOM at high temperatures (El-Hendawy, 2006). In charcoal, the bands between 1100 and 500 cm^{-1} are prevalently attributed to mineral compounds (Madejová, 2003). In addition, some charcoals are characterized by the presence of a weak band at ca. 2220 cm^{-1} , which was assigned to CN stretching vibration of iso-cyanate, nitrile and cyanamide groups (Francioso, et al., 2009; Francioso, et al., 2011; Nocentini, et al., 2010).

Conclusions

A number of studies have proved that MIR spectroscopy is a powerful tool for analysis of a large number of soil samples. In general, several qualitative features can be obtained from a single soil spectrum analysis: i) identification of functional groups, e.g. carbohydrates, lignin, cellulose, fats and proteinaceous substances; ii) identification of primary (quartz, feldspars) and secondary (silicates, clays, aluminosilicates) soil minerals. Mathematical spectra processing, e.g. second derivative or spectral subtraction give important information on not visible bands in the original spectrum. Moreover, the PCA and PLS provide additional support for the quantitative determination of several features or properties of a large number of soil samples. The creation of a MIR spectral library of soils is the most pressing issue to convert this technology into routine analyses.

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References

- Abdulla, H.A.N., Minor, E.C., Dias, R.F., Hatcher, P. G., (2010) Changes in the compound classes of dissolved organic matter along an estuarine transect: a study using FTIR and ¹³C NMR. *Geochimica Cosmochimica Acta*, 74(13), 3815-3838.
- Aguiar, N.O., Novotny, E.H., Oliveira, A.L., Rumjanek, V.M., Olivares, F.L., Canellas, L.P., (2013) Prediction of humic acids bioactivity using spectroscopy and multivariate analysis. *Journal of Geochemical Exploration*, 129, 95-102.
- Aochi, Y. O., Farmer, W. J., (2011) Effects of surface charge and particle morphology on the sorption/desorption behaviour of water on clay minerals. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 374(1-3), 22-32.
- Artz, R.R.E., Chapman, S.J., Campbell, C.D., (2006) Substrate utilization profiles of microbial communities in peat are depth dependent and correlate with whole soil FTIR profiles. *Soil Biology and Biochemistry*, 38(9), 2958-296.
- Artz, R.R.E., Chapman, S.J., Robertson, A.H.J., Potts, J.M., Laggoun-Defarge, F., Gogo, S., Comont, L., Disnar, J.R., (2008) FTIR spectroscopy can be used as a screening tool for organic matter quality in regenerating cutover peatlands. *Soil Biology and Biochemistry*, 40(2), 515-527.
- Baigorri, R., Fuentes, M., Gonzalez-Gaitano, G., Garcia-Mina, J. M., Almendros, G., Gonzalez-Vila, F. J., (2009). Complementary multianalytical approach to study the distinctive structural features of the main humic fractions in solution: gray humic acid, brown humic acid, and fulvic acid. *Journal Agricultural and Food Chemistry*, 57(8), 3266-3272.
- Bardy, M., Fritsch, E., Derenne, S., Allard, T., Do Nascimento, N.R., Bueno, G.T., (2008) Micromorphology and spectroscopic characteristics of organic matter in waterlogged podzols of the upper Amazon basin. *Geoderma* 145(3-4), 222-230.
- Barje, F., El Fels, L., El Hajjouji, H., Amir, S., Winterton, P., Hafidi, M., (2012) Molecular behaviour of humic acid-like substances during co-composting of olive mill waste and the organic part of municipal solid waste. *International Biodeterioration & Biodegradation*, 74,17-23.

- Bauer, M., Blodau, C., (2009) Arsenic distribution in the dissolved, colloidal and particulate size fraction of experimental solutions rich in dissolved organic matter and ferric iron. *Geochimica Cosmochimica Acta*, 73(3), 529-542.
- Bellon-Maurel, V., Mc Bratney, A., (2011) Near-infrared (NIR) and mid-infrared (MIR) spectroscopic techniques for assessing the amount of carbon stock in soils- Critical review and research perspectives. *Soil Biology and Biochemistry*, 43(7), 1398-1410.
- Bishop, J.L., Lane, M.D., Dyar, M.D., Brown, A.J., (2008) Reflectance and emission spectroscopy study of four groups of phyllosilicates: smectites, kaolinite-serpentines, chlorites and micas. *Clay Minerals*, 43, 35-54.
- Bornemann, L., Welp, G., Amelung, W., (2010) Particulate organic matter at the field scale: rapid acquisition using mid-infrared spectroscopy. *Soil Science Society of America Journal*, 74, 1147-1156.
- Bruckman, V.J., Wriessnig, K., (2013) Improved soil carbonate determination by FT-IR and X-ray analysis. *Environmental Chemistry Letters*, 11(1), 65-70.
- Calderón, F.J., Reeves III, J.B., Collins, H.P., Paul, E.A., (2011a) Chemical differences in soil organic matter fractions determined by diffuse reflectance mid-infrared spectroscopy. *Soil Science Society of America Journal*, 75(2), 568-579.
- Calderón, F.J., Mikha, M.M., Vigil, M.F., Nielsen, D.C., Benjamin, J.G., Reeves III, J.B., (2011b) Diffuse-reflectance mid-infrared spectral properties of soils under alternative crop rotations in a semi-arid climate. *Communications in Soil Science and Plant Analysis*, 42(17), 2143-2159.
- Capriel, P., (1997) Hydrophobicity of organic matter in arable soils: influence of management. *European Journal of Soil Science*, 48(3), 457-462.
- Cecillon, L., Certini, G., Lange, H., Forte, C., Strand, L.T., (2012) Spectral fingerprinting of soil organic matter composition. *Organic Geochemistry*, 46, 127-136.
- Chang, C.W., Laird, D.A., Mausbach, M.J., Hurburgh, C.R. Jr., (2001) Near-infrared reflectance spectroscopy - principal components regression analysis of soil properties. *Soil Science Society of America Journal*. 65(2), 480-490.
- Chen, Y., Mastalerz, M., Schimmelmann, A., (2012) Characterization of chemical functional groups in macerals across different coal ranks via micro-FTIR spectroscopy. *International Journal of Coal Geology*, 104, 22-33.
- Cheng, C., Lehmann, J., Thies, J.E., Burton, S.D., Engelhard, M.H., (2006) Oxidation of black carbon by biotic and abiotic processes. *Organic Geochemistry*, 37(11), 1477-1488.
- Cox, R., Peterson, H.L., Young, J., Cusik, C., Espinoza, E.O., (2000) The forensic analysis of soil organic by FTIR. *Forensic Science International*, 108(2), 107-116.
- D'Acqui, L.P., Pucci, A., Janik, L.J., (2010) Soil properties prediction of western Mediterranean island with similar climatic environments by means of mid-infrared diffuse reflectance spectroscopy. *European Journal of Soil Science* 61(6), 865-876.
- Demyan, M.S., Rasche, F., Schulz, E., Breulmann, M., Muller, T., Cadisch, G., (2012) Use of specific peaks obtained by diffuse reflectance Fourier transform mid-infrared spectroscopy to study the composition of organic matter in a Haplic Chernozem. *European Journal of Soil Science* 63(2), 189-199.
- Dorado, F., Garcia, P.B., de Lucas, A., Ramos, M.J., Romero, A., (2010) Hydrocarbon selective catalytic reduction of NO over Cu/Fe-pillared clays: diffuse

- reflectance infrared spectroscopy studies. *Journal of Molecular Catalysis A: Chemical* 332(1-2), pp. 45-52.
- D'Orazio, V., Senesi, N., (2009) Spectroscopic properties of humic acids isolated from the rhizosphere and bulk soil compartments and fractionated by size-exclusion chromatography. *Soil Biology and Biochemistry* 41(9), 1775-1781.
- Du, C.W., Linker, R., Shaviv, A., (2007) Characterization of soils using photoacoustic mid-infrared spectroscopy. *Applied Spectroscopy* 61(10), 1063-1067.
- Du, C., Zhou, J., (2009) Evaluation of soil fertility using infrared spectroscopy: a review. *Environmental Chemistry Letters* 7(2), 97-113.
- Duboc, O., Zehetner, F., Djukic, I., Tatzber, M., Berger, T.W., Gerzabek, M.H. (2012) Decomposition of European beech and black pine foliar litter along an alpine elevation gradient: mass loss and molecular characteristics. *Geoderma* 189-190, 522-531.
- Egli, M., Mavris, C., Mirabella, A., Giaccai, D., (2010) Soil organic matter formation along a chronosequence in the moreratsch proglacial area (Upper Engadine, Switzerland). *Catena* 82(2), 61-69.
- El-Hendawy, A.A., (2006) Variation in the FTIR spectra of a biomass under impregnation, carbonization and oxidation conditions. *J. Anal. Appl. Pyrolysis* 75(2), 159-166.
- Ellerbrock, R.H., Kaiser, M., (2005) Stability and composition of different soluble soil organic matter fractions - evidence from delta C-13 and FTIR signatures. *Geoderma* 127(3-4), 28-37.
- Ellerbrock, R.H., Gerke, H.H., and Böhm, C., (2009) In situ DRIFT characterization of organic matter composition on soil structural surfaces. *Soil Science Society of America Journal* 73(2), 531-540.
- Fernandez-Getino, A.P., Hernandez, Z., Piedra Buena, A., Almendros, G., (2013) Exploratory analysis of the structural variability of forest soil humic acids based on multivariate processing of infrared spectral data. *European Journal of Soil Science* 64(1), 66-79.
- Ferrari, E., Francioso, O., Nardi, S., Saladini, M., Dal Ferro, N., Morari, F., (2011) DRIFT and HR MAS NMR characterization of humic substances from a soil treated with different organic and mineral fertilizers. *Journal of Molecular Structure* 998(1-3), 216-224.
- Francioso, O., Sánchez-Cortés, S., Casarini, D., Garcia-Ramos, J.V., Ciavatta, C., Gessa, C., (2002) Spectroscopic study of humic acids fractionated by means of tangential ultrafiltration. *Journal of Molecular Structure* 609(1-3), 137-147.
- Francioso, O., Montecchio, D., Giocchini, P., Cavani, L., Ciavatta, C., Trubetskoj, O., Trubetskaya, O., (2009) Structural differences of Chernozem soil humic acids SEC-PAGE fractions revealed by thermal (TG-DTA) and spectroscopic (DRIFT) analyses. *Geoderma* 152(3-4), 264-268.
- Francioso, O., Sanchez-Cortes, S., Bonora, S., Roldan, M.L., Certini, G., (2011) Structural characterization of charcoal size-fractions from a burnt *Pinus pinea* forest by FT-IR, Raman and surface-enhanced Raman spectroscopies. *Journal of Molecular Structure* 994(1-3), 155-162.
- Francioso, O., Certini, G., Ciavatta, C., (2012) Organic matter investigation by direct analysis of charcoal fractions using diffuse reflectance FT-IR spectroscopy. In: *Functions of natural organic matter in changing environment*, Hangzhou, Springer, pp. 580-582.

- Ghosh, S., Wang, Z.Y., Kang, S., Bhowmik, P.C., Xing, B.S., (2009) Sorption and fractionation of a peat derived humic acid by kaolinite, montmorillonite, and goethite. *Pedosphere* 19(1), 21-30.
- Griffiths, P.R., Fuller, M.P., (1982) Mid infrared spectrometry of powdered samples. In: R.J., Clark, R.E., Hester, eds. (1982) *Advances in Infrared and Raman Spectroscopy* Heyden and Son, London, pp.63-129.
- Griffiths, P.R., De Haseth, J. A., (2007) *Fourier Transform Infrared Spectroscopy*. Wiley-Interscience, New Jersey.
- Grim, R.E., Kulbicki, G., (1961) Montmorillonite - high temperature reactions and classification. *American Mineralogist* 46, 1329-1369.
- Grinand, C., Barthes, B.G., Brunet, D., Kouakoua, E., Arrouays, D., Jolivet, C., Caria, G., Bernoux, M., (2012) Prediction of soil organic and inorganic carbon contents at a national scale (France) using mid-infrared reflectance spectroscopy (MIRS). *European Journal of Soil Science* 63(2), 141-151.
- Grube, M., Lin, J.G., Lee, P.H., Kokorevicha, S., (2006) Evaluation of sewage sludge-based compost by FT-IR spectroscopy. *Geoderma* 130(3-4), 324-333.
- Haberhauer, G., and Gerzabek, M.H., (1999) Drift and transmission FT-IR spectroscopy of forest soils: an approach to determine decomposition processes of forest litter. *Vibrational Spectroscopy* 19(2), 413-417.
- Huber-Humer, M., Tintner, J., Bohm, K., Lechner, P., (2011) Scrutinizing compost properties and their impact on methane oxidation efficiency. *Waste Management* 31(5), 871-883.
- Jahn, B.R., Linker, R., Upadhyaya, S.K., Shaviv, A., Slaughter, D.C., Shmulevich, I., (2006) Mid-infrared spectroscopic determination of soil nitrate content. *Biosystems Engineering* 94(4), 505-515.
- Janik, L.J., Skjemstad, J., Shepherd, K., Spouncer, L., (2007a) The prediction of soil carbon fractions using mid-infrared-partial least square analysis. *Australian Journal of Soil Research* 45(2), 73-81.
- Janik, L.J., Merry, R.H., Forester, S.T., Layon, D.M., Rawson, A., (2007b) Rapid prediction of soil water retention using mid infrared spectroscopy. *Soil Sci. Soc. Am. J.* 71, 507-514.
- Jerzykiewicz, M., (2013) The effect of Hg(II) ions on the free radicals of humic substances and their model compounds. *Chemosphere* 92, 445-450.
- Jing, C.Y., Korfiatis, G.P., Meng, X.G., (2003) Immobilization mechanisms of arsenate in iron hydroxide sludge stabilized with cement. *Environ. Sci. Technol.* 37, 5050-5056.
- Kaiser, M., Ellerbrock, R.H., Gerke, H.H., (2007) Long-term effects of crop rotation and fertilization on soil organic matter composition. *Eur. J. Soil Sci.* 58, 1460-1470.
- Kaiser, M., Walter, K., Ellerbrock, R.H., Sommer, M., (2011) Effects of land use and mineral characteristics on the organic carbon content, and the amount and composition of Na-pyrophosphate-soluble organic matter, in subsurface soils. *Eur. J. Soil Sci.* 62, 226-236.
- Knicker, H., Gonzalez-Vila, F.J., Polvillo, O., Gonzalez, J.A., Almendros, G., (2005) Fire-induced transformation of C- and N-forms in different organic soil fractions from a Dystric Cambisol under a Mediterranean pine forest (*Pinus pinaster*). *Soil Biol. Biochem.* 37, 701-718.
- Legodi, M.A., de Waal, D., Potgieter, J.H., Potgieter, S.S., (2001) Rapid determination of CaCO₃ in mixtures utilizing FT-IR spectroscopy. *Miner. Eng.* 14, 1107-1111.

- Leue, M., Ellerbrock, R.H., Banninger, D., Gerke, H.H., (2010) Impact of soil microstructure geometry on DRIFT spectra: comparisons with beam trace modeling. *Soil Phys.* 74,1976-1986.
- Linker, R., (2011) Application of FTIR spectroscopy to agricultural soil analysis. In: G., Nikolic, ed. (2011) *Fourier Transforms - New Analytical Approaches and FTIR Strategies*. InTech, pp. 385-404.
- Linker, R., Weiner, M., Shmulevich, I., Shaviv, A., (2006) Nitrate determination in soil pastes using attenuated total reflectance mid-infrared spectroscopy: improved accuracy via soil identification. *Biosystems Engineering* 94 (1), 111-118.
- Ludwig, B., Nitschke, R., Terhoeven-Urselmans, T., Michel, K., Flessa, H., (2008) Use of mid-infrared spectroscopy in the diffuse-reflectance mode for the prediction of the composition of organic matter in soil and litter. *J. Plant Nutr. Soil Sci.* 171, 384-391.
- Lumsdon, D.G., Fraser, A.R., (2005) Infrared spectroscopic evidence supporting heterogeneous site binding models for humic substances. *Environ. Sci. Technol.* 39, 6624-6631.
- Madejová, J., (2003) FTIR techniques in clay mineral studies. *Vibr. Spectrosc.* 31,1-10.
- Marquardt, D.W., (1963) An algorithm for least-squares estimation of nonlinear parameters. *J. Soc. Ind. Appl. Math.* 11, 431-441.
- Matějková Š., Šimon T., (2012) Application of FTIR spectroscopy for evaluation of hydrophobic /hydrophilic organic components in arable soil. *Plant Soil Environ.* 58, 192-195.
- Minasny, B., McBratney, A.B., Tranter, G., Murphy, B.W., (2008) Using soil knowledge for the evaluation of mid-infrared diffuse reflectance spectroscopy for predicting soil physical and mechanical properties. *Eur. J. Soil Sci.* 59, 960-971.
- Mohamed-Ziegler, I., Billes, F., (2002) Vibrational spectroscopic calculations on pyrogallol and gallic acid. *J. Mol. Struct.* 618, 259-265.
- Nakamoto, K., (1997) *Infrared and Raman spectra of inorganic and coordination compounds. Part B.* John Wiley & Sons, Inc. New York USA, 5nd ed.
- Nault, J.R., Preston, C.M., Trofymow, J.A., Fyles, J., Kozak, L., Siltanen, M., Titus, B., (2009) Applicability of diffuse reflectance Fourier transform infrared spectroscopy to the chemical analysis of decomposing foliar litter in Canadian forests. *Soil Sci.* 174, 130-142.
- Neves-Fernandes, A., Giovanela, M., Esteves, V.I., de Sousa Sierra, M.M., (2010) Elemental and spectral properties of peat and soil samples and their respective humic substances. *J. Mol. Struct.* 971, 33-38.
- Nguyen, T., Janik, L.J., Raupach, M., (1991) Diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy in soil studies. *Aust. J. Soil Res.* 29, 49-67.
- Nocentini, C., Certini, G., Knicker, H., Francioso, O., Rumpel, C., (2010) Nature and reactivity of charcoal produced and added to soil during wildfire are particle-size dependent. *Org. Geochem.* 41, 682-689.
- Osono, T., Hobara, S., Hishinuma, T., Azuma, J., (2011) Selective lignin decomposition and nitrogen mineralization in forest litter colonized by *Clitocybe* sp. *Eur. J. Soil Biol.* 47, 114-121.
- Pandey, A.K., Pandey, S.D., Misra, V., (2000) Stability constants of metal-humic acid complexes and its role in environmental detoxification. *Ecotoxicol. Environ. Saf.* 47, 195-200.

- Piccolo, A., Conte, P., Trivellone, E., Van Lagen, B., Buurman, P., (2002) Reduced heterogeneity of a lignite humic acid by preparative HPSEC following interaction with an organic acid. Characterization of size-separates by Pyr-GC-MS and H-1-NMR spectroscopy. *Environ. Sci. Technol.* 36, 76-84.
- Pirie, A., Singh, B., Islam, K., (2005) Ultra-violet, visible, near-infrared and mid-infrared diffuse reflectance spectroscopic techniques to predict several soil properties. *Aust. J. Soil Res.* 43, 713-721.
- Reeves III, J.B., (2010) Near- versus mid-infrared diffuse reflectance spectroscopy for soil analysis emphasizing carbon and laboratory versus on-site analysis: where are we and what needs to be done? *Geoderma* 158, 3-14.
- Reeves, J.B., (2012) Mid-infrared spectral interpretation of soils: is it practical or accurate? *Geoderma* 189, 508-513.
- Reeves, J.B., Francis, B.A., Hamilton, S.K., (2005) Specular reflection and diffuse reflectance spectroscopy of soils. *Appl. Spectrosc.* 59, 39-46.
- Reeves, J.B., Smith, D.B., (2009) The potential of mid- and near-infrared diffuse reflectance spectroscopy for determining major-and trace-element concentrations in soils from a geochemical survey of North America. *Appl. Geochem.* 24, 1472-1481.
- Reza, A.H.M.S., Jean, J.S., Lee, M.K., Kulp, T.R., Hsu, H.F., Liu, C.C., Lee, Y.C., (2012) The binding nature of humic substances with arsenic in alluvial aquifers of chain an plain, southwestern Taiwan. *J. Geochem. Expl.* 114, 98-108.
- Richter, N., Jarmer, T., Chabrilat, S., Oyonarte, C., Hostert, P., Kaufmann, H., (2009) Free iron oxide determination in Mediterranean soils using diffuse reflectance spectroscopy. *Soil Sci. Soc. Am. J.* 73, 72-81.
- Salati, S., Scaglia, B., di Gregorio, A., Carrera, A., Adani, F., (2013) Mechanical biological treatment of organic fraction of MSW affected dissolved organic matter evolution in simulated landfill. *Bioresour. Technol.* 142,115-120.
- Sarkhot, D.V., Comerford, N.B., Jokela, E.J., Reeves, III J.B., Harris, W., (2007) Aggregation and aggregate carbon in a forested southeastern coastal plain spodosol. *Soil Sci. Soc. Am. J.* 71,1779-1787.
- Senesi, N., Loffredo, E., (2001) Soil humic substances In: *Biopolymers M.*, Hofrichter, A., Steinbuchel, eds (2001) Wiley -Vch, Weinheim Vol. 1 pp. 247–299.
- Senesi, N., D'Orazio, V., Ricca, G., (2003) Humic acids in the first generation of Eurosoils. *Geoderma* 116, 325-344.
- Sharma, P., Ofner, J., Kappler, A., (2010) Formation of binary and ternary colloids and dissolved complexes of organic matter, Fe and As. *Environ. Sci. Technol.* 44, 4479-4485.
- Simpson, A.J., Kingery, W.L., Hayes, M.H.B., Spraul, M., Humpfer, E., Dvortsak, P., Kerssebaum, R., Godejohann, M., Hofmann, M., (2002) Molecular structures and associations of humic substances in the terrestrial environment. *Naturwissenschaften* 89(29), 84-88.
- Smidt, E., Meissl, K., (2007) The applicability of Fourier transform infrared (FT-IR) spectroscopy in waste management. *Waste Management* 27(2), 268-276.
- Solomon, D., Lehmann, J., Kinyangi, J., Liang, B., Schäfer, T., (2005) Carbon K-edge NEXAFS and FTIR-ATR spectroscopic investigation of organic carbon speciation in soils. *Soil Science Society of America Journal* 69(1), 107-119.
- Sorak, D., Herberholz, L., Iwascek, S., Altinpinar, S., Pfeifer, F., Siesler, H.W., (2012) New developments and applications of handheld Raman, Mid-

- infrared, and Near-infrared spectrometers. *Applied Spectroscopy Reviews* 47(2), 83-115.
- Spaccini, R., Piccolo, A., Haberhauer, G., Stemmer, M., Gerzabek, M.H., (2001) Decomposition of maize straw in three European soils as revealed by DRIFT spectra of soil particle fractions. *Geoderma* 99(3-4), 245-260.
- Spence, A., Kelleher, B.P., (2012) FT-IR spectroscopic analysis of kaolinite-microbial interactions. *Vibrational Spectroscopy* 61, 151-155.
- Stevenson, F.J., (1994) *Humus chemistry: genesis, composition, reactions*. Wiley-Interscience, New York.
- Stumpe, B., Weihermuller, L., Marschner, B., (2011) Sample preparation and selection for qualitative and quantitative analyses of soil organic carbon with mid-infrared reflectance spectroscopy. *European Journal of Soil Science* 62(8), 849-862.
- Swift, R.S., (1996) Organic matter characterization (chap. 35). In: *Methods of Soil Analysis: Part 3-Chemical Methods*, D.L., Sparks ed., (1996) Soil Sci. Soc. Am. Book Series, SSSA and ASA, Madison, WI, pp. 1018-1020.
- Tatzber, M., Stemmer, M., Spiegel, H., Katzlberger, C., Haberhauer, G., Gerzabek, M.H., (2007) An alternative method to measure carbonate in soils by FT-IR spectroscopy. *Environmental Chemistry Letters* 5(1), 9-12.
- Tatzber, M., Stemmer, M., Spiegel, H., Katzlberger, C., Haberhauer, G., Gerzabek, M.H., (2008) Impact of different tillage practices on molecular characteristics of humic acids in a long-term field experiment - An application of three different spectroscopic methods. *Science of the Total Environment* 406(1-2), 256-268.
- Tatzber, M., Stemmer, M., Spiegel, H., Katzlberger, C., Zehetner, F., Haberhauer, G., Roth, K., Garcia-Garcia, E., Gerzabek, M.H., (2009) Decomposition of carbon-14-labeled organic amendments and humic acids in a long-term field experiment. *Soil Science of America Journal* 73(3), 744-750.
- Tatzber, M., Mutsch, F., Mentler, A., Leitgeb, E., Englisch, M., Gerzabek, M., (2010) Determination of organic and inorganic carbon in forest soil samples by mid-infrared spectroscopy and partial least squares regression. *Applied Spectroscopy* 64(10), 1167-1175.
- Tremblay, L., Alaoui, G., Leger, M.N., (2011) Characterization of aquatic particles by direct FTIR analysis of filters and quantification of elemental and molecular compositions. *Environmental Science Technology* 45 (22), 9671-9679.
- Verchot, L.V., Dutaur, L., Shepherd, K.D., Albrecht, A., (2011) Organic matter stabilization in soil aggregates: understanding the biogeochemical mechanisms that determine the fate of carbon inputs in soils. *Geoderma* 161 (3-4), 182-193.
- Vergnoux, A., Guiliano, M., Di Rocco, R., Domeizel, M., Theraulaz, F., Dolmen, P., (2011) Quantitative and mid-infrared changes of humic substances from burned soils. *Environmental Research* 111 (2), 205-214.
- Viscarra Rossel, R.A., Walvoort, D.J.J., McBratney, A.B., Janik, L.J., Skjemstad, J.O., (2006) Visible, near infrared, mid infrared or combined diffuse reflectance spectroscopy for simultaneous assessment of various soil properties. *Geoderma* 131 (1-2), 59-75.
- Vlaev, L., Damyanov, D., Mohamed, M.M., (1989) Infrared spectroscopy study of the nature and reactivity of a hydrate coverage on the surface of γ -Al₂O₃, *Colloids Surfaces* 36 (3), 427-437.

Wang, S.L., Mulligan, C.N., (2009) Enhanced mobilization of arsenic and heavy metals from mine tailings by humic acid. *Chemosphere* 74 (2), 274-279.

Zhang, Y., Du, J., Zhang, F., Yu, Y., Zhang, J., (2011) Chemical characterization of humic substances isolated from mangrove swamp sediments: the Qinglan area of Hainan island, China. *Estuarine Coastal Shelf Science* 93 (1), 220-227.