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Article

Detection of mercury and other metals in mercury contaminated soils using mid-infrared spectroscopy

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Abstract

The Oak Ridge Reservation, established in 1942, was the designated site for the construction of the atomic bomb. During a 20-year period from 1944-1963 radioactive and toxic chemical pollutants, especially mercury compounds were released into the surrounding waterways. Mercury in the soil environment can undergo numerous chemical transformations. Conventional methods for detection of total soil mercury in contaminated environments are based on time-consuming sample preparation and costly sample analysis. The possibility for determination of total soil –Hg concentration and other elements in contaminated soils using the mid-infrared (MIR) region (4000 – 600 cm^{-1}) has been investigated. Principal component analysis (PCA) was used to identify patterns or differences in soil spectral data and partial least squares (PLS) regression was used to develop models for several metals in soil samples. Pearson correlation identified nine elements (Sr, Ni, Cu, Cd, V, Ti, Fe, Ba, Rb) and total carbon that were significantly correlated with total soil-Hg. Our calibration models showed high *r* for Hg, and Sr ($r \geq .90$) and relatively moderate *r* for Cu and Ni ($r > .80$). Results support the conclusion that mid-infrared spectroscopy could aid conventional method analyses of soils heavily contaminated with certain heavy metals after a robust model is developed.

Keywords heavy metals; mercury; soil; spectroscopy.

1 Introduction

Mercury pollution has become an important current issue due to its environmental effects at a global scale. Solubility, mobility, and bioavailability of mercury in terrestrial and aquatic ecosystems are strongly controlled by mercury speciation in both soil solution and solid-phase components (Han et al., 2006a). Mercury transport and distribution in the environment originate from natural (i.e. outgassing, wild fires, geothermal surfaces or volcanoes) and anthropogenic sources (i.e. fossil fuels, smelting lead, zinc ores) (Boening, 2000; Nriagu and Pacyna, 1988; Revis et al., 1989; Schroeder and Munthe, 1998). Various species of mercury exist in soils (i.e. elemental mercury, organic and inorganic mercury) and their potential toxicity depends on their concentration and species present in the soil solution (Revis et al., 1989). Mercury in soils is firmly bound to organic matter or precipitated as sulfide, and found in trace concentration in soil solution (Schuster, 1991).

Due to anthropogenic and natural input, many watersheds have been affected by heavy metals (Sayyed and Sayadi, 2011; Anim et al., 2012), like mercury that discharged into waterways such as creeks, lakes and streams. One such case is East Fork Poplar Creek (EFPC) in Oak Ridge, TN, where in the 1950’s and 1960’s large amounts (~ 1,080 metric tons) of mercury compounds were discharged into EFPC from the U S. Department of Energy's Oak Ridge Tennessee Site (Bashor and Turri, 1986; Han et al., 2006a; Revis et al., 1989). East Fork Poplar Creek's head water begins at the Y-12 Facilities located on the Oak Ridge Reservation. During the 1950s and early 1960s, mercury was used to separate lithium isotopes during the production of nuclear weapons (Han et al., 2006a). This 15-mile long creek flows through the city of Oak Ridge in Anderson County and empties into the Clinch River in Roane County, TN. Levels of total Hg in the floodplain soils along the creek ranged from 0.5 to 3000 mg kg^{-1} in 1984 (Revis et al., 1989). Several streams of various sizes (White Oak Creek, Mitchell Branch, McCoy Branch, Bear Creek, Poplar Creek, and East Fork Poplar Creek) which run through the Oak Ridge Reservation have been heavily impacted by radionuclides, trace metals (especially mercury), and polychlorinated biphenyls. Following remediation (i.e. pump-and-treat, in-situ anaerobic bioremediation and hydrofracture) of EFPC and other tributaries by the U.S. Department of Energy and Science Application International Corporation (USEPA, 1989; SAIC, 1994), the total remaining soil Hg ranged from 0 to 200 mg kg^{-1} along transects, with some areas > 200 mg kg^{-1}.

Conventional methods for total mercury detection in soil samples are rife with problems. Not only do they require harsh chemicals such as tin chloride ($SnCl_2$), sodium borohydride ($NaBH_4$), or aqua regia (Cl-H.H-N-O_3) in acid solutions which procreates additional waste, they can also be labor intensive processes, and quite costly. These methods include inductively coupled plasma-mass spectrometry (ICP-MS), cold vapor atomic absorption spectroscopy (CVAAS) and atomic emission spectroscopy (AES). The detection limit for mercury for each method mentioned above is 0.001 ppb, and is limited to quantifying total elemental concentrations (Clevenger et al. 1997; Han et al. 2006b). Feo and Aller (2001) found the detection limit for mercury species in whole bacterial cells using Fourier transform infrared spectroscopy was 0.02 ng ml^{-1} (~1 ppb).

Infrared spectroscopy can be used to identify many types of organic and inorganic compounds in the form of solids, liquids and gases. Infrared spectrums are only obtained from compounds that form polar molecular bonds. The infrared region is divided into three regions: the near-, mid- and far-infrared. The mid-infrared (MIR) region, with wave number from 4000 cm^{-1} to 600 cm^{-1}, can be used to obtain reflectance spectra from a variety of opaque samples (fabrics, soil, powders, polymers, etc.,) with minimum sample preparation by using an Attenuated Total Reflectance (ATR) accessory.

Soils are heterogeneous, with many soil properties dependent on mineral and soil organic matter composition (Janik et al., 1998). Various soil components such as smectite, kaolin, illite, quartz, and organics (protenaceous, aliphatic, lipid, carboxyl and aromatic compounds) absorb in the mid-infrared and near-infrared (NIR) region, and exhibit spectral patterns with peaks at vibrational frequencies of molecular functional groups (Janik et al., 1998). Quartz and kaolinite clays occur in more compact soil with high bulk density and have strong infrared bands around 1100 – 1000 cm^{-1} (Si-O) and 3690 – 3620 cm^{-1}, respectively. Soil organic matter has spectral peaks due to alkyl $-CH_2$ at 2930-2850 cm^{-1}, bands for protein amide OC-NH around 1680 and 1530 cm^{-1}, carboxylate anion COO^- at 1600 and 1400 cm^{-1}, and carboxylic acid COOH around 1720 cm^{-1} (Janik et al., 1998) . The prediction of mercury and several major and trace elements by near-infrared and mid-infrared spectroscopy has previously been reported (Janik et al., 1998). The author found that the calibration for Hg was poor, R^2 0.109 and root mean square error of 0.033, with no independent validation test set. It should also be noted that Hg concentrations in soil samples were very low (0.01 to 0.7 mg kg^{-1}). The authors concluded that near-infrared and mid-infrared were not adequate techniques for reducing the need for conventional analysis of soil samples at this concentration range.

The objective of this study was to examine the potential use of MIR in the quantitative determination of total mercury and other heavy metals in soil samples within the floodplain of a mercury contaminated site. The concentrations of multiple elements in these soil samples were determined by inductively coupled plasma

(ICP), and Hg was determined by cold vapor atomic absorption spectroscopy. The resulting data were used to build and validate models using MIR spectra of the samples.

2 Methods

2.1 Soil sampling

During June 2007, three blocks B1 (N 36° 00.52′, W 084° 14′), B2 (N 36° 00.33′, W 084° 16.82′) and B3 (N 35° 95.243′ W 084° 38.19′) were established within the floodplain of East Fork Poplar Creek (EFPC) perpendicular to the creek bank. The Natural Resources Conservation Service has classified soils along EFPC as Inceptisols. These Newark silt loams are somewhat poorly drained and range from moderately acid to moderately alkaline. Historical data for soil total Hg concentration along EFPC obtained from Science Application International Corporation (SAIC, 1994), was used to establish plots along the creek. Three Hg contamination levels, low (0-50 mg kg^{-1}), medium (50-200 mg kg^{-1}) and high (>200 mg kg^{-1}) were established within each of the blocks, and circular plots were randomly placed within each of these areas. Plot size was 168.1 m^2 (0.017 hectare), with 3 plots each for low and medium levels and one high level within Block 1 (1A, 1B, 1D, 1E, 1F, 1G,1H) and Block 3 (3A, 3B, 3C, 3D, 3E, 3F, 3G). Block 2 (2A, 2B, 2C) was smaller in area and contained one plot in each contamination level. The high/medium/low classification of some plots was later changed based on the results of our soil analysis. Due to remediation efforts along EFPC during the late 1980’s, there were few areas remaining in which to establish high plots. Soils were sampled during June and October 2007 and June and October 2008. Three 2 cm diameter by 30.5 cm deep soil cores were randomly collected from each plot. The soil samples from each plot were mixed together in the field, placed in storage bags and taken back to the lab where the soil samples were stored in the freezer until analysis. Sub-samples from this heterogeneous mixture were used for total Hg analysis and physiochemical composition of EFPC soils.

2.2 Soil sample preparation, ICP and mercury analysis

All soil samples were air dried for 2 days to prevent volatilization of certain Hg species that occur above 30 °C. They were then finely ground and passed through a 250 µm (60 –mesh) sieve. Total elemental analysis was determined as described by Nadkarni (1984), using microwave oven digestion with modifications. Total elemental analysis of the digested soil samples was analyzed by inductively coupled atomic emission spectrometry (ICP). Exchangeable cations (Ca, K, Mg, Pb, Cd, Mn, Fe, Zn, Ni and Cu) were determined by extraction with 1 N ammonium acetate ($1NH_4OAc$, pH 7.0). The pH of the $1NH_4OAc$ was adjusted by adding concentrated ammonium hydroxide. Exchangeable were analyzed by ICP. Cation exchange capacity (CEC) was determined by extraction with 2 N ammonium followed by distillation. Total nitrogen (N) and carbon (C) was determined on a Thermo Eager 3000 analyzer. Soil pH was measured by mixing 1:1 volume by weight soil (20 g) and deionized water into a 50 ml falcon tube. Samples were brought up to final volume (40 ml) with additional deionized water, shaken for one minute and allowed to settle for one hour before pH was read using a pH meter.

Samples were analyzed for total mercury concentration by cold vapor atomic absorption spectroscopy (CVAAS) by Western Kentucky University, Institute of Combustion Science and Environmental Technology. Only soil samples collected in October of 2008 were analyzed for total mercury.

2.3 Spectral analysis

Ground and sieved (~60 mesh) soil samples were pelleted using the Carver Hydraulic Press (Carver, Inc.). Briefly, 0.3 g of each soil sample were placed in a KBr die, and pressed for 4 minutes at 5000 pounds. Three pellets were made for each soil sample with a pellet thickness of 1.0 mm. Pellets were scanned in the mid-IR on a Spectrum One (PerkinElmer Instruments LLC, Shelton, CT) FT-IR Spectrometer equipped with a

Universal ATR. Pellets were scanned from 4000 to 600 cm^{-1} at 1 cm^{-1} resolution with 64 scans per spectrum. A total of 12 spectra were collected per pellet.

2.4 Statistical analysis and chemometrics

Pearson product moment correlation coefficient was used to identify correlations between CEC, pH, average C, N, Hg, Al, Ba, Cd, Cr, Cu, Fe, K, Mn, Nd, Ni, Sr, Ti, V, Zn, Pb, Rb, S and cations (Ca, Mg, Na, P). Multivariate analyses of the mid-infrared soil spectral data were performed using principal component analysis (PCA) and partial least-squares (PLS) regression in Unscrambler v. 9.2 software (CAMO Software Inc., Woodbridge, NJ). PCA identifies patterns in spectral data, allowing the clustering of data and reducing the number of dimensions without the loss of information. The mid-infrared spectra were collected from 10 (1B, 1D, 1E, 1G, 1H, 3A, 3C, 3D, 3F, 3G) of the 17 plots sampled. Problems occurred with seven soil samples during pressing so these were not analyzed. All spectra were modified by reduction (averaging) of wavenumber by 4, averaging of the initial sample set by 3 ($n = 360$ to $n = 120$), and mean normalized. Additional spectral pretreatments using first and second derivatives with a 9 point smoothing point average were tested. PCA (SPSS, 2008) was run initially on the full spectral range (4000-600 cm^{-1}) to characterize soil spectra and detect outliers before establishing the regression model. However due to a lack of apparent spectral features above 1400 cm^{-1}, data above 1600 cm^{-1} were removed for all further analyses. PLS is a bilinear modeling method where spectral data (X-variables) were projected onto a small number of PLS components. In estimating the latent variables, the response variables (Y-variable(s)) were used to ensure that the first components were the most relevant for predicting the Y-variables (Martin et al., 2005). There are two versions of PLS regression algorithm, where the PLS1 examines one y-variable and PLS2 examines multiple y-variables at a time. Multiple y-variables (elements) were significantly correlated to total soil mercury, so a PLS2 was performed to develop calibration and validation models for each correlated element.

The required number of samples to calibrate an infrared multivariate model depended on the complexity of the samples, where an appropriate multivariate model for k (> 3) variables (k is the number of variables) should contain a minimum of $6(k + 1)$ spectra (ASTM 2005). Even though the number of samples to produce an appropriate multivariate model for k (> 3) variables should normally contain a minimum of $6(k + 1)$ spectra, here we performed a cross validation because it can be a more efficient way of utilizing small sample numbers. There are two types of cross validations, segmented cross validation and full cross validations. Even though segmented is a faster method, here we chose to use full cross validation which improves the relevance and power of the analysis. To ensure that the calibration and validation models produced were appropriate for each y-variable analyzed, the regression coefficients plot for each Y variable was compared. The parameters used to qualify the results were the correlation (r), root mean square error of calibration (RMSEC) and root mean square error of validation (RMSEV).

3 Results and Discussion

3.1 Soil analytes

Table 1 shows the summary statistics for the analytes examined for soil sampled from EFPC. Total mercury ranged from 0.70 to 758.65 mg kg^{-1}. In addition to mercury, strontium (Sr), tritium (T), uranium (U), technetium (Tc) and plutonium (Pu) were discharged into EFPC from the Y-12 Facilities. Nine metals (Ba, Cd, Cu, Fe, Ni, Rb, Sr, Ti, V), and carbon were positively correlated to $p < 0.05$, total soil mercury. The majority of metal ions significantly correlated to mercury are transition metals (Cd, Cu, Fe, Ni, Ti and V) and being “class B” metals (Pearson classification) tend to associate with each other. Furthermore the absorption of metal ions at the solid/aqueous solution is controlled exclusively by the “free” metal ion concentration, but also by much stronger adsorbed hydroxo, sulfato, carbonato and other metal complex species (Elliott and Huang,

Table 1 ICP analysis of mercury contaminated soil and Spearman's correlation between mercury, ICP analytes, pH, and CEC

	Minimum	Maximum	Mean	Corr. Coeff.	Sig. $^{(2\text{-tailed})}$
Topsoil 25.4"					
pH	5.66	8.04	7.12	0.740**	0.001
CEC	0.13	12.09	7.77	0.001	0.999
Analytes					
Al $_{\text{mg kg}^{-1}}$	28525	63575	47420	0.846**	< 0.001
Ba $_{\text{mg kg}^{-1}}$	30575	57000	41810	0.392	0.119
Ca $_{\text{mg kg}^{-1}}$	29650	177600	84950	0.887**	< 0.001
Cd $_{\text{mg kg}^{-1}}$	10	25	13.5	0.919**	< 0.001
Cr $_{\text{mg kg}^{-1}}$	20	95	48.5	0.833**	< 0.001
Cu $_{\text{mg kg}^{-1}}$	0.97	125	48	0.956**	< 0.001
Fe $_{\text{mg kg}^{-1}}$	6940	29325	20380	0.919**	< 0.001
K $_{\text{mg kg}^{-1}}$	7215	15595	9715	-0.042	0.874
Mg $_{\text{mg kg}^{-1}}$	3870	12725	8095	0.650**	0.005
Mn $_{\text{mg kg}^{-1}}$	140	1935	755	0.272	0.291
Nd $_{\text{mg kg}^{-1}}$	10	25	17	0.412	0.101
Ni $_{\text{mg kg}^{-1}}$	2.02	95	29	0.892**	< 0.001
P $_{\text{mg kg}^{-1}}$	240	1025	605	0.529*	0.029
Sr $_{\text{mg kg}^{-1}}$	20	40	24	0.934**	< 0.001
Ti $_{\text{mg kg}^{-1}}$	1235	2115	1655	0.623**	0.008
V $_{\text{mg kg}^{-1}}$	20	60	41	0.716**	0.001
Zn $_{\text{mg kg}^{-1}}$	10	20	88.5	0.868**	< 0.001
Pb $_{\text{mg kg}^{-1}}$	25	70	55	0.807**	< 0.001
Rb $_{\text{mg kg}^{-1}}$	20	80	56.5	0.907**	< 0.001
S $_{\text{mg kg}^{-1}}$	80	295	195	0.841**	< 0.001
C $_{\text{mg kg}^{-1}}$	12000	45600	26800	0.850**	< 0.001
N $_{\text{mg kg}^{-1}}$	600	2400	1800	0.321	0.208

ICP analysis for total extractable analytes. Number of sampled plots n=17, level. ** Correlation is significant at the 0.01 level. * Correlation is significant at the 0.05 level. (Table adapted from Jean-Philippe et al., 2011).

1979). Soil samples obtained from EFPC are Newark series consisting of somewhat poorly drained soils formed in mixed alluvium and are moderately acid to alkaline. Soil pH was significantly positively correlated ($p < 0.01$) to total soil mercury and ranged from 5.66 to 8.04. Metal ions hydrolyzed onto various oxides as well as other surfaces tend to follow a common trend with solution pH (Guy et al., 1975). Because of this minimum to no adsorption is observed with low pH (Guy et al., 1975), whereas abrupt increases in adsorption over a narrow pH range do occur depending on the metal under observation (James et al., 1973). Five of the metals (Ba, Cd, Cu, Ni, and Ti) positively correlated with mercury were also positively correlated to pH. Mercury (Hg^{2+}) ion exhibits a high affinity for sulfide especially in anoxic waters and sediments (Morel et al., 1998). Schuster (1991) found that mercury in soils is firmly bound to organic matter or precipitated as sulfide, and is found in trace concentrations in soil solution. Sulfur content in plots along EFPC sampled ranged from 0.16 to 0.59 mg kg^{-1} and was not significantly correlated to total mercury. Barnett and Turner (2001) sampled 20 soils from EFPC and found a significant correlation ($p < 0.0001$) between sulfur and total mercury content but not with total carbon. Total sulfur and mercury concentration in plots sampled ranged between 50 – 1700 mg kg^{-1}, and 15 to 2630 mg kg^{-1}, respectively. The differences in sulfur and mercury totals were related to sampling depth, with deeper soil samples having higher sulfur and mercury concentrations. The authors did not examine other potential analytes. Besides mercury several other natural and artificial heavy metal contaminates were also released in EFPC such as strontium (Sr), plutonium (Pu), tritium ($_1H_2$), uranium (U), ruthenium (Ru), and technetium (Tc). Certain metals have been shown to influence one another's uptake in animals and plants, and toxicity in natural ecosystems (Casini and Depledge, 1997). Mercury has been shown to influence lead, zinc (Gray, 1974) and iron (Fowler et al., 1975) uptake and/or toxicity in invertebrates in aquatic environments. In terrestrial environments organic matter and iron oxides are two important mercury sorbents (Gabriel and Williamson, 2004). Higher organic C has also resulted in absorption of Hg in soil (Miretzky et al., 2005). Kinniburgh and Jackson (1978) reported that roughly more than 90% Hg (II) was absorbed by iron (Fe). Iron and carbon are two of several elements in this study shown to be significantly correlated to mercury.

3.2 MIR spectra

Shown in Fig. 1 is the mid-IR spectra from EFPC soil samples obtain for the highest (1D, 216.2 mg kg^{-1}Hg) and lowest (3C, 0.705 mg kg^{-1} Hg) 10 plots sampled for total mercury. Principal component analysis (PCA) was initially on the full spectral range (4000-600 cm^{-1}) to characterize soil spectra and detect outliers before establishing the regression model. However, due to lack of apparent spectral features above 1400 cm^{-1}, data above 1600 cm^{-1} were removed (Fig. 1 & Fig. 2b). Figs 2a & 2b are the PCA score and loading plots for the 10 mercury soil plots sampled. The first two principal components of the PCA account for the greatest amount of total variation (98%) with principal component 1 (PC1) containing 94% and principal component 2 (PC2) 4% of the observed variation. Interestingly, plots samples with total soil mercury concentration < 7 mg kg^{-1} clustered together and include, 1B (0.945 mg kg^{-1} Hg), 3C (0.705 mg kg^{-1} Hg), and 3F (6.33 mg kg^{-1} Hg) (Fig. 2a). The loading plot, Fig. 2b shows the important bands responsible for classification of the soil samples are 995, 911, 791, 775, 691 cm^{-1} which are assigned to C-H stretching vibrations, and 1167, 1123, 1063, 971, 927, 847, 775, and 695 cm^{-1} attributed to C-H and C-O stretching vibrations.

The Pearson correlation shows nine (Ba, Cd, Cu, Fe, Ni, Rb, Sr, Ti, V) of the twenty-two metals and total carbon were significantly correlated to soil total-Hg concentrations. Due to the significant correlation of these metals and carbon with mercury, we investigated the ability to determine these analytes in soils using a multivariate regression technique, PLS-2, which analyzes multiple y-variables with spectral information. Table 2 summarizes the results for the calibration models developed with mid-infrared spectra. The best models (high r, low RMSEC and RMSEP) to predict Hg and Sr ($r \geq .90$), Cu and Ni ($r > .80$), Fe, Cd, C_{total}, Rb, V, Ti, and Ba ($r < .80$) are obtained with general pretreatment methods.

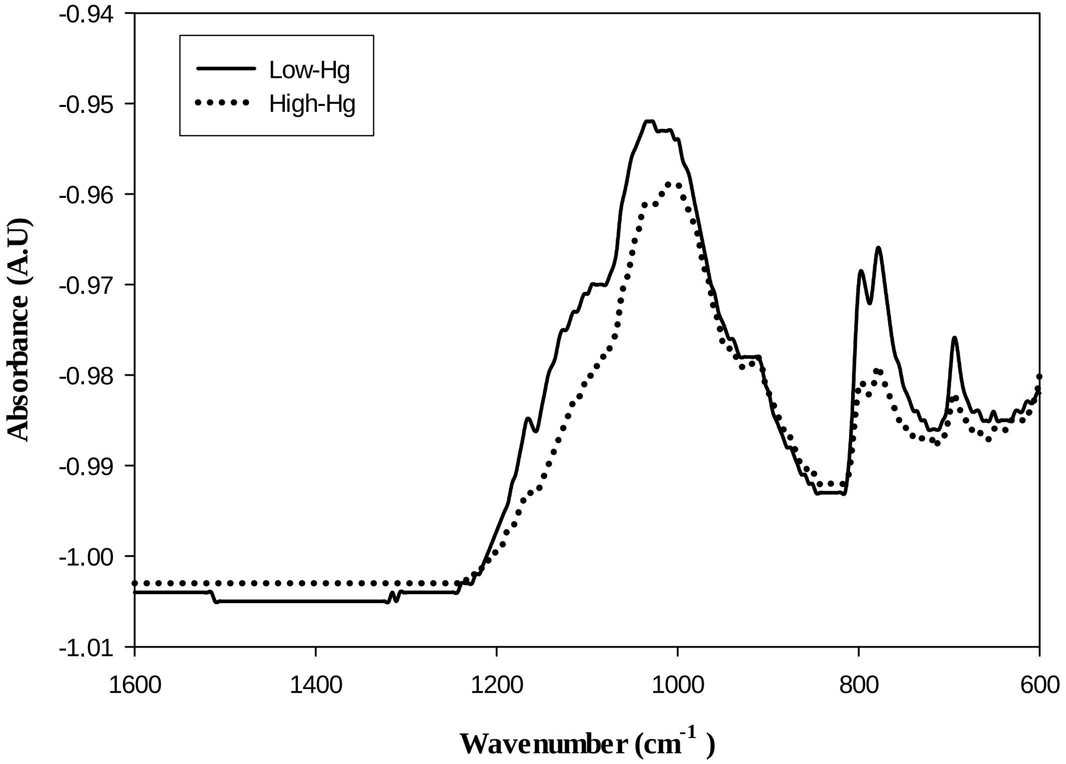
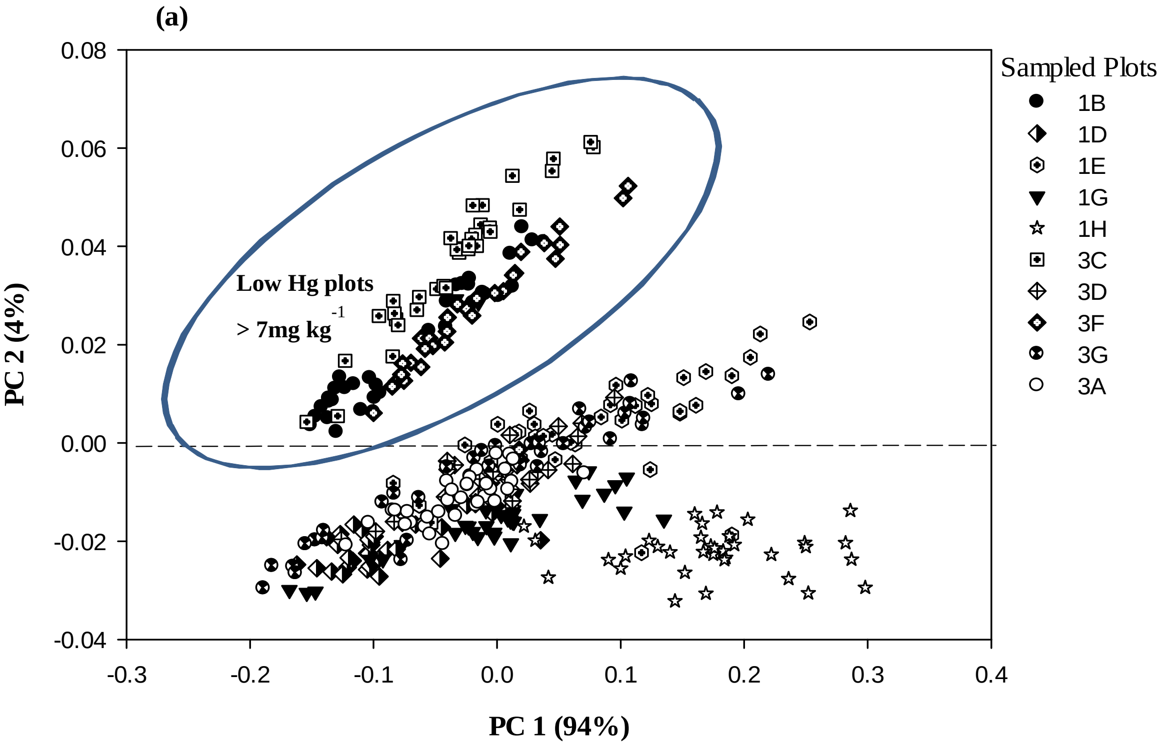


Fig. 1 Mid-infrared spectra of the highest and lowest mercury soil samples along EFPC



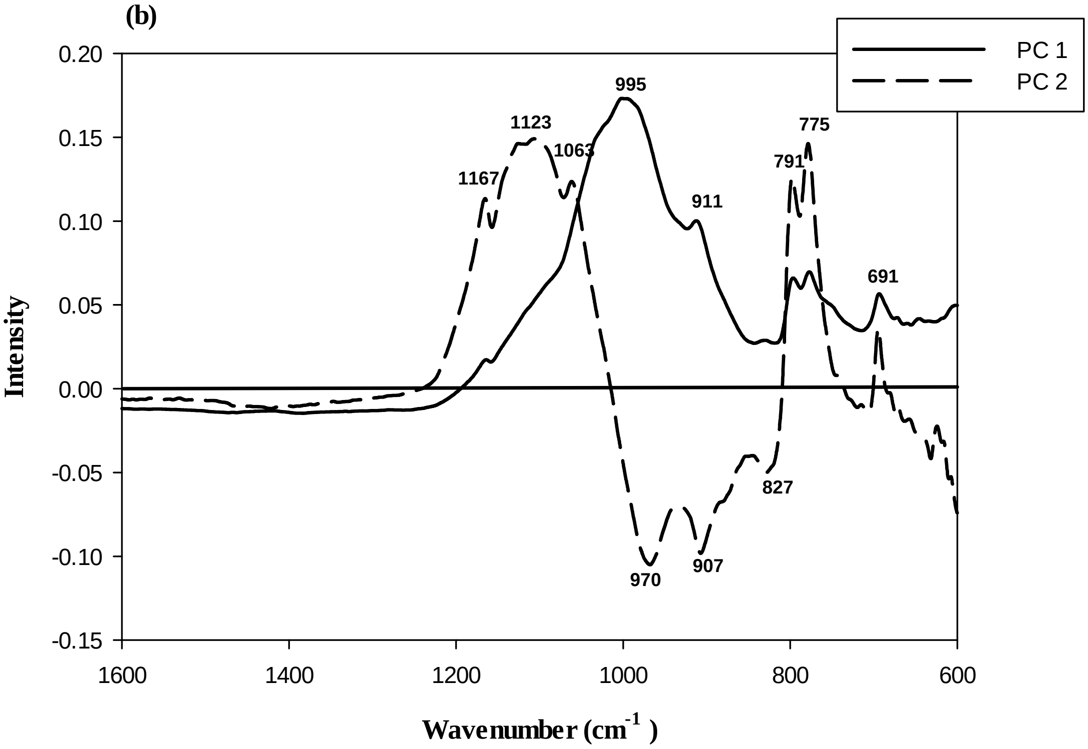


Fig. 2 (a) PCA score plot of MIR spectra (b) PC 1 and PC 2 loading plots for 10 mercury soil plots sampled

Table 2 PLS-2 models developed for Hg, Sr, Ni, Cu, Cd, Fe, V, Ti, Rb, Ba, C_{total}

				Full cross-validation			
Element			***Pre-treated**	**Calibration**		**Validation**	
	Min	Max	no. PC	r	RMSEC	r	RMSEP
Hg_{ppm}	0.7	758.65	5	0.93	22.7	0.91	25.8
Sr_{ppm}	0.04	0.08	3	0.90	0.003	0.88	0.003
Cu_{ppm}	0.001	0.25	3	0.87	0.02	0.85	0.03
Ni_{ppm}	0.004	0.19	5	0.86	0.01	0.82	0.01
Fe_{ppm}	13.88	58.65	5	0.79	7.49	0.76	7.9
$C_{total\ mg\ g^{-1}}$	0.63	2.34	3	0.78	0.29	0.76	0.3
Cd_{ppm}	0.02	0.05	4	0.78	0.003	0.76	0.004
Rb_{ppm}	0.04	0.16	3	0.75	0.02	0.74	0.02
Ti_{ppm}	2.47	4.23	5	0.7	0.23	0.69	0.25
V_{ppm}	0.04	0.12	5	0.64	0.01	0.6	0.01
Ba_{ppm}	61.15	114	5	0.52	8.90	0.39	9.7

All spectra were averaged and mean normalized.

Table 3 Regression coefficients for Fe, C, Cd, Rb, Ti, V, and Ba

Element	Regression coefficients (cm^{-1})
Fe	1168 1075 1002 877 823 796 77 5 723 689 671
C	1168 1075 1002 925 877 823 796 775 721 689 668
Cd	1177 1075 1029 977 912 877 823 800 775 723 691 671
Rb	1168 1129 1054 1022 877 825 800 775 721 691 673
Ti	1179 1150 1073 1031 954 912 875 823 800 775 721 689
Ba	1433 1133 1029 1010 979 912 877 802 721 687
V	1433 1137 1073 1077 1006 977 912 877 831 818 802 766 743 723 689 675 668 654

The relevant regression coefficients for the highest *r* calibration and validation models were obtained for Hg, Sr, Cu, and Ni. Examination of the results for Hg, where sample distribution was marginal, showed some low (< 21 mg kg^{-1}) samples to be poorly determined with several samples at values ~ 6%, to have ~21% Hg content in the calibration. The validation (*r*) set resulted in over-prediction of several samples, ~6% to be over-predicted by ~ 20% Hg content. Results for Cu were similar, several samples < 1% were slightly over-predicted to have ~2% Cu content in both calibration and validation sets. Even though Hg and Cu calibration and validation models were *r* > 90 and 80, the ability for the models to capture relatively low concentrations in these samples was poor.

The calibration results for Sr and Ni were fairly accurate in predicting these metals (Table 2). The majority of the metals analyzed did not consist of a wide range of concentration, which made these metals difficult to predict. Regression coefficients for metals with models < 80 are listed in Table 3. Reeves and Smith (2009) reported that due to the diversity of samples (> 700) there was an inability to capture a relevant calibration and validation models for most metals sampled. The authors did report good calibration models for Ni or Mg when sample concentrations were < 100 mg kg^{-1}. The calibration and validation *r* for Ti and Ba were below < 80 but these models were still able to detect these metals (Table 2). Several researchers have developed calibration models for Fe, Cu, Ni, Cd (Malley and Williams, 1987; Reeves and Smith, 2009) and total carbon (Michel and Ludwig, 2010) using the mid- and near-infrared region. Strong stretching and vibrational bands at 1340-1470 cm^{-1}, 675-995 cm^{-1} and 1030-1167 cm^{-1} indicates C-H and C-O bonds, respectively. The majority of analytes sampled had prominent bands in these regions.

4 Conclusions

Traditionally, conventional methods for detecting heavy metals in contaminated samples are labor intensive and relatively expensive. The objective of this study was to examine the potential use of MIR in the quantitative determination of total mercury and other heavy metals in soil samples within the floodplain of a mercury contaminated site. Soil samples were obtained from 10 plots initially designated as high (> 200 mg/kg Hg), medium (50-200 mg/kg Hg) or low (< 50 mg/kg Hg). In general, results show that quantitative analysis based on mid-IR spectroscopy could be used to develop calibration models that can use spectral data to distinguish contaminated from uncontaminated samples. Inaccurate prediction could be made if metal concentrations are below certain levels as seen in Hg and Cu calibration and validation models, due to over-fitting of spectral data. Reeves and Smith (2009) noted that a larger sample size may reduce the problems associated with over-fitting. The *fingerprint* region 1200 to 600 cm^{-1} is very useful in identifying small differences in the structure and constituents of molecules of interest (Skoog et al., 1998). A close match between several spectra in this fingerprint region constitutes strong evidence for the identity of compounds in the spectra. Several analytes (Hg, Sr, Ni, Cu, Cd, Ti, and C_{total}) have sharp bands between this region (691, 726, 783, 798, 799, 726 cm^{-1}). The majority of single bonds give rise to absorption bands within these frequencies and, due to similarities in their energies strong interactions occur between neighboring bonds. Absorption is thus a composite of competing interactions and depends on the overall structure of the molecule (Skoog et al., 1998). Exact interpretation of spectra in this region poses a problem due to the complexity of the spectra, but it is the complexity that leads to unique structure and eventual identification.

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