

A spectroscopic approach to assess trace–heavy metal contents in contaminated floodplain soils *via* spectrally active soil components

Michael Vohland^{1*}, Christian Bossung¹, and Heinz-Christian Fründ²

¹ Remote Sensing and Geoinformatics, Faculty of Geography and Geosciences, University of Trier, 54286 Trier, Germany

² Department of Agricultural Sciences and Landscape Architecture, Fachhochschule Osnabrück (University of Applied Sciences), 49009 Osnabrück, Germany

Abstract

Soil samples from grassland plots in the Hase floodplain near Osnabrück (NW Germany) were analyzed using visible and near-infrared laboratory spectroscopy (VNIRS) by means of an ASD FieldSpec II Pro FR- spectroradiometer (spectral range 0.4–2.5 μm), paralleled by atomic-absorption spectrometry (AAS), automated combustion for C_{org} quantification, and texture analysis. By AAS, contents of Cu, Zn, and Pb were found to be clearly elevated which is due to industrial effluents into the river in the 19th and 20th century. As these heavy metals (HMs) cannot be assessed directly by VNIRS, it was one major task to clarify whether they can be quantified indirectly using intercorrelations with spectrally active soil components. A second goal was to identify the specific spectroscopic predictive mechanism which may also be applicable to assess trace-HM contents of other soil samples similar to those investigated here. For the latter, C_{org} was found to be most indicative, whereas the binding of the metals to other constituents (Fe oxides, clay) was not utilizable in the spectroscopic approach. The measured spectra were subjected to a multiplicative scatter correction and afterwards used to establish partial least-squares regression (PLSR) models to estimate the contents of the different soil constituents. For C_{org} , very reliable estimates were obtained for both calibration and validation samples (in the validation, r^2 amounted to 0.90 and the percentage root mean square error [RMSE] was equal to 30.6%). Estimation accuracies obtained by PLSR for the trace HMs were considerably lower (r^2 between 0.56 and 0.71, percentage RMSE > 50%), which can be traced back to moderate correlations with C_{org} as main spectral determinant. According to these results, VNIRS can be applied as rapid and precise screening method for C_{org} to complement traditional analytical methods and to be used efficiently for a large number of samples. The method of VNIRS may also be applied for an indirect estimation of C_{org} -associated metals to address their spatial variability, for example. This issue appears to be of high importance for digital soil mapping by imaging spectroscopy in the local to medium scale.

Key words: trace heavy metals / soil organic carbon / VNIR spectroscopy / partial least-squares regression / multiplicative scatter correction

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1 Introduction

Over the last two decades, visible and near-infrared spectroscopy (VNIRS) has evolved into an important nondestructive tool to characterize soils and to assess soil properties quantitatively, *e.g.*, the carbonate content, the organic C (C_{org}), total N, Fe oxide minerals, hygroscopic moisture, or clay content (Dalal and Henry, 1986; Deaton and Balsam, 1991; Ben-Dor and Banin, 1995; Chang and Laird, 2001; McCarty et al., 2002; Udelhoven et al., 2003; Brown et al., 2006). Compared to conventional laboratory analysis, VNIRS is accepted as rapid and potentially cost-effective method. Additionally, it can be applied in the field by portable spectroradiometers (Couillard et al., 1997; Wu et al., 2007). The predictive accuracy of VNIRS is determined by both the spectral “fingerprints” of the studied materials and an adapted preprocessing strategy for the spectral data (Ben-Dor and Banin, 1995). Assessing the predictive power of VNIRS for soil heavy-metal

(HM) contamination is an important objective, as high levels of some trace heavy metals may be ecotoxicologically relevant and harmful when passing the food chain (Wu et al., 2007). The study presented here focused on soils of a river floodplain where high concentrations of Cu, Pb, and Zn are significant. As a transition element with an incomplete d-subshell, Cu provides a specific absorption feature in the VNIR domain. However, as shown by contamination experiments performed by Wu et al. (2007), very high Cu concentrations will be necessary (>4000 mg kg^{-1}) to exhibit its inherent absorption feature. Thus, under real-world soil conditions, Cu and the featureless metals Pb and Zn cannot be assessed directly by VNIRS. Nonetheless, trace HMs in soils are predictable indirectly when correlated with spectrally active soil components (Fe oxides, organic matter [OM], clay). Based on that, statistical models between VNIR spectra and HM



* Correspondence: Prof. Dr. M. Vohland;
e-mail: vohland@uni-trier.de

concentrations have been established in some studies investigating freshwater sediments (Malley and Williams, 1997), alluvial soils (Kooistra et al., 2001; Wu et al., 2007), agricultural soils (Malley et al., 2000), soils of a metal mining region (Siebielec et al., 2004), and soils contaminated by a mining accident (Kemper and Sommer, 2002). In these case studies, different prediction mechanisms were identified. For example, Malley and Williams (1997) found OM to be responsible for the prediction of sediment HM concentrations, and Kooistra et al. (2001) identified both clay and OM to be most essential for the HM assessment. On the other hand, Wu et al. (2007) clearly demonstrated that Fe oxides form the major predictive mechanism. However, these results cannot be generalized, as soil properties (e.g., the soil C_{org} content) differed distinctly in-between these studies.

In this study, soil samples were taken from grassland plots. In fact, they show a very wide range of both C_{org} (0.37%–9.24%) and clay contents (0%–37.8%). Thus, with reference to the studies cited above, it is one objective to investigate whether the trace-HM contents of these samples can actually be assessed by VNIRS. Furthermore, it is explored statistically whether a valid prediction mechanism can be identified.

2 Material and methods

The soil samples were taken in the floodplain of the Hase river along a section of approx. 11 km, located downstream the city of Osnabrück (NW Germany). We restricted soil sampling to grassland plots, as permanent grassland is the most widespread land-use type in the Hase floodplain, and selected points inside the individual parcels randomly; in this way, a total of 109 points widely spread in the study area was specified (Fig. 1).

For each of the selected points, a humus-profile auger of Eijkelkamp (Giesbeek, The Netherlands) with a length of 40 cm was used to take a sample from a depth of 10–20 cm (below the main rooting zone). The profiles frequently showed signs of plowing with significant turns at a profile depth of 20–25 cm; humose horizons occurred at all depths. Thus, sampling was extended for a total of 40 points by taking soil material from a second profile depth (27–37 cm) additionally. All sampling positions were located by GPS measurements (GPS III Plus, Garmin, Olathe, Kansas, USA).

The C contents of the samples were determined by automated combustion at 1300°C using the ELTRA CS 500 instrument (ELTRA, Neuss, Germany). A correction for inorganic C was not necessary, as all samples were free of carbonate. To correct for C derived from past industrial and mining activities in the study region, an inert C fraction was determined from subsamples that had been kept at 375°C for 12 h before combustion at 1300°C according to Gustafsson et al. (1997). Organic C was thus operationally defined as the total C content minus the inert C fraction. The concentrations of the trace metals Cu, Pb, Zn, and the major elements Fe and Mn were measured, after a complete digestion of 0.1–0.2 g soil material with 3 mL concentrated HNO_3 and 1 mL H_2O_2 (suprapur) in high-pressure bombs (Berghof,

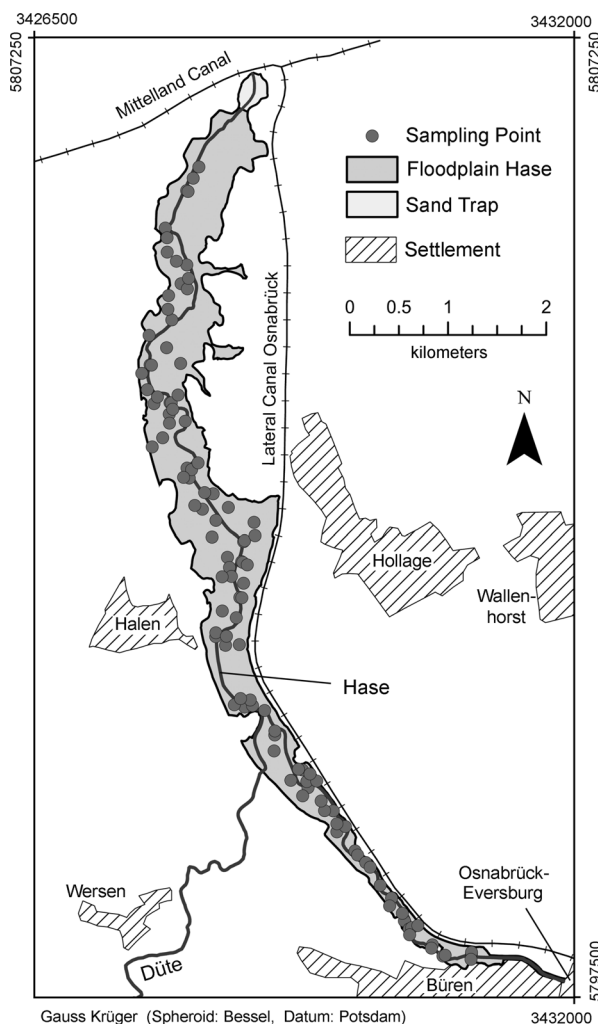


Figure 1: Study area and sampling points.

Eningen, Germany), with an atomic-absorption spectrometer (AAS) (Spectra AA-10; Varian, Palo Alto, California, USA). For texture analysis, a combined mesh-and-pipette analysis (designed after Köhn) was applied.

Roughly 80 g of each sample were used for the spectroscopic approach in the spectral laboratory. Here, each air-dried sample was bisected, one subsample was crushed to pass a 2 mm sieve, the other carefully homogenized by grinding in an agate mortar. For the bidirectional reflectance measurements of both subsamples, we used an ASD FieldSpec II Pro FR spectroradiometer (Analytical Spectral Devices, Boulder, Colorado, USA) and a reflectance standard of known reflectivity (Spectralon®). From the ASD instrument, spectral readings were retrieved in 1 nm increments over the 0.4–2.5 μm wavelength range. A 1000 W quartz-halogen lamp was applied for the illumination of the sample and the reference panel. Viewing and illumination geometry were held constant for all measurements (nadir view, 30° illumination zenith angle). From the raw spectral readings for each sample, we obtained the absolute bidirectional reflectances by taking account of the certified reflectivity of the Spectralon® standard.

Because a preliminary analysis showed clear multicollinearities (Fig. 2), data were reduced by resampling the measured spectra to 5 nm resolution and by statistical factoring. For the latter, the PLS (partial least squares) approach was applied to define variables that are uncorrelated to one another. As this factoring is based on the variance of both the spectral information and the target variable, it usually exploits the information that is inherent in the data efficiently for a powerful prediction. Partial least-square regressions were used in this study for both types of samples (sieved and homogenized) to examine the relation between measured reflectances and soil properties. To eliminate effects of nonspecific scattering of radiation at the surface of particles, a multiplicative scatter correction (MSC) has been performed. In the MSC, the light scattering is estimated for each sample relative to that of an ideal sample that we obtained by the usual procedure of averaging the measured data set over the complete wavelength range. Each spectrum is afterwards corrected in a way that all samples appear to have the same scatter level as the reference spectrum. For a further description of this method, see *Isaksson and Næs (1988)* and *Næs et al. (1990)*. After preprocessing, PLS regressions were calibrated for the samples of the upper soil horizon (10–20 cm profile depth, $n = 109$); for validation, these PLS models were applied to the samples taken from 27–37 cm soil depth ($n = 40$).

3 Results

Retrieved soil properties and trace-metal contents are listed in Tab. 1. In general, correlations between the soil variables are significant, but on a moderate to low level. Highest correlations can be found between Pb and Zn, and Fe and the clay fraction (Tab. 2).

The measured raw spectra partly provide redundant information due to clearly pronounced multicollinearities; especially in the near infrared (NIR) at wavelengths >1030 nm, reflectance values are highly correlated with each other (see 2D

correlations plotted for the sieved samples in Fig. 2 b). Spectra of sieved and homogenized samples provide similar information, as they do almost not differ in course, but only in the level of reflectance (Fig. 2 a). For both, the same typical absorption features do occur (at 1.45, 1.95, and 2.2 μm) that are induced by combined and overtone modes of H–O–H and OH– fundamental vibrations (*Hunt and Salisbury, 1970*).

The spectral response of each parameter can easily be illustrated by correlation analysis between the concentrations of the target variables and the measured reflectances of each spectral channel of the ASD instrument (Fig. 3 and 4). From these correlation spectra, two groups of soil variables can be identified. A first group is made by the contaminant HMs, in which we found the best and most stable correlations for the C_{org} . Here, the optimum value of r was -0.79 (Fig. 3), which

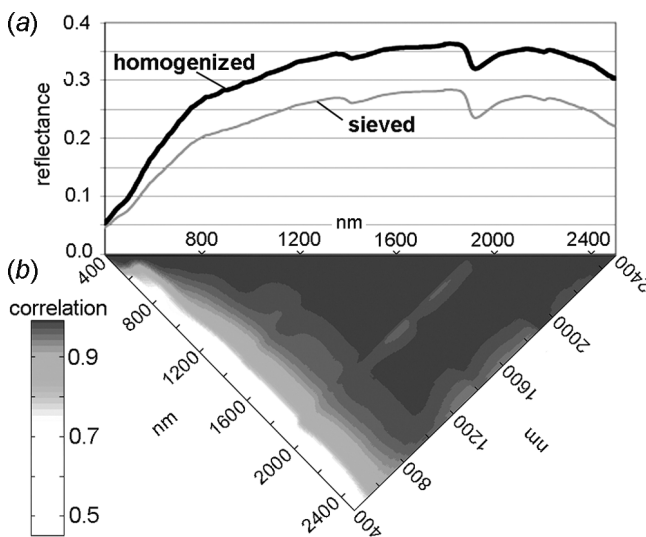


Figure 2: 2D-correlation plot (b) for the measured reflectances (sieved samples, $n = 149$) and mean measured spectra (a) for both sieved and homogenized samples ($n = 149$).

Table 1: Soil properties and trace-metal concentrations of the investigated soil samples downstream of Osnabrück ($n = 149$).

	PH (CaCl_2)	Inert C (%)	C_{org} (%)	C_{ua} (mg kg^{-1})	Pb^a (mg kg^{-1})	Zn^a (mg kg^{-1})	Clay (%)
Mean	5.4	0.29	2.98	278	165	388	11.9
Range	4.2–7.1	0.01–3.55	0.37–9.24	8–1823	0–605	40–1322	0–37.8
Var coef ^b	7.0	158.3	54.4	111.5	77.1	76.0	55.1

^a mean background level of soils in the Hase valley upstream of Osnabrück (*Bailly et al., 1993*): Cu: 10–15, Pb: 25–35, Zn: 50–65

^b coefficient of variation in%

Table 2: Correlation matrix of examined soil properties ($n = 109$).

	C_{org}	Cu	Pb	Zn	Fe	Mn	Clay
C_{org}^a	1.00	0.67	0.66	0.65	0.62	0.29	0.71
Cu	0.67	1.00	0.67	0.73	0.21 ^b	0.28	0.31
Pb	0.66	0.67	1.00	0.91	0.40	0.53	0.46
Zn	0.65	0.73	0.91	1.00	0.38	0.60	0.45
Fe	0.62	0.21 ^a	0.40	0.38	1.00	0.40	0.80
Mn	0.29	0.28	0.53	0.60	0.40	1.00	0.43
clay	0.71	0.31	0.46	0.45	0.80	0.43	1.00

^a correlation between Cu and Fe significant at the 0.05 level, all other correlations at the 0.01 level

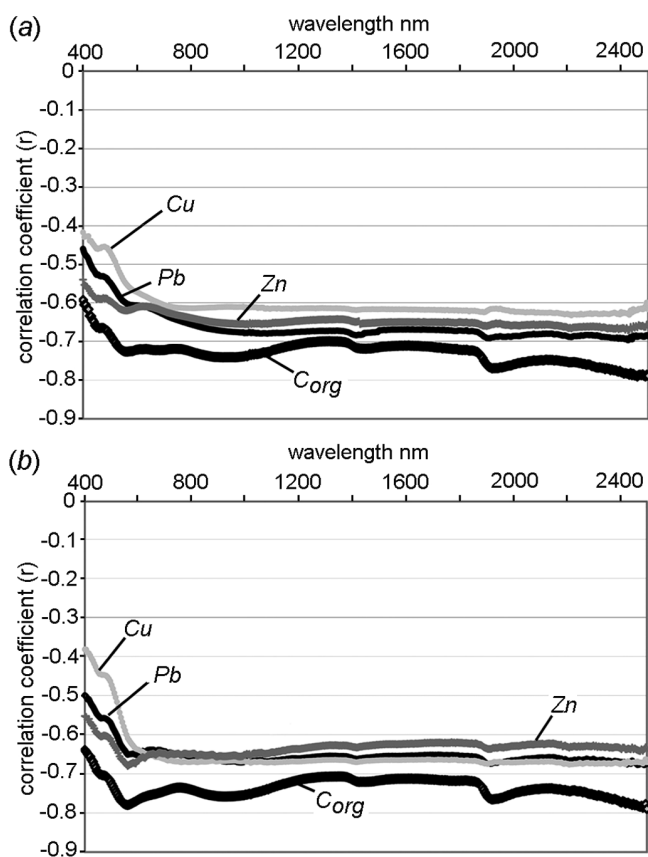


Figure 3: Correlation spectra for C_{org} , Cu, Pb, and Zn (sieved [a] and homogenized [b] soil samples, $n = 149$).

was not influenced by the selected preprocessing strategy (sieved, homogenized, raw spectra or spectra corrected for multiple scattering). Comparing the maximum correlations between soil constituents and spectroradiometer measurements, a general order of $C_{org} \gg Zn, Pb > Cu$ was found. In total, the differences of the correlation spectra between Cu, Pb, and Zn were small. By contrast, the correlation spectra for Fe, Mn, and clay are clearly different from those of the first group (Fig. 4), and these variables may all be assigned to a second group of soil parameters. For this group, an order of $Fe \gg clay \gg Mn$ can be identified for the maximum correlation coefficients.

As correlation spectra identify both direct or indirect correlations with the measured spectra, they may be helpful to reveal coherences between the variables; for spectrally nonactive constituents, possible predictive mechanisms *via* spectrally sensitive

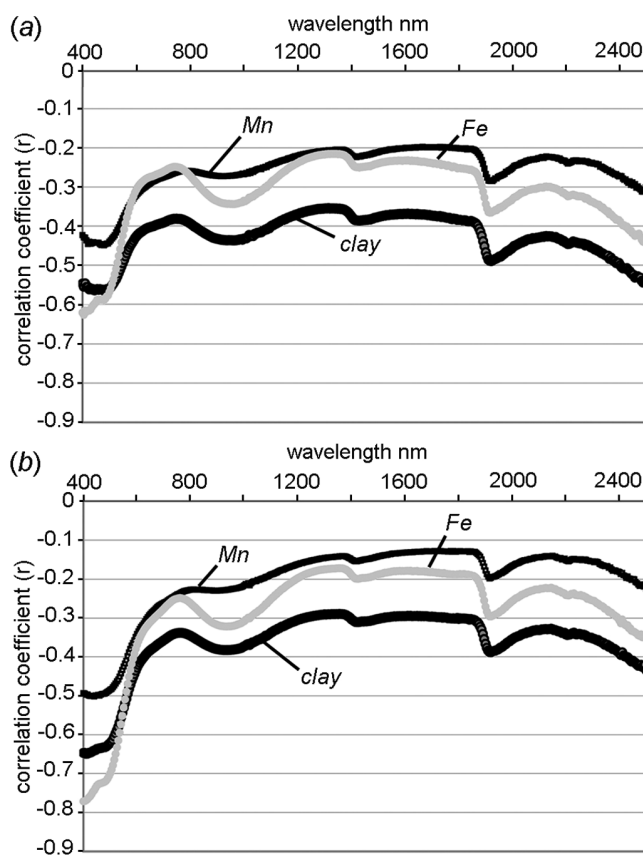


Figure 4: Correlation spectra for clay, Fe, and Mn (sieved [a] and homogenized [b] soil samples, $n = 149$).

variables may be identified, which will be referred to later on in the analysis of the PLS regression models.

For the calibration of the PLS regression models, the 109 samples of the upper sampling depth were used. To determine an optimum number of latent variables, an internal validation was performed based on the method of leaving-one-out cross-validation (CV); the model providing the lowest $RMSE_{CV}$ was selected. For C_{org} , the best estimates were clearly obtained when exploiting the spectra of the sieved samples after MSC (Tab. 3).

This turned out to be the same for all HMs and the clay fraction which were all estimated most reliable from sieved samples after scatter correction. Coefficients of determination and RMSE prove the prediction of C_{org} to be most promising; poorest RMSE results were obtained for Cu (Tab. 4). How-

Table 3: Results of the PLS regression analysis for C_{org} (sampling depth 10–20 cm, $n = 109$).

Spectral data	n of latent variables	r^2 ^a	RMSE (% C_{org})	rRMSE ^b	RMSE _{CV} (% C_{org})	rRMSE _{CV} ^b
Sieved, raw	9	0.676	0.903	0.288	1.298	0.415
Sieved, MSC	8	0.860	0.588	0.188	0.889	0.284
Homogenized, raw	9	0.661	0.929	0.297	1.434	0.458
Homogenized, MSC	8	0.804	0.700	0.224	1.108	0.354

^a all correlations significant at the 0.01 level

^b relative RMSE (quotient of RMSE and mean of C_{org} [3.13%] in the upper horizon)

Table 4: Results of the PLS regression from spectral data for all soil properties (sieved samples after MSC; sampling depth 10–20 cm; $n = 109$).

Metal	Mean (mg kg ⁻¹)	n of latent variables	r^2 ^a	RMSE	rRMSE	RMSE _{CV}	RRMSE _{CV}
Cu	276.7	7	0.753	151.4	0.547	220.5	0.797
Pb	164.2	7	0.756	58.1	0.354	85.4	0.520
Zn	377.0	9	0.810	117.5	0.312	213.2	0.566
Fe	20,526	7	0.840	4,960	0.242	7,255	0.353
Mn	826.2	8	0.706	363.3	0.440	578.2	0.700
clay	12.17 ^b	6	0.647	4.149	0.341	5.102	0.419

^a all correlations significant at the 0.01 level

^b in%

ever, the RMSE increased significantly for nearly all metals in the cross-validation. Cross-validated estimates for the trace HMs are illustrated by Fig. 5. Here, values of r^2 are between 0.50 and 0.60 which is considered to be generally usable for an approximate screening (Malley et al., 2004).

In the PLS regression models, the number of latent variables used for prediction was relatively high (n was 6 to 9, Tab. 3 and 4). To identify the most significant spectral information for each soil constituent, we concentrated on the first two factors that already capture most of the explained variation (in all cases >50%) and examined the coefficients in the respective regression model $Y = X B_{PLS} + E$ (with Y = estimates for chemical variables, X = spectral information, and E = error term) (Fig. 6). For comparison, all variables were standardized between 0 and 1 before PLS modeling.

In fact, the PLS coefficients for the trace metals are very similar; the graphs for Pb and Zn are almost identical, and the Cu graph deviates marginally (Fig. 6). This again indicates that these metals do not provide distinguishable and therefore diagnostic reflectance patterns. Furthermore, as they are represented by nearly identical spectral information, the same optically active variables must be significant. From the analysis of the PLS coefficients, we find C_{org} to be most indicative; similar spectral regions are in fact exploited to obtain the contents of both C_{org} and trace metals. Nevertheless, not more than 45% of the metals' variances are retrievable by C_{org} (Tab. 2), but there is no other spectrally active soil component to provide a key to a more reliable estimation; in fact, the B_{PLS} coefficients of Fe, Mn, and clay do not reveal any clear correspondence with those of the trace metals (Fig. 6).

For the external validation, the already calibrated PLS models were applied to the spectra of those samples that had been taken from 27–37 cm soil depth. Statistical analysis showed the C_{org} concentrations of both soil depths to differ significantly (Mann-Whitney U test, $p < 0.05$; mean C_{org} 10–20 cm = 3.13%, mean C_{org} 27–37 cm = 2.49%), but the results of the PLS regression for C_{org} kept stable in the validation (r^2 amounted to 0.90, and the rRMSE was rather low at 0.306, Tab. 5). In total, RMSE values for the different soil constituents (Tab. 5) were now similar to those that had been retrieved by the internal cross-validation (Tab. 3 and 4). For the contaminant trace metals, results for Pb and Zn were satisfactory (Tab. 5, Fig. 7); for Cu, a high correlation coefficient between estimates and measurements was cancelled out by high error terms (RMSE, rRMSE).

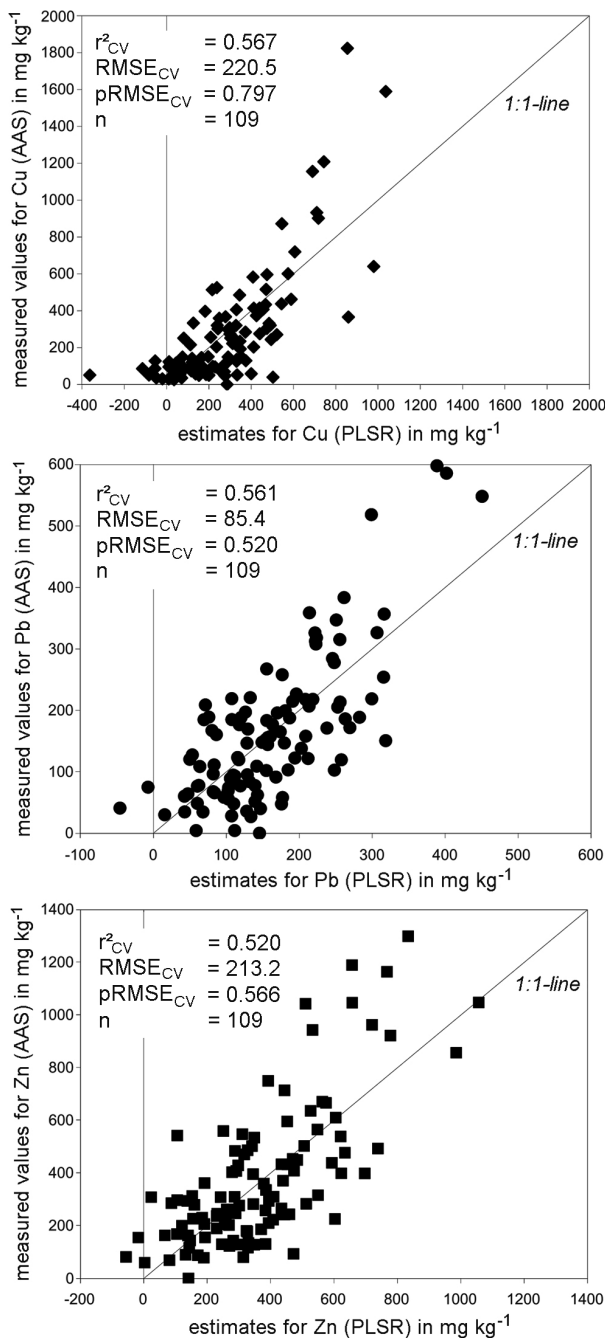


Figure 5: Cross-validated estimates for Cu, Pb, and Zn retrieved by PLS regression vs. concentrations measured by AAS.

Table 5: Validation of the PLS models (sieved samples from 27–37 cm soil depth after MSC, $n = 40$).

	C _{org}	Cu	Pb	Zn	Fe	Mn	Clay
mean ^a	2.57	248.9	168.7	426.9	20.402	731.4	11.10
r ² ^b	0.90	0.71	0.62	0.56	0.67	0.23	0.46
RMSE ^a	0.789	207.5	97.9	248.0	7.744	541.5	4.89
rRMSE	0.306	0.834	0.580	0.581	0.380	0.740	0.440

^a in% (C_{org}, clay) or mg kg⁻¹ (all other variables)

^b all correlations significant at the 0.01 level

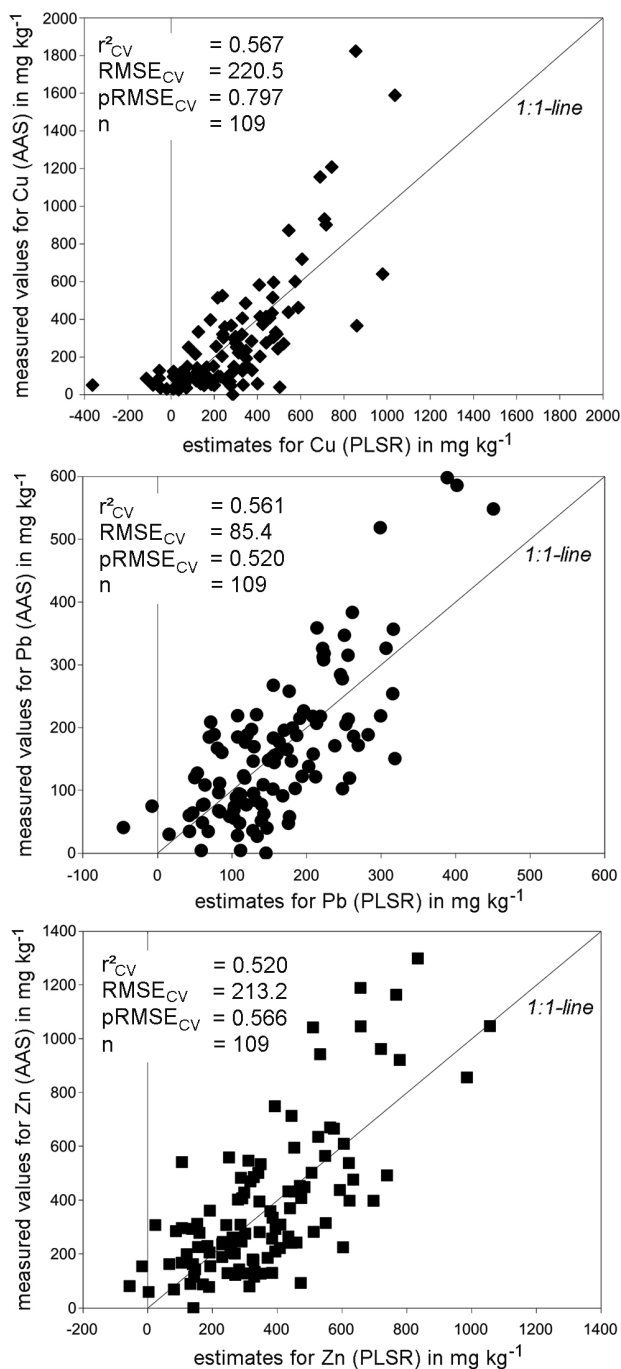


Figure 6: Plot of B_{PLS} for the studied soil constituents when two latent variables are used in the PLS predictive model.

In addition to a pure laboratory approach, that mostly aims at a reliable prediction of the contamination level for each sample, the spatial distribution of HM concentrations inside the study area is another issue of major concern. Here, information referring to the path of immission may be very helpful for assisting in an improved spatial analysis. However, in case of multiple sources of contamination, these information are normally not fully available or reconstructable. For the samples collected in the Hase floodplain, we quantified two possible spatial variables by GIS analysis—the flow path from the city of Osnabrück and the distance from the river channel. Statistically, we found only moderate relationships between the metal concentrations and both variables. Correlations were not significant in an univariate analysis, but when used together with C_{org}, in a multivariate analysis, one (for Cu and Zn) or even both (for Pb) of the positional variables turned out to be significant. Nevertheless, r^2 was generally <0.55 in case of the upper soil depth, but well-defined multivariate models could be found for the sample depth of 27–37 cm (Tab. 6). To test the quality of the PLS-based spectroscopic assessment of C_{org}, we used both measured and also estimated C_{org} values in these multivariate regressions. Using C_{org} estimates instead of measured values, the results diminished slightly only for Zn, but kept stable for Pb and also Cu (Tab. 6, Fig. 7). This again proves the robustness of C_{org} estimation based solely on spectroscopy.

4 Discussion

4.1 Sample preprocessing

In general, the sieved soil samples proved to be more appropriate for the statistical prediction of soil constituents from the measured spectra than the samples homogenized in a mortar. This is of relevance as the sieved samples are more similar to *in situ* conditions with pronounced shadowing effects induced by soil aggregates (Bowers and Hanks, 1965). Nevertheless, more aggregated samples are strongly affected by the scattering of radiation at the particles' surfaces which can be eliminated by including a MSC in the preprocessing of the spectra. For this, the scattering effects were assumed to be wavelength-independent, and the average spectrum of the calibration set was used as ideal sample. As one basic assumption for MSC, the chemical differences between the samples should be relatively small (De Noord, 1994), which was not true for our study. However, Isaksson and Næs (1988) and Næs et al. (1990) found the MSC to be appropriate and also very effective for samples with clearly

Table 6: Results for (multiple) linear regression modeling of the trace metals Cu, Pb, and Zn using C_{org} (measured and spectrometrically estimated) and positional variables (27–37 cm soil depth, $n = 40$).

modeled by	Cu		Pb		Zn	
	r^2 a	RMSE ^b	r^2 a	RMSE ^b	r^2 a	RMSE ^b
C_{org} (measured)	0.60	181.2	0.60	97.3	0.58	226.9
C_{org} (measured), flow path, distance from river channel	0.66	159.6	0.66	87.6	0.69	201.3
C_{org} (estimated by PLS regression), flow path, distance from river channel	0.62	169.5	0.67	86.8	0.59	229.3

a all correlations significant at the 0.01 level

b in $mg\ kg^{-1}$

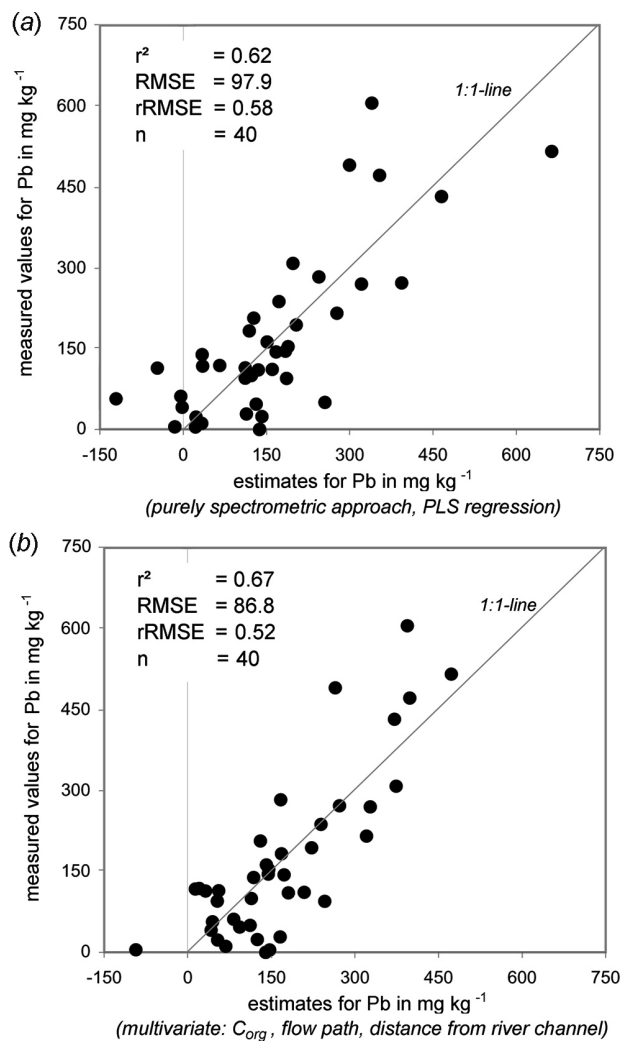


Figure 7: Estimates for Pb (27–37 cm soil depth) in a purely spectral approach (a) (obtained by externally calibrated PLS regression as documented in Tab. 5) and by multiple linear regression using C_{org} from PLS analysis and positional variables (b) ($n = 40$).

varying target variable values. One critical point of the MSC refers to the fact that the ideal sample is formed by the calibration set itself and not independently. This may produce artificial effects, and the large increase of the r^2 for C_{org} after MSC compared to the raw spectra without further preprocess-

ing might partly result from that. On the other hand, the good robustness in the validation ($r^2 = 0.90$) proves the efficiency of this method as the scatter correction for the validation samples was performed independently from the calibration set.

4.2 Spectroscopic assessment of the soil parameters

For the quantification of the trace heavy metals, we found by correlation spectra and PLS coefficients that the spectrally active C_{org} fraction is the key variable for an indirect spectroscopic approach. This spectral predictive mechanism was also found in some other studies (e.g., Malley and Williams, 1997; Dupuy and Douay, 2001), but differs from the results of Wu et al. (2007) and Kooistra et al. (2001) for alluvial soils. Based on high correlations with Fe, Wu et al. (2007) obtained reliable estimates for a set of trace HMs (Ni, Cr, Co, Cu, As; $r^2_{CV} \geq 0.67$); nevertheless, the contents of C_{org} were clearly lower (the mean was 1.27%) than in the Hase floodplain.

A study very similar to the one presented here was carried out by Kooistra et al. (2001) in two floodplains along the river Waal in The Netherlands. Here, both clay and OM contents were identified as major spectrally active soil components for the indirect determination of Cd and Zn concentrations. Based on PLSR, the prediction accuracy for Zn was clearly higher than in our study ($RMSE_{CV}$ 81 $mg\ kg^{-1}$ vs. 213 $mg\ kg^{-1}$ with moderately lower total concentrations of Zn in the Waal region).

For OM, Kooistra et al. (2001) achieved a $RMSE_{CV}$ of 1.7%, that is in line with the one determined in our study (1.5%, calculated from C_{org}). In the Hase floodplain, the estimates for C_{org} were very reliable for both the calibration and the validation samples. Based on these results, VNIRS may be applied efficiently for a rapid and also precise C_{org} screening of large soil sets.

4.3 Interactions and covariation between C_{org} and trace metals

Attention should be paid to the fact that the binding of heavy metals to the organic fraction is variable and may depend on size fraction and contamination level. Parat et al. (2002)

found a high correlation only in the coarse fractions of copper-contaminated vineyard soils, and concluded that the decomposition of OM is prevented by biotoxic Cu concentrations. This coincides with the results of *Ducaroir* and *Lamy* (1995) who found high contents of toxic trace metals to associate with an accumulation of C_{org} in the coarser-size fractions. However, high trace-metal contents were also found in the clay fraction in both studies. Here, accumulation is due to organo–mineral associations (with Fe as main agent) and inorganic bindings (mostly Fe oxides); thus, Fe could be indirectly responsible for most of the trace metals in the clay fraction (*Parat et al.*, 2002). In case of our samples, the accumulation of Fe in the clay fraction (*Mulders*, 1987; *Parat et al.*, 2002) was clearly comprehensible by very similar correlation spectra, and the spectral responses allowed a stable Fe assessment. Nevertheless, these spectral “fingerprints” could apparently not be turned to make the trace-metal assessment more reliable.

In the Hase floodplain, Cu is the dominating contaminant with concentrations on average about 10 times the precautionary value of the German Soil Protection and Contaminated Sites Ordinance (*BbodSchV*, 1999), and the maximum exceeding this value by >60 times. The concentrations of Zn are approx. 5 (maximum 20) times and those of Pb 3 (maximum 18) times the precautionary values. Although Cu has an extraordinary high tendency to accumulate in OM (*Hiller and Brümmer*, 1997), a relation between soil C_{org} and Cu seems to take place only at elevated Cu concentrations > 100–200 mg Cu per kg dry weight (*Minnich and McBride*, 1986; *Vavoulidou et al.*, 2005; *Sauvé*, 2006; *Fründ et al.*, 2007). Therefore, the spectral assessment of trace metals may be most feasible at contaminated floodplains aiding in the identification of hot-spot areas and contamination gradients. Its applicability in other situations like vineyards or areas with airborne metal immissions has yet to be investigated.

The relation between C_{org} and trace metals in the studied floodplain may also be due to the dynamics of deposition during flood events. It may be possible that trace metals are deposited in depressions by sedimentation, while C_{org} is accumulated at the sample place because of wet conditions associated with an overall reduced decomposition rate. Copper, Zn, and Pb are usually highly cross-correlated in contaminated soils showing a positive relation to C_{org} (*Valsecchi et al.*, 1995; *Dai et al.*, 2004). Further studies are necessary to explore which kind of relation between C_{org} and trace metals is happening.

5 Conclusion

Our study has shown that a spectroscopic assessment of trace metals in contaminated floodplain soils is in principle feasible by means of C_{org} that has been identified to form the major predictive mechanism. As one advantage, the spectroscopic approach requires much less working time than classical analysis. For the 149 samples analyzed, both measurement and preprocessing of the spectra was done in two days. For the chemical determination of C_{org} , a working time of at least one week has to be estimated, and the analysis of HMs requires another two to three weeks. This saving of time is

partly traded off by reduced accuracies. Thus, the spectral assessment of soil samples cannot replace but rather will complement the classical chemical analysis. The benefits result from the practicable processing of a large number of samples and the saving of chemicals. However, a calibration by information obtained from chemical analysis is mandatory.

In terms of a spatial analysis, an airborne or spaceborne hyperspectral sensor may be useful for the screening of large areas and the reproduction of the spatial distribution pattern of C_{org} and associated soil variables.

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