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# Study of heavy metal contamination in river floodplains using the red-edge position in spectroscopic data

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**Abstract.** One of the major environmental problems resulting from the regular flooding of rivers in Europe, is the heavy metal contamination of soils. Various studies have shown that soil contamination may influence plant physiology and, through changes in leaf pigment concentrations, influence reflectance spectra. The main objective of this case study was to study whether the red-edge position (REP) of vegetation spectra may provide information on soil contamination by heavy metals in river floodplains. The use of the maximum first derivative, smoothing methods (like polynomial fitting and the inverted Gaussian function), and interpolation methods based on just a few spectral bands were evaluated for a test site in the floodplain of the river Waal in the Netherlands. On selected transects heavy metal concentrations of soil samples and reflectance spectra of the growing vegetation using a field spectroradiometer were measured. A significant, negative correlation between the REP and heavy metal concentration was found using the maximum first derivative method ( $R^2 = 0.64$ ). The first derivative spectra in this study showed the presence of more than one peak within the red-edge region, as found by other authors. This phenomenon requires further detailed research using very fine spectral measurements.

### 1. Introduction

Many European rivers regularly flood vast areas of agricultural land. One of the major environmental problems with these floods is heavy metal contamination of soils. As an example, sediments of river floodplains in the Netherlands show significant levels of heavy metal concentrations such as cadmium (Cd), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn) (Beurskens *et al.* 1994, Middlekoop 2000). High levels of heavy metal concentrations may influence plant growth in a negative way and, if these heavy metals end up in agricultural crops or in grazing lands, they pose a serious health threat. Goetz *et al.* (1983) have shown that stress factors like heavy metal uptake will influence reflectance spectra at the leaf and canopy level. Field studies have demonstrated that changes in vegetation spectra can be metal-induced due to geochemical stress (Collins *et al.* 1983, Kooistra *et al.* 2003) or the occurrence of old waste deposit sites (Lehmann *et al.* 1991, Sommer *et al.* 1998).

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Remote Sensing *(gamma)* RES35803.3d 30/1/04 12:36:16 Rev 7.51n/W (Jan 20 2003) **The Charlesworth Group, Huddersfield 01484 517077**  Spectral changes occurred in both visible and near-infrared parts of the spectrum. As a result, optical remote sensing potentially offers tools to detect and monitor heavy metal contamination of soils in an indirect way.

The spectral signature of leaves is dominated by chlorophyll in the visible (VIS) region of the electromagnetic spectrum, by the cell structure in near-infrared (NIR) regions and by water content in the short-wave infrared (SWIR) regions. In addition to these variables, at the canopy level the leaf area index (LAI), the amount of green biomass and the leaf angle distribution determine the spectral signature. From a remote sensing point of view the illumination and observation geometry are also important. Many studies have focused on the use of vegetation indices, calculated as combinations of NIR and red reflectance, for estimating and monitoring vegetation characteristics. These indices correlated well with plant variables such as biomass, LAI and the fraction of absorbed photosynthetically active radiation (Baret and Guyot 1991, Broge and Leblanc 2000, Daughtry *et al.* 2000).

<u>Clevers (1999)</u> showed that imaging spectrometry might provide additional information at the red-edge region, not covered by the information derived from a combination of a NIR and a VIS broad spectral band. He concluded that, concerning high spectral resolution data, this seems to be the major contribution of imaging spectrometry to vegetation studies. The remote sensing of foliar chemical concentrations, other than chlorophyll and water, has not been very successful due to among other things the presence of water in living leaf tissue.

Collins (1978) and Horler et al. (1983) were among the first researchers to point out the importance of the red-NIR wavelength transition for vegetation studies. At red wavelengths reflectance is low due to absorbance by chlorophyll pigments while in NIR wavelengths reflectance is high due to scattering inside the leaf and multiple reflections inside the canopy, resulting in a steep rise in reflectance between 670 and 780 nm. Both the position and the slope of this red-edge change under stress conditions, resulting in a shift of the slope towards shorter wavelengths (Horler et al. 1983, Wessman 1994). The red-edge position (REP) is defined as the position of the inflection point of the red-NIR slope. This REP shift due to stress conditions can be caused both by a decrease in leaf chlorophyll concentration and by a decrease in LAI (see Clevers and Jongschaap 2001). These are the main variables determining the REP. The REP can be studied by plotting  $dR/d\lambda$ , the first derivative of reflectance (R) with respect to wavelength ( $\lambda$ ), as a function of  $\lambda$ . Alternatively, in many studies simple functions have been fitted to the reflectance spectrum in the red-edge region, and subsequently the wavelength belonging to the maximum slope has been extracted from such an analytical expression.

In order to investigate the potential applications of high-spectral-resolution remote sensing data in the red-edge region for assessment of heavy metal contamination in river floodplains, a study was conducted using a field spectroradiometer. The main objective of this study was to investigate whether the rededge of vegetation spectra could provide information on variation in soil contamination by heavy metals. In addition, it was studied which method for determining the REP was most suitable.

# 2. Methodology for determining the red-edge position (REP)

The inflection point is defined as the maximum slope (maximum first derivative) of the reflectance spectrum in the red-edge region. Derivative spectra may be

calculated using:

$$\left(\frac{\mathrm{d}R}{\mathrm{d}\lambda}\right)_{\lambda} = \frac{R_{\lambda} - R_{(\lambda-1)}}{\Delta\lambda} \tag{1}$$

where  $R_{\lambda} - R_{(\lambda-1)}$  is the difference in reflectance measured across a single wavelength increment centred at  $\lambda$ , and  $\Delta \lambda$  is the wavelength increment.

Accurate determination of the REP requires a large number of spectral measurements in narrow bands. However, the calculated REP will depend on the spectral sampling interval applied and the REP will always be one of the wavelengths or the midvalue of the sampling interval employed by the remote sensing sensor used (thus depending on definition:  $\lambda$ ,  $(\lambda-1)$  or  $(\lambda+(\lambda-1))/2$ ). To overcome this dependency on the sampling interval high-order curve fitting techniques have been employed to fit a continuous function to the derivative spectrum (Horler *et al.* 1983, Demetriades-Shah and Steven 1988, Demetriades-Shah *et al.* 1990). However, existing curve fitting techniques are very complex. Dawson and Curran (1998) presented a technique based upon a three-point Lagrangian interpolation technique for locating the REP in spectra that have been sampled coarsely. This same technique may be used for interpolating the REP between fine spectral samples yielding more accurate REP estimates within the spectral sampling interval. It fits a second-order polynomial curve to three spectral bands, from which the REP is determined.

Although an increasing number of airborne and space borne imaging spectrometers have become available, their spectral resolution is not fine enough for an accurate determination of the REP using derivative spectra. Therefore, fitting a mathematical function to a few measurements in the red-edge region is often applied to estimate the REP. The above-mentioned Lagrangian technique of Dawson and Curran (1998) is an example. Recently, Dawson (2000) observed an artefact when using the Lagrangian technique on a reduced number of spectral bands. The REP was more sensitive to spectral variation when it was derived from a combination of reduced band positions than when calculated from continuous spectra. Clevers *et al.* (2002) also observed a discontinuity in the REP, when plotted as a function of the chlorophyll concentration, using this technique. In this paper, this technique will only be used for the fine spectral resolution data; that is to refine equation (1).

Clevers and Büker (1991) fitted a simple third-order polynomial function to the red-edge spectrum:

$$R(\lambda) = c_0 + c_1\lambda + c_2\lambda^2 + c_3\lambda^3 \tag{2}$$

The REP can then simply be calculated by determining the maximum first derivative of this function. A major disadvantage of a third-order polynomial is its symmetry around the REP by definition.

Broge and Leblanc (2000) applied a sixth-order polynomial to derive the REP:

$$R(\lambda) = c_0 + c_1 \lambda + c_2 \lambda^2 + c_3 \lambda^3 + c_4 \lambda^4 + c_5 \lambda^5 + c_6 \lambda^6$$
(3)

In this way, they captured potential asymmetry of the red-edge. The REP was determined from the maximum first derivative in the 690–740 nm range.

Hare et al. (1984) described a so-called inverted Gaussian fit to the red-infrared

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slope, thus smoothing the reflectance spectrum:

$$R(\lambda) = R_s - (R_s - R_o) \exp\left(\frac{-(\lambda_o - \lambda)^2}{2\sigma^2}\right)$$
(4)

where  $R_s$  is the maximum or 'shoulder' spectral reflectance at the NIR plateau,  $R_o$  is the minimum reflectance at the chlorophyll absorption well,  $\lambda_o$  is the wavelength at the reflectance minimum and  $\sigma$  is the Gaussian shape parameter. The REP can be calculated as:

$$\mathbf{REP} = \lambda_o + \sigma \tag{5}$$

Several authors (Bonham-Carter 1988, Demarez and Gastellu-Etchegorry 2000, Lucas *et al.* 2000, Patel *et al.* 2001) have used this approach.

Guyot and Baret (1988) applied a simple linear model to the red-infrared slope. This method assumed that the reflectance curve at the red-edge can be simplified to a straight line between 700 and 740 nm. The reflectance of the REP was then estimated as being halfway the reflectance in the NIR at about 780 nm and the reflectance minimum of the chlorophyll absorption feature at about 670 nm. Subsequently, the REP was estimated by linearly interpolating between measurements at 700 and 740 nm, following:

$$\operatorname{REP} = 700 + 40 \left( \frac{\{(R_{670} + R_{780})/2 - R_{700}\}}{R_{740} - R_{700}} \right)$$
(6)

where  $R_{670}$ ,  $R_{700}$ ,  $R_{740}$  and  $R_{780}$  are the reflectance values at 670, 700, 740 and 780 nm wavelength, respectively, and the constants 700 and 40 result from interpolation in the 700–740 nm interval.

Finally, Baret *et al.* (1992) proposed an *a priori* polynomial equation, based on only three spectral bands, as an estimate of the inflection point. They used model simulations to select optimal spectral bands at 672  $(r_1)$ , 710  $(r_2)$  and 780  $(r_3)$  nm, and subsequently to fit a polynomial equation to the maximum second derivative, resulting in:

$$REP = c_0 + c_1r_1 + c_2r_2 + c_3r_3 + c_4r_1^2 + c_5r_2^2 + c_6r_3^2 + c_7r_1r_2 + c_8r_1r_3 + c_9r_2r_3 + c_{10}r_1r_2r_3$$
(7)

# 3. Material and methods

### 3.1. Test site and field sampling

The test site for the case study was located in the Afferdensche and Deestsche Waarden floodplain along the river Waal, the main branch of the river Rhine in the Netherlands (figure 1). This floodplain has an area of 250 ha, where ecological rehabilitation is being applied by transforming farmland into wetlands. During the past decades, large amounts of contaminated sediment have been deposited in the floodplain because of winter floods. Studies on soil quality in the floodplain have revealed great spatial variability of soil metal concentrations (Kooistra *et al.* 2001). At the scale of the study site, vegetation composition and coverage are relatively homogeneous and characterized by grasslands with patches of herbaceous vegetation.

For the current study, nine transects of 50 m each were located in areas with grassland (figure 1). Most transects were located in areas with heavy metal contamination, as known from previous studies (Kooistra *et al.* 2001). Three

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Figure 1. Location of the study site and of the transects sampled within the Afferdensche en Deestsche Waarden floodplain along the river Rhine in the Netherlands.

transects (No.6, 7 and 8) were positioned in an area that has recently been excavated and had very low vegetation cover.

Six equidistant soil samples were collected along each transect, so they were 10 m apart. Within the field-of-view (FOV) of the spectroradiometer (§3.3) three scoops from the soil top 10 cm were taken (yielding between 500 and 1000 g soil), homogenized, stored in a plastic bag and taken to the laboratory for chemical analysis. In addition, a qualitative description of the vegetation for every sampling point was made. No vegetation biophysical measurements (such as biomass, LAI and chlorophyll concentration) were performed in the field. All the fieldwork took place within three days at the beginning of August 2001.

### 3.2. Chemical analysis

In addition to the Cd, Cu, Ni, Pb and Zn concentrations, moisture content and organic matter content of the soil samples was measured. Moisture content was determined by oven-drying the soil samples at  $105^{\circ}$ C for 24 hours and measuring the weight loss. The organic matter content was obtained by loss-on-ignition (Houba *et al.* 1989). The total metal concentrations were determined by drying approximately 20 g of field-moist soil material at  $105^{\circ}$ C for 24 hours, grinding the dried soil material in a mortar and removing particles larger than 2 mm by sieving. Dried soil samples (1 g) were treated with a HNO<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> solution using the microwave digestion method. After mineralisation, total metal concentrations were measured by means of ICP-AES spectrometry (Kooistra *et al.* 2001).

### 3.3. Field reflectance measurements

For all sample points described in §3.1, detailed spectral measurements were collected at the beginning of August 2001. An Analytical Spectral Devices (ASD) FieldSpec FR spectroradiometer was used to measure vegetation reflectance spectra within 2 hours of local solar noon. The radiometer had a  $25^{\circ}$  FOV and a 1 nm spectral resolution within the 400 to 2500 nm spectral range. The fibre optics of the spectroradiometer was mounted on a tripod looking from nadir at a height of 1 m above the target. This resulted in a measurement area of  $0.15 \text{ m}^2$ . Every measurement was recorded as the average of 15 readings. Every target measurement was preceded by a reference measurement over a standardized white spectralon panel. By dividing the measured target radiance spectrum by that of the spectralon panel, the reflectance spectrum was obtained.

# 4. Results and discussion

Eighteen measurement points were classified in the field as being homogeneous grasslands with annual bluegrass (*Poa annua* L.) and perennial ryegrass (*Lolium perenne* L.) as dominant species. Table 1 shows that the metal concentrations were strongly correlated with each other, and in most cases also with soil moisture and organic matter. Most results will be illustrated for Pb, but similar results were obtained for all heavy metals in this study.

#### 4.1. Spectral signatures

Figure 2 illustrates the spectral signature of a vegetation sample with a low to medium contamination level (about 200 mg Pb per kg dry matter) and a vegetation sample with a high contamination level (about 400 mg Pb per kg dry matter). It is striking that the sample with the high contamination level showed a higher NIR reflectance than the sample with the lower contamination level. In the field, the sample with the high contamination level showed tall grass vegetation with a high biomass level. From table 1 we may conclude that the samples with the higher contamination level also had higher soil moisture and organic matter contents. From this we may conclude that soils with a high organic matter and moisture content were favourable for growth of the grass, and at the same time favoured fixation of heavy metals in the soil. In this data set no negative influence of heavy metal concentration on biomass of grasslands was observed. Figure 3 shows the positive relationship between Pb concentration and NIR reflectance for the grassland samples. This, however, may not be a causal relationship, but an effect of other soil properties (like moisture and organic matter).

	Ni	Cd	Cu	Zn	Pb	OM	moisture
Ni	1						
Cd	0.781**	1					
Cu	0.895**	0.944**	1				
Zn	0.800**	0.863**	0.913**	1			
Pb	0.812**	0.955**	0.978**	0.916**	1		
ОМ	0.895**	0.803**	0.832**	0.679**	0.779**	1	
moisture	0.814**	0.501*	0.590**	0.429	0.499*	0.850**	1

Table 1. Correlation coefficients between the metal concentrations, soil moisture content and organic matter content (OM) for the grassland samples within the study area (n=18).

\*p<0.05, \*\*p<0.01

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Figure 2. Example of a spectral signature measured over a grassland area with a high heavy metal contamination level and one with a low to medium heavy metal contamination level.

Figure 2 also shows a lower red reflectance for the grassland sample with the medium contamination level. This sample clearly showed a lower biomass level from field observation. We would expect the grassland with the lower biomass level to have a higher red reflectance (Lillesand and Kiefer 2000). It appeared to be that the sample with the higher biomass level (higher NIR reflectance) and the high metal contamination level had a higher red reflectance. Metals may have a negative



Figure 3. Relationship between Pb concentration and NIR reflectance (at 780 nm) for the grassland samples within the study area.

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effect on the chlorophyll concentration, and thus have caused a higher red reflectance. This would be consistent with the commonly reported effect that heavy metal treated plants contain lower chlorophyll concentrations than healthy plants (Horler *et al.* 1980, 1983). As stated before, no chlorophyll concentrations were measured in this case study, so the effect of heavy metals on chlorophyll could not be proven.

#### 4.2. Derivative spectra

In the previous subsection we found a positive relationship between the heavy metal concentration and the NIR reflectance. Although a high NIR reflectance often coincides with a low red reflectance, we found sample points with a relatively high red reflectance and a high contamination level. This suggested the existence of an effect of heavy metal contamination on chlorophyll concentration, as was also found by Horler *et al.* (1980, 1983). The two opposite effects of high biomass and low chlorophyll concentration on the red reflectance yielded no clear relationship between metal concentration and red reflectance.

Figure 4 illustrates the derivative spectra for the signatures shown in figure 2. This figure shows a rapid increase of the first derivative towards about 700 nm. Then the slope of the first derivative decreased and subsequently it again increased towards 720 nm. Spectra with low vegetation cover showed a maximum around 700 nm. The two spectra in figure 2 showed a double peak around 720 nm. The derivative spectrum with the higher derivative values matched the spectral signature with the steeper slope in the red-edge region. This was the grassland sample with the high biomass level (and the high contamination level). Although one would expect a higher REP value for this sample in comparison to the sample with the lower biomass level (medium contamination level), the reverse effect was observed. This suggests that the REP of vegetation may be related to the level of heavy metal contamination in the soil.

As stated in §2, other authors have found two peaks (around 705 and 725 nm) in



Figure 4. First derivative spectra of the reflectance spectra illustrated in figure 2.

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the derivative spectra of vegetation (Horler *et al.* 1983, Boochs *et al.* 1990, Miller *et al.* 1990, Filella and Peñuelas 1994, Lamb *et al.* 2002). Boochs *et al.* (1990) used a spectroradiometer with 2 nm bandwidth and observed that the second peak sometimes consisted of two individual peaks. Lamb *et al.* (2002) found one peak between 720 and 730 nm in their experimental data. However, they used a spectroradiometer with a spectral resolution of about 3.5 nm. Filella and Peñuelas (1994) observed only one peak at the position of the second peak, but they used a spectroradiometer with a bandwidth of 8 nm. Miller *et al.* (1990) neither obtained the very fine spectral detail while using a laboratory spectroradiometer with 4 nm bandwidth.

Since we used a spectroradiometer with a spectral resolution of only 1 nm, it was possible to find finer spectral information. Another possibility is that our double peak around 720 nm was caused by measurement inaccuracy. Figure 4 shows a relative minimum in the first derivative spectra between 720 and 721 nm. However, this dip was not found in all grassland spectra. Moreover, this feature had a width of several measurements and this width varied between the different measurements. So, it was not evident that this is a systematic measurement error. Figure 5 shows results after application of a 3 band moving average filter, thus simulating measurements with a spectroradiometer with a spectral resolution of 3 nm. The double peak around 720 nm was less evident, but still present. This 'smoothing' resulted in similar REP results as without smoothing.

# 4.3. Relationship between REP and heavy metal concentrations

Table 2 gives the correlation coefficients between the various methods described in §2 for deriving the REP and the heavy metal concentrations using the 18 grassland samples. In all cases highest correlations were found when using the maximum first derivative for calculating the REP. The Lagrangian technique described in §2 was used for interpolating between the spectral sampling points.



Figure 5. Simulated first derivative spectra for a spectroradiometer with 3 nm spectral resolution (based on the reflectance spectra of figure 2).

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	Ni	Cd	Cu	Zn	Pb
Maximum first derivative	-0.502*	-0.688**	-0.736**	-0.697**	-0.802**
3 <sup>rd</sup> order polynomial	-0.140	-0.225	-0.179	-0.072	-0.206
6 <sup>th</sup> order polynomial	-0.178	-0.228	-0.184	-0.079	-0.203
Inverted Gaussian fit	-0.187	-0.252	-0.212	-0.098	-0.227
Linear interpol. method	-0.152	-0.272	-0.224	-0.112	-0.260
3-point interpol. method	0.105	-0.035	0.050	0.166	0.003

Table 2. Correlation coefficients between the various REP measures and the heavy metal concentrations for the grassland samples within the study area (n=18).

p < 0.05, p < 0.01

Figure 6 illustrates the relationships between the REP using the various calculation methods and the Pb concentration for the grassland samples. The maximum first derivative method showed a significant negative correlation with the Pb concentration (as well as with the other heavy metals, cf. table 2). All other procedures for calculating the REP did not yield significant correlations. They either apply a rigorous smoothing to the spectral measurements or only use a very limited number of spectral measurements (3 or 4). As a result, only the derivative method makes full use of the fine spectral information present in the spectroradiometer data.

#### 5. Conclusions

In this study the maximum first derivative of grassland spectral signatures in the red-edge region yielded a significant, negative correlation with the heavy metal level in the soil of floodplains. High heavy metal concentrations primarily occurred in soils with a high organic matter and soil moisture content. These soils yielded grasslands with a high NIR reflectance (high biomass level). This could not explain the negative correlation between REP and heavy metal concentration for the grassland samples, because an increase in biomass would yield a larger REP. Although no chlorophyll measurements were available for this study, the hypothesis is that the heavy metal contamination in the soil had a negative effect on the chlorophyll concentration of the leaves. This effect was, for instance, also found by Horler *et al.* (1980, 1983). A lower leaf chlorophyll concentration between REP and heavy metal correlation between REP and heavy metal correlation between REP and heavy metal concentration causes a lower REP (Clevers *et al.* 2002). This would explain the negative correlation between REP and heavy metal concentration.

The first derivative spectra of the grassland samples in this study confirmed the presence of more than one peak within the red-edge region. The data showed a peak around 700 nm and another peak between 716 and 722 nm. Many samples even showed two peaks in the latter region. This double peak can only be observed if a very fine spectral resolution (1-3 nm bandwidth) is used. Boochs *et al.* (1990) and Llewellyn *et al.* (2001) also observed these multiple peaks. Most other studies did not use such a high spectral resolution and did not observe more than two peaks in total.

All methods for estimating the REP in this study, except for the maximum first derivative method, did not make full use of the very fine spectral resolution of the used spectroradiometer. They applied either a function (polynomial or Gaussian function), which smoothed the spectral signature in the red-edge region, or they even used only three or four fixed wavelength positions for deriving the REP. As a



Figure 6. Relationship between the REP based on various methods and the Pb concentration for the grassland samples within the study area. (a) the maximum first derivative method, (b) the 3rd order polynomial method, (c) the 6th order polynomial method, (d) the inverted Gaussian method, (e) the linear interpolation method, and (f) the 3-point interpolation method.

Remote Sensing (*gamma*) RES35803.3d 30/1/04 12:37:00 Rev 7.51n/W (Jan 20 2003) The Charlesworth Group, Huddersfield 01484 517077 result, the correlation between these estimated REP values and the heavy metal concentration was not significant.

This study showed that spectral signatures measured with a spectral resolution of 1-3 nm may provide very fine spectral information in the derivative spectra at the red-edge region for detecting metal-induced stress in river floodplains. Multiple peaks occurred in the derivative spectra. The subdivision of the second peak in subpeaks, as observed in this study, requires further investigation.

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