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Spectrometric analyses in comparison to the physiological condition of heavy metal stressed floodplain vegetation in a standardised experiment

Research Article

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Abstract: Floodplain ecosystems are affected by flood dynamics, nutrient supply as well as anthropogenic activities. Heavy metal pollution poses a serious environmental challenge. Pollution transfer from the soil to vegetation is still present at the central location of Elbe River, Germany. The goal of this study was to assess and separate the current heavy metal contamination of the floodplain ecosystem, using spectrometric field and laboratory measurements. A standardized pot experiment with floodplain vegetation in differently contaminated soils provided the basis for the measurements. The dominant plant types of the floodplains are: *Urtica dioica*, *Phalaris arundinacea* and *Alopecurus pratensis*, these were also chemically analysed. Various vegetation indices and methods were used to estimate the red edge position, to normalise the spectral curve of the vegetation and to investigate the potential of different methods for separating plant stress in floodplain vegetation. The main task was to compare spectral bands during phenological phases to find a method to detect heavy metal stress in plants. A multi-level algorithm for the curve parameterisation was developed. Chemo-analytical and ecophysiological parameters of plants were considered in the results and correlated with spectral data. The results of this study show the influence of heavy metals on the spectral characteristics of the focal plants. The developed method (depth CR1730) showed significant relationship between the plants and the contamination.

Keywords: vegetation indices • plant stress • heavy metals • floodplain • spectrometric measurements

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1. Introduction

Floodplain ecosystems are affected by flood dynamics, nutrient supply in addition to anthropogenic activities. Heavy metal pollution poses a serious environmental challenge. Comprehensive studies of the material load of the water, the sediments and the soils in the catchment area of the Elbe already exist [1]. As a result of extreme flooding the impact of pollution has become a topic of significant scientific and public interest. Pollution transfer from the soil into the food chain, through the vegetation is still present in the central region of Elbe River, Germany [2].

A number of studies have concluded that vegetation changes its spectral reflectance by geochemical stress [3–7]. Within the range of green reflectance at 550 nm or the range of chlorophyll absorption near 670 nm physiological disturbances modify the spectral behavior. Similarly, the spectral increase between 670 nm and 750 nm as well as the position of the red edge showed up variations by geochemical stress. These shifts were minor both within longer and shorter wavelengths [3, 8]. The results of investigations into the effects in heavy metal-loaded plants differed depending on the region, plant type and method used [9, 10]. However, no standard method for detection of heavy metal stress in plant was developed, because many environmental parameters interact and complicate the detection of the stress factors. Few studies of spectral analysis of heavy metal-affected plants took place in floodplain ecosystems [7, 11].

The goal of this study was to assess and separate the current heavy metal contamination of the floodplain ecosystem using spectrometric field and laboratory measurements. The toxicological effects of the soils were indirectly derived from the spectral characteristics of the floodplain vegetation [12]. Algorithms for parameterization and/or separation from stress characteristics of the floodplain vegetation were developed. Using different vegetation indices and methods it was possible to determine the red edge position. The spectral curves of the vegetation were normalized, in order to examine the potential of the methods for the detection of heavy metal stress. On the one hand plant physiological properties were estimated by determination of the chlorophyll and heavy metal content, on the other hand indicators for the soil quality were parameterized.

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2. Measurements and methods

2.1. Pot experiment

A standardized pot experiment with floodplain vegetation in differently contaminated soils provided the basis for the measurements (Figure 1). Soil material from the three morphologic units of the floodplain was used and set in 10-litre pots. Stinging nettle (*Urtica dioica*), Reed canarygrass (*Phalaris arundinacea*) and Meadow foxtail (*Alopecurus pratensis*) were selected as the dominant plant types of the floodplains in this region. These were then planted in the pots. In total 27 pots were used (3 species $\times$3 replicates $\times$3 soil types). Standardised irrigation and nutrient supply were used to control for other natural factors that might influence the results, this allowed us to determine the correlations between the spectral behavior and the heavy metal contamination of the focal plants. The heavy metal contamination of soil type A (lower terrace) was 56 mg kg^{-1} of Arsenic, 7 mg kg^{-1} of cadmium and 152 mg kg^{-1} of lead. Soil type B (plateau) contained 28 mg kg^{-1} of Arsenic, 1 mg kg^{-1} of cadmium and 60 mg kg—1 of lead, while soil type C (depression) was 48 mg kg^{-1} of Arsenic, 4 mg kg^{-1} of cadmium and 187 mg kg^{-1} of lead.

Figure 1. Pot experiment at the test station of the Helmholtz-Centre for Environmental Research.

Spectral sampling was taken using the FieldSpec Pro FR from ASD® between April and September 2008. Toxicological effects of the soil were indirectly investigated by the spectral responses of the plants. Plant physiological parameters, such as chlorophyll content (Minolta SPAD-502) and chemical parameters such as heavy metals were also measured.
For the sequential extraction of mobile, plant-available

heavy metals ammonium nitrate was calculated (DIN standard 19730). The analyses determined the contents of cadmium, chromium, copper, manganese, nickel, lead, iron and zinc. The aqua regia dissolution determines the heavy metal total contamination of the soil (DIN standard 11466). The inductively coupled plasma mass spectrometry and an inductively coupled plasma optical emission spectrometry were used for the analysis. The use of a pot experiment allowed the underlaying stress factors to be excluded, so that only heavy metals could explain the variation between the plants.

2.2. Spectral measurements

Field and laboratory spectrometric measurements were accomplished via an ASD FieldSpec Pro FR. Different development stages and influences in the spectral signal could be found. The investigation discovered that heavy metal stress could be detected and parameterized during the season. Altogether approx. 400 spectra were measured, distributed in seven terms. At the beginning of each measurement an alignment with a reference standard (Spectralon) took place. All data measurements of the spectral reflectance of a surface were measured relative to the reference surface (relative measurements). The laboratory measurements served as a comparison for the validation of the field surveys. The spectrometer laboratory of the Institute for Geosciences is a photographic darkroom with a pre-installed lighting source.

2.3. Methods

2.3.1. Stress parameterization stage 1

In the investigation different forms of the standardisation for spectral curves were used, vegetation indices in the first stage of the stress parameterization. Relevant subranges of the spectrum were also examined. These vegetation indices described different object characteristics such as vitality, biomass, content of chlorophyll, water, lignin, cellulose and protein [9, 12–14]. This stage of the analysis showed the degree of change of the reflectance signal. The parameter water (e.g. dryness) as well as the vitality of the plants (biomass, content chlorophyll, chlorophyll/carotinoid ratio, xanthophyll cycle, light use efficiency, senescence) were examined. The stress analysis demonstrated sensitive ranges of the spectrum. The plant components such as nitrogen, lignin and cellulose were determined via other vegetation indices. Variations in the spectral signal uncovered the content of the parameters and represented stress reactions. The reflectance range from the red to the infrared was examined, and could prove to be an indicator for plant stress. In particular, the main turning point , the red edge position (REP), the maximum upward gradient within this range, showed shifts caused by exogenous effects [3, 15]. The REP is determined by the first derivative of the function curve. Important characteristics of a signature curve are their position, depth, expansion (FWHM), form, local minima and maxima as well as the main turning points. By standardization procedures like the continuum transformation the measured values were converted into a uniform scale level, so that a comparison of the spectral curves was possible [16]. The division of the continuum ranges refers to the spectral sections, in which local minima are present and conclusions on plant components are possible. The section of the continuum curve for 970 nm and 1730 nm was examined. Figure 2 shows the methods used in the first stage.

2.3.2. Stress parameterization stage 2

In the second stress parameterising stage the results of the method were evaluated using the coefficient of variation. The entire measuring time as well as the different contamination degrees of the soil was selected as the data range. The coefficient of variation (C_v) was defined as the relative standard deviation, i.e. the standard deviation divided by the mean. Using the coefficient of variation the sensitivity of the methods could be described and pre-selected for the stress parameterising (sensitivity test). Afterwards the methods were compared with the plant parameters such as chlorophyll content and heavy metal content. A high sensitivity and correlation gave the methods for heavy metal stress detection.

3. Results and discussion

By the coefficient of variation of the methods water indices could be identified to be non-sensitive while the pigment and foliar chemistry indices (Table 3) and the derivation of the curve (REP) were more sensitive for spectral variations. The water indices (DSWI, MSI, WBI) could be determined indirectly via the leaf water content in the standardised pot experiment. Only small differences (Cv Ø 5%) were found in the index values, in the range of the sensitive wavelengths (water bands) for the phenological period from April to August. Therefore, water could be excluded as a stress factor. The pigment indices (NPCI, LCI, PRI, NDVI, NPQI, SIPI) showed larger variations during the period (Cv Ø 35%). In the stress parameterization the cell structural changes were examined. The results showed high variations in the reflectance signal, especially with the PSRI and CAI with a Cv of 115.88% and 46.16%. In the case of the PSRI the high standard

Table 1. The used methods of the investigation.

Methode	Abbreviation	Parameter
	Pigment Indices	
Normalized Phaeophytinization *Index*	NPQI	Chlorophyll
Normalized Difference Vegetation Index	NDVI	Vitality, biomass
Leaf Chlorophyll Index	LCI	Chlorophyll
Photochemical Reflectance Index	PRI	Light use efficiency
Structure Insensitive Pigment Index	SIPI	Ratio carotinoids/chlorophyll
Normalized Pigment Chlorophyll Index	NPCI	Ratio total pigment/chlorophyll
	Foliar Chemistry Indices	
Normalized Difference Nitrogen Index	NDNI	Nitrogen
Plant Senescence Reflectance Index	PSRI	Ratio carotinoids/chlorophyll
Cellulose Absorption Index	CAI	Cellulose
Normalized Difference Lignin Index	NDLI	Lignin
	Water Indices	
Water Band Index	WBI	Water
Moisture Stress Index	MSI	Water
Disease Water Stress Index	DWSI	Water
	Other Methods	
Red Edge Position (first derivation)	REP	Red edge position
Continuum removal analysis at 970 nm	CR970	Water
Continuum removal analysis at 1730 nm	CR1730	Lignin, protein

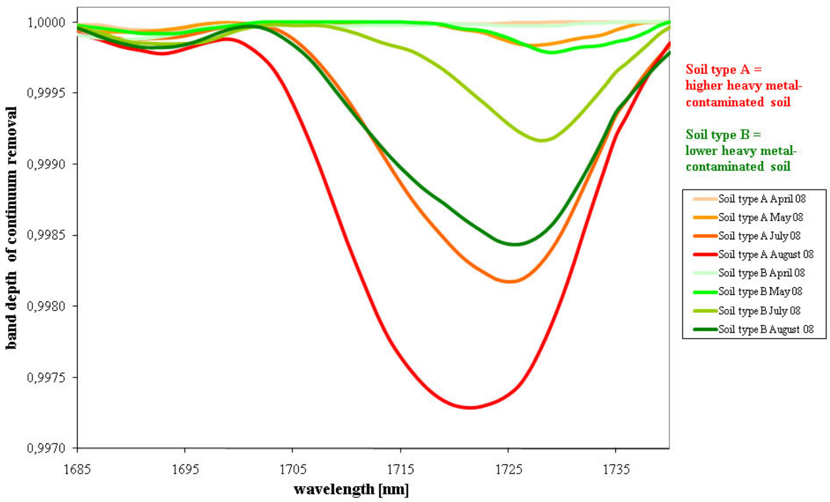

Figure 2. Variations of the depth of the continuum removal near 1730 nm between different contaminated soils.

deviation originated from the change from the negative to the positive range around 0. On the other hand NDNI (nitrogen content) and NDLI (lignin content) reported small changes. The sensitive range of the red light and near infrared (Red-Edge) was not included in this comparison, because it concerns another physical unit/dimension. The deviations from the average value 711 are 11 nm, which are described in the literature as a high change [15]. With the help of the continuum removal analysis the depth and position of the bands were determined. Here the range of the bands showed a high change of the depth (Cv % 129.86) in the measuring time by 1730 nm. Conversely,

Table 2. Coefficient of variation of the methods.

Index	Coefficient of variation	Index	Coefficient of variation	Index	Coefficient of variation
CR1730	128.86	NPQI	32.08	NDVI	6.72
PSRI	115.88	CR970	25.06	NDLI	6.58
NPCI	85.61	LCI	21.73	DSWI	5.20
PRI	58.50	MSI	7.54	SIPI	4.50
CAI	46.16	NDNI	7.11	WBI	1.06

the CR range of the small water bands had negligible differences with a Cv 25.06% around 970 nm and thus the plants showed small fluctuations in the leaf water content. The usability of the methods was also tested by the coefficient of determination between the chlorophyll (Table 3) and the heavy metal content which was in high accordance with the sensitivity results. The methods were compared with the analytic investigations. These correlations offer the possibility of examining the quality of the methods. High correlations could be determined between the physiological condition and the spectral characteristics (NPCI, LCI, CR1730, PRI, REP). Figure 3 shows the relationship between the depth at CR 1730 Nm and the relative chlorophyll content (SPAD). The depth of the CR1730 is low with high content of chlorophyll and rises potentially with the reduction of the analysis values. Likewise the REP shifted to higher wavelengths in the beginning of June, parallel to this the chlorophyll values of the plants became lower. The water indices didn't show significant correlations. Initial investigations with samples from the heavy metal analyses showed dependence to the high-significantly tested methods NPCI and the depth of the CR1730. By removing chlorophyll content the heavy metal stress factor was the singular explanation for the spectral changes in the pot experiment.

Table 3. Coefficient of determination of the methods.

Index	Coefficient of determination	Index	Coefficient of determination	Index	Coefficient of determination
NPCI	0.91	CAI	0.52	SIPI	0.28
REP	0.80	NDVI	0.44	NPQI	0.24
PRI	0.75	CR970	0.35	WBI	0.20
CR1730	0.74	MSI	0.32	DSWI	0.09
LCI	0.71	PSRI	0.29	NDLI	0.02

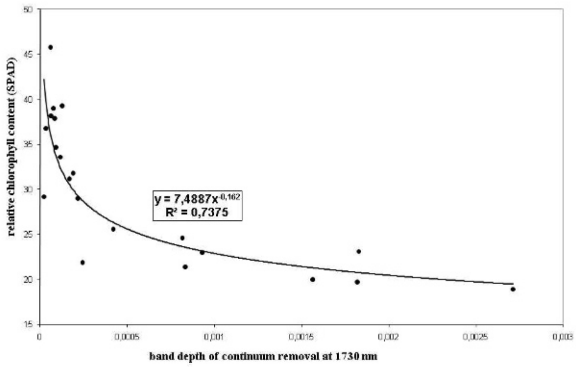

Figure 3. Coefficient of determination (exponential) (R^2 = 0.74) between depth of CR1730 and the relative chlorophyll content (SPAD).

4. Conclusion

The results have shown the usability of different sensitivity methods. The standardized experimental set up showed that heavy metal stress in plants can be separated from water and nutrient stress. The NPCI, PRI, REP and CR1730 proved to be sensitive for heavy metal stress. These methods were also highly correlated to stress-related physiological parameters. The band depth of continuum removal in the part of spectrum near 1730 nm was determined as a potential indicator for heavy metal stress detection. The reason for the correlation could be the lignin or protein production in the plant metabolism influenced by stress [17]. Further investigations are needed to explain the relationship between plant physiological and spectral interactions.

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