SPECTROMETRIC ANALYSES IN COMPARISON TO THE PHYSIOLOGICAL CONDITION OF HEAVY METAL STRESSED FLOODPLAIN VEGETATION IN A STANDARDISED EXPERIMENT

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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. The pollution transfer from the soil over the vegetation into the food chain is still very 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 like Urtica dioica, Phalaris arundinacea and Alopecurus pratensis were also chemically analysed. Different vegetation indices and methods for estimating red edge position were employed to normalise the spectral curve of the vegetation and to investigate the potential 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 into the results and correlated with spectral data. The results of this study show the influence of heavy metals causing changes in the spectral characteristics of the plants. The developed method (Depth CR1730) showed significant relations to heavy metal contamination of the plants.

1. MOTIVATION AND OBJEKTIVS

Floodplain ecosystems are affected by flood dynamics, nutrient supply as well as anthropogenic activities. Especially heavy metal pollution poses a serious environmental challenge. Comprehensive investigations exist for the material load of the water, the sediments and the soils in the catchment area of the Elbe (Friese et al., 2000). By the extreme floods the topic pollution impact has moved into the scientific and public interest. The pollution transfer from the soil through the vegetation into the food chain is still present at the central region 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. The toxicological effects of the soils were indirectly derived from the spectral characteristics of the floodplain vegetation (Kumar, 2001). Algorithms for parameterization and/or separation from stress characteristics of the floodplain vegetation were developed. By different vegetation indices and methods it was possible to determine the red edge position. The spectral curves of 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 by determination of the chlorophyll and heavy metal content on the other hand indicators for the soil quality could be parameterized.

2. MEASUREMENTS AND METHODS

2.1 Pot experiment

standardized experiment with А pot vegetation floodplain in differently contaminated soils provided the basis for the dioica. measurements (Fig. 1). Urtica **Phalaris** arundinacea and Alopecurus pratensis were selected as dominant plant types of the floodplains. Spectral sampling was taken with FieldSpec Pro FR from ASD[®]. Toxicological effects of the soil were indirectly investigated by the spectral responses of the plants. Plant physiological parameters like chlorophyll content (Minolta SPAD-502) and other chemical parameters (heavy metals) were also measured. By the pot experiment the overlaying of stress factors was excluded, so that only heavy metals could be the factor of the variation between the plants.



Figure 1. Pot experiment in the test station of the Helmholtz-Centre for Environmental Research Leipzig-Halle

2.2 Spectral measurements

Within the growing season of 2008 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 pointed out that heavy metal stress could be detected and be 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 as measurement of the spectral reflection of a surface were accomplished to the reference surface (relative measurements). The laboratory measurements served for to the comparison and 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 spectrum examined. the were These vegetation indices described different object characteristics such as vitality, biomass, content of chlorophyll, water, lignin, cellulose and protein (Götze et al., 2007, Kumar et al., 2001). This stage of the analysis showed the degree of change of the reflection 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 examines. The stress analyzes 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 pointed out the content of the parameters and represented stress reactions in such a way. The reflection 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 (red edge position, REP), the maximum upward gradient within this range showed shifts caused by exogenous effects (Horler et al., 1983, Pinar & Curran, 1996). 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 ensured (Erasmi, 2002). The division of the continuum ranges refers to the spectrum sections, in which local minima are there and conclusions on plant components are possible. The part of the continuum curve for 970 nm and 1730 nm was examined. The Fig: 2 shows the used methods of the first stage.

2.3.2 Stress parameterization stage 2

In the second stress parameterizing stage the results of the method were evaluated by means of the coefficient of variation. The entire measuring times as well as the different contamination degrees of the soil were selected as data range. The coefficient of variation (Cv) was defined as the relative standard deviation, i.e. the standard deviation was divided by the average value. Hereby the sensitivity of the methods could be described and pre-selected for the stress parameterizing (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. Pigment Indices Normalized Difference Vegetation Index (NDVI) Leaf Chlorophyll Index (LCI) Photochemical Reflectance Index (PRI) Structure Insensitive Pigment Index (SIPI) Normalized Phaeophytinization Index (NPQI) Normalized Pigment Chlorophyll Index (NPCI) Foliar Chemistry Indices Normalized Difference Nitrogen Index (NDNI) Normalized Difference Lignin Index (NDLI)

Cellulose Absorption Index (CAI)

Plant Senescence Reflectance Index (PSRI)

Water Indices

Water Band Index (WBI)

Moisture Stress Index (MSI)

Disease Water Stress Index (DWSI)

Other Methods

Red Edge Position (REP first derivation)

Continuum removal analysis at 970 nm (CR970)

Continuum removal analysis at 1730 nm (CR1730)

Figure 2. The used methods of the investigation

3. RESULTS

By the coefficient of variation of the methods water indices could be identified to be nonsensitive while the pigment and foliar chemistry indices (Tab. 3) as well as 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 \emptyset 5%) of the index values showed up in the phenological period from April to August in the range of the sensitive wavelengths (water bands). Therefore water could be excluded as stress factor. The pigment indices (NPCI, LCI, PRI, NDVI, NPQI, SIPI) showed larger variations during the period (Cv Ø 35%).

Index	Coefficient of variation	Index	Coefficient of variation	Index	Coefficient of variation
CR1730	129,86	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

Table 3. Coefficient of variation of the methods

In the parameterization stress the cellstructural changes were examined. The showed high variations in results the reflection signal, in particular with the PSRI and CAI with a Cv of 115,88 % and 46,16 %. In the case of the PSRI the high standard 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 into this comparison, since it concerns another physical unit/dimension. The deviations from the average value 711 are 11 nm, which are described as a high change in the literature (Pinar & Curran, 1996). 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 (Fig. 4). On the other hand the CR range of the small water bands had negligible differences with a Cv 25,06 % around 970 nm and to 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 (Tab. 5) 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 methods on their quality.



Figure 4. Variations of the depth of the continuum removal near 1730 nm between different contaminated soils

Index	R ²	Index	R ²	Index	R ²
NPCI	0,91	CAI	0,52	SIPI	0,28
REP (Abl.)	0,80	NDVI	0,44	NPQI	0,24
PRI	0,75	CR970 Depth	0,35	WBI	0,20
CR1730 Depth	0,74	MSI	0,32	DSWI	0,09
LCI	0,71	PSRI	0,29	NDLI	0,02

Table 5. Coefficient of determination of the methods

High correlations could be determined between the physiological condition and the spectral characteristics (NPCI, LCI, CR1730, PRI, REP). Fig. 6 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. First investigations with samples from the heavy metal analyses showed dependence to the high-significantly tested methods NPCI and the depth of the CR1730. By the removing chlorophyll content the stress factor heavy metal was the reason for the spectral changes in the pot experiment.



Figure 6. Coefficient of determination between depth of CR1730 and the relative chlorophyll content (SPAD)

4. CONCLUSIONS AND OUTLOOK

The results have shown different sensitivity methods. The heavy metal stress in plants of the standardized experiment could be separated from water and nutrient stress. The NPCI, PRI, REP and CR1730 proved to be sensitive for heavy metal stress. These methods have also a high correlation to stressrelated 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 synthesis influenced by stress but further investigations are required.

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