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Characterization of Archaeological Soils and Sediments Using VIS Spectroscopy

Geoarchaeology; soil science; soil colour; VIS-spectra; geochemistry.

Introduction

Ancient topsoil horizons have rarely been preserved in situ, but prehistoric pits filled with former topsoil material are common features at most archaeological excavation sites. One attribute of these features is routinely evaluated: differences in soil colour are used to estimate the age of the archaeological context. In the Lower Rhine Basin (NW-Germany) a dark-brownish pit filling would date to the Neolithic period, a grey-brownish filling to the Iron Age and a light-grey filling would be considered Roman.[1] For archaeological research, these changes in soil colour are of enormous importance because often the absence of artefacts or other dateable material does not allow the use of any other dating method. Examples are the prehistoric settlements Langweiler 2, 8 and 9 in the Lower Rhine Basin, where 21–43% of all pits in the settlement areas did not contain any artefacts. Their classification as Neolithic was based exclusively on the colour of the pit fillings.[2]

A standardized method to describe the soil colour would be the use of Munsell Soil Colour Charts, as it is common practice in Soil Science.[3] However, the description of soil colour with Munsell Soil Colour Charts is an estimation that limits its use for archaeological dating and quantitative modelling. The disadvantages are that not every possible colour is found in the charts and that different light exposures lead to shifts in the perception of colours. An objective and fast method to determine colour is spectrophotometry, i.e. the measurement of the wavelength of light reflected by a sample in the visible range (VIS). Correlations between soil colour and chemical properties can be measured, since spectrophotometers produce numerical values that make statistical analyses possible.[4] The multivariate statistical tools for calibrating spectrometric information against soil properties have recently been developed and applied, mainly for near- and mid-infrared spectroscopy. These methods allow the characterization of a large number of soil variables without elaborate sample preparation.[5]

The colour of soil material is the result of soil-forming processes and related to soil characteristics,[6] and thus an indicator for soil attributes of material preserved in past times. Soil compounds that are typically found in settlement pit fillings and that are an indicator for human activities are, for example, an increased amount of organic matter or charcoal. Schulze et al.[7] described the correlation between colour lightness and organic matter concentration in soils with comparable texture and on similar parent material.

1 Kuper 1979; Lüning 1998; Krahn 2006.
2 Boelicke 1988.
3 Ad-hoc-AG Boden 2005.
4 Barrett 2002; Viscarra Rossel et al. 2006a.
5 Janik, Merry, and Skjemstad 1998; Viscarra Rossel et al. 2006b.
6 Bigham and Ciolkosz 1993.
7 Schulze et al. 1993.

Charred organic matter could be the colouring agent in black soils. Spielvogel et al.[8] found a significant correlation between luminance values and concentrations of aromatic carbon compounds in soils. The measurement of soil colour and charred organic matter concentration before and after an experimental burning revealed the correlation between biomass burning and darkening of soil colour.[9] The red-brown colouring of a soil depends on type, composition and amount of iron oxides which cover a specific spectrum of colours. Scheinost and Schwertmann[10] were able to determine the different types of iron oxides in soil samples via spectrophotometry.

Human influence on soil formation is mainly driven by the addition or subtraction of specific soil compounds. Wet-chemical methods are used to detect those variations in soil composition, e.g. the BPCA molecular marker method to detect charcoal carbon in soils,[11] but the analyses can be expensive or time-consuming. Spectroscopic methods estimate soil characteristics of large numbers of samples from a smaller set of samples which is used for calibration. We tested the measurement of soil colour spectra, or VIS spectra, as a novel and rapid analytical tool in geoarchaeological research in two regions and on at least two excavation sites per region. To the best of our knowledge, the reasons for the soil colour changes in pit fillings over time have not been investigated and explained yet.

Material and Methods

In order to calibrate the method, we used two calibration sets which allowed us to test a large set of samples with known properties: (i) a range of topsoil material (87 samples) from loess-derived soils which have been measured on black carbon,[12] and (ii) a range of paleosoil sequences (198 samples) from the Balearic islands with known $CaCO_3$ and Fe contents.[13]

Archaeological soil samples were taken from excavation sites in two regions which are characterized by soils developing from loess: (i) NW-Germany, between the cities of Aachen, Cologne and Bonn, where Luvisols dominate (Paffendorf and Arnoldsweiler sites, 96 samples), and (ii) Central Germany (Saxony-Anhalt, Colbitz, Köthen and Kleinpaschleben sites, 313 samples) where chernozem-like soils are present. Hydromorphic soils that are characterized by oxidation and reduction were not investigated. We sampled pit fillings from Early Neolithic to Roman Age, or Iron Age, respectively, that represent former top soil material. Chronological information is not available for many samples yet, because archaeological documentation and interpretation of the excavated features is still ongoing.

Soil colour was measured using a spectrophotometer in the laboratory for dried, homogenised but not milled soil samples in triplicates (Konica Minolta CM-5) and in the field in-situ on the surface of a profile or planum (Konica Minolta CM-700d) by detecting the diffused reflected light under standardised observation conditions (2° standard observer, illuminant C). The colour spectra were obtained in the 360 to 740nm range, in 10nm increments. The spectral information was used to build predictive models from the measured VIS spectra of sample sets with known properties (laboratory analysis) based on Partial Least Squares Regression (PLSR) using the software ParLes (v3.1).[14] Predictions were calculated using sub-samples of all measured samples, a prediction set and a test sample set.

8 Spielvogel, Knicker, and Kögel-Knabner 2004.
9 Eckmeier et al. 2007.
10 Scheinost and Schwertmann 1999.
11 Brodowski et al. 2005.
12 Published in Rodionov et al. 2010.
13 Wagner, Günster, and Skowronek 2011 and unpublished data.
14 Viscarra Rossel 2008.

The measured VIS spectra were also converted into Munsell values and L*a*b* values (CIE 1976 Standard Observer) which indicate the extinction of light on a scale from L* 0 (absolute black) to L* 100 (absolute white), from green (-a*) to red (+a*) or from blue (-b*) to yellow (b*). The use of colour indexes allows for soil colour description as it is used, e.g. in sedimentology.[15] Total carbon (C) contents of the soil fine earth were measured using a CN elemental analyzer. Organic C (Corg) was determined by subtraction of anorganic C from total C. Carbonate ($CaCO_3$) content was determined after dissolution with HCl (10%) using a Scheibler unit. The content of black carbon (BC) in fine-earth samples was determined as benzene polycarboxylic acids (BPCA) according to the method described by Brodowski et al.[16]

Results

The two calibration sets showed that VIS spectra could be used to build PLSR models that were able to predict the values that have been measured in the laboratory. For the recent top soils from loess-derived soils, measured organic carbon contents and black carbon contents correlated highly with the predicted values ($R^2 = 0.87$ for Corg and $R^2 = 0.78$ for BC), while the relation of Corg and BC to the luminance (L*) value using an exponential regression model is weaker ($R^2 = 0.36$ for Corg, $R^2 = 0.55$ for BC). For the Balearic paleosoils, the correlation between measured and PLSR-predicted values was also high for $CaCO_3$ ($R^2 = 0.85$) and for total Fe contents that have been corrected for clay content (Fe index $R^2 = 0.81$). Using only the colour indexes, a linear regression between $CaCO_3$ content and L* reached $R^2 = 0.60$ and between chromaticity values a* and Fe index $R^2 = 0.53$, while L* and Corg content did not show any correlation.

First results for the archaeological samples showed a pattern which is less distinct than the calibration sets. Corg concentrations did not effect the brightness of pit fillings ($R^2 = 0.23$ for Corg and L* for the Rhineland) as strongly as the BC concentrations ($R^2 = 0.42$ for BC and L*). Using linear regression models with colour indexes ($R^2 = 0.18$ for Corg and L* for Saxony-Anhalt) resulted in weaker correlations than using the PLS regression ($R^2 = 0.45$). Soil colours are clearly different between the two investigated regions. In between archaeological periods, colours are different, too, although the differences are small. Fig. 1 shows the colours of pit fillings from the sites in the Rhineland (A) and from Saxony-Anhalt (B), respectively. The lightness and the chromaticity of the pit fillings from different periods are different but overlapping. Pit fillings from Neolithic pits in both regions are clearly darker (L* -5.2 from the average of younger pit fillings in Saxony-Anhalt and -2.9 in the Rhineland) and redder (a* +0.5 from the average of younger pit fillings in Saxony-Anhalt and +1.5 in the Rhineland) than samples from younger periods, although the soil development and the recent soil types are different. Since the luminance did not correlate with Corg contents in all archaeological sample sets, other factors seem to have a stronger influence on soil colours, e.g. charcoal content or the presence of iron oxides.

Conclusions

VIS spectra can be used as an analytical tool after the method has been calibrated. The presence of charcoal highly correlated with the lightness of soils, while in the samples with lower concentrations of organic matter and high contents of $CaCO_3$, the presence of iron oxides and carbonates mediated soil colours. For the pit fillings, we found that

15 Debret et al. 2011.
16 Brodowski et al. 2005.

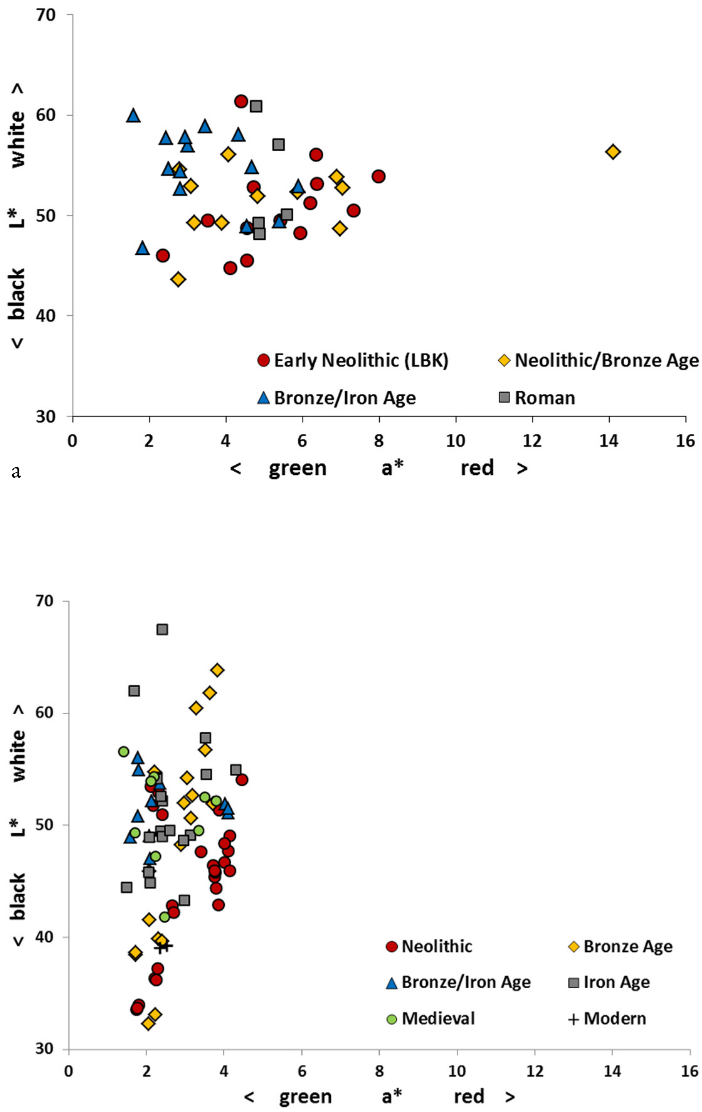

Fig. 1 | Soil colour expressed as luminance (L*) and chromaticity (a*) for archaeologically dated pit fillings sampled at excavations in the Rhineland (a), and Saxony-Anhalt (b).

the amount of charred organic matter influenced soil colour more than total soil organic matter. The differences in soil colour between archaeological periods will be of special interest: did we see pedogenetic features or differences in the original soil material? The tendency of Neolithic samples to have redder soil colours is a new finding which was visible only by using spectrophotometric measurements. Further investigation will include the consideration of iron oxides and additional black carbon measurements for the archaeological sample sets.

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