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НОВЫЕ МЕТОДЫ И РЕЗУЛЬТАТЫ ИССЛЕДОВАНИЙ ЛАНДШАФТОВ В ЕВРОПЕ, ЦЕНТРАЛЬНОЙ АЗИИ И СИБИРИ

Монография в 5 томах

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This monograph shall inform you about up to date methodologies and recent results in landscape research. It is intended as a guide for researchers, teachers, students, decision makers, stakeholders interested in the topic of landscape science and related disciplines. It provides information basis for decision makers at various levels, from local up to international decision bodies, representing the top level of landscape science in a very short form.

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Chapter I/30: DIFFUSE REFLECTANCE INFRARED FOURIER TRANSFORM (DRIFT) SPECTROSCOPY FOR MAPPING ORGANIC MATTER COMPOSITION AT INTACT MACROPORE SURFACES IN STRUCTURED SOILS

Глава I/30: Спектроскопия диффузного отражения инфракрасного преобразования Фурье (DRIFT) для картирования состава органического вещества на неповреждённых макропорных поверхностях в структурированных почвах

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ABSTRACT. The mm-scale distribution of organic matter (OM) at macropore surfaces such as biopore walls and crack coatings can affect preferential flow, transport, and element turnover but is poorly understood and difficult to determine. The diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy in the mid-infrared range offers a possibility to determine the organo-mineral composition and organic carbon (OC) content of soils. We applied DRIFT spectroscopy in a mapping technique to obtain spectral information from intact macropore surfaces at the mm-to-cm scale. In combination with complementary measurement techniques, the spatial distribution of OM functional groups and of the OC content was described and predicted via partial least squares regression. With these techniques, the spatial distributions of OC content and OM and mineral composition in terms of the functional groups can be described at the mm-scale along intact macropore surfaces (i.e., inter-aggregate cracks, worm and root biopores) in structured soils. These macropore-specific distributions should be considered when modeling and interpreting preferential flow, transport, and turnover processes.
RESULTS. Распределение органического вещества (OM) в мм-масштабе на макропорных поверхностях, таких как биопоровые стенки и трещиноватые покрытия, может влиять на предпочтительный поток, транспорт и оборот элементов, но это плохо изучено и трудно определить. Спектроскопия диффузного отражения инфракрасного Фурье-преобразования (DRIFT) в среднем инфракрасном диапазоне позволяет определить органо-минеральный состав и содержание органического углерода (OC) в почвах. Мы применили DRIFT - спектроскопию в методе картографирования для получения спектральной информации с неповрежденных макропорных поверхностей в масштабе от мм до см. В сочетании с дополнительными методами измерения пространственное распределение функциональных групп органического вещества (OM) и содержания органического углерода (OC) было описано и предсказано с помощью частичной регрессии наименьших квадратов. С помощью этих методов пространственные распределения содержания OC, OM и минерального состава в терминах функциональных групп могут быть описаны в мм-масштабе вдоль интактных макропоровых поверхностей (т. е. межагрегатных трещин, биопор червя и корня) в структурированных почвах. Эти макропористые распределения следует учитывать при моделировании и интерпретации процессов преходящего потока, транспорта и оборота.

KEYWORDS: preferential flow, soil organic matter, infrared spectroscopy, clay coatings
Ключевые слова: преференциальный поток, органическое вещество почвы, инфракрасная спектроскопия, покрытия глины

INTRODUCTION
The surfaces of earthworm burrows, root channels, cracks, and soil aggregates form the interface between the porous matrix and the macropores that can act as preferential flow paths [1, 2]. This interface has been identified as a biogeochemical ‘hotspot’ [3] because it provides favorable conditions for an increased turnover of organic matter (OM) by soil microorganisms. Macropore surfaces are often covered with OM, clay, and clay-organic complexes, the latter particularly occurring in the illuvial horizons of Luvisols (Bt-horizons). In structured subsoil horizons, the content of organic carbon (OC) and the composition of OM in coatings and biopore walls can strongly differ from that of the bulk soil [4, 5, 6]. The OM composition and OC content of macropore surfaces may influence preferential flow as well as macropore-matrix mass transfer [7] by affecting physico-chemical interface properties such as wettability [8] and cation exchange capacity [9]. One major implication of the heterogeneous spatial distribution of OM components and OC contents at the mm-scale in structured subsoils is that OM-related processes and properties cannot be described with mean values of OM obtained from mixed bulk soil samples [10]. Despite the importance, limited information on the spatial OM distribution along intact macropore surfaces are available mainly because these information is difficult to obtain due to problems with handling the thin and vulnerable coatings; thus quantitative effects of coating properties on preferential flow, transport, and element turnover processes are still severely limited.

The diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy in the mid-infrared range (wave lengths 2.5 – 25 μm) has been used to determine the OM composition [11] and OC contents of in soils [12]. The OM composition can be evaluated by the proportions of functional groups such as C-H, C-O, C=O, O-H, N-H, which have wave length-specific absorption bands in the infrared. In addition, signals from functional groups of soil minerals, such as Si-O and O-H, can be found in the spectra. In combination with partial least squares regression (PLSR) [13], DRIFT spectra were used in numerous studies to predict basic soil parameters [14]. However, in all these studies, mixed samples separated from the structural surfaces were analyzed, without characterizing a more detailed spatial distribution of OM and OM-related properties of these surfaces.

AIM OF THE METHOD
The DRIFT mapping method was developed for a two-dimensional mm-scale characterization of OM compounds and the quantification of OC at intact structural surfaces [4]. Another aim was to expand the possibilities of DRIFT spectral analysis by combining DRIFT spectral data with a complementary measurement data by statistical techniques such as PLSR.
PRINCIPLE AND PROCEDURE

Sampling and preparation: Soil blocks of approximately 20 cm x 30 cm x 10 cm edge lengths were cut or broken out of the soil pits using a spade and packed in tinfoil to prevent possible evaporation or cracking. From these blocks, smaller sub-samples or clods of about 5 to 10 cm edge length were manually separated along existing surface cracks. Sections of up to 8 x 10 cm^2 were separated by scraping material off from the surrounding clod and from below using a knife to reduce the sample thickness to maximal 15 mm. The sides of these samples containing intact surfaces of coated and uncoated cracks and biopores were stabilized with wrapped tinfoil, fixed at aluminum plates, and dried in a desiccator.

DRIFT mapping: For the DRIFT mapping of intact sample surfaces, the aluminum plates with the fixed samples are installed in an XY-positioning table coupled with a DRIFT device, which is installed in a FTIR spectrometer. The DRIFT spectra can be measured at the intact sample surfaces either at specific single points or along transects which can be combined to measurement grids (Fig. 1). The maximum resolution of the measurement grid (i.e., the minimum distance) is 1 mm by 1 mm; while the diameter of the IR beam is about 1.5 mm. Coarser grid resolutions can be used depending on the scientific issue and time effort. At sample surfaces with a distinctive micro-topography, the focus of the DRIFT device has to be adjusted for every individual measurement point in order to reduce micro-topographic effects on the DRIFT signal intensity and resolution [15]. At smooth surfaces the focus is adjusted in the average surface elevation of the samples.

Spectra analysis: The DRIFT spectra are recorded from at least 16 co-added scans between wave number (WN) 4000 and 400 cm\(^{-1}\) (mid-infrared range) at a spectral resolution of 4 cm\(^{-1}\), and corrected for ambient air using a background spectrum of a gold target (99 %; Infragold). The spectra are converted to Kubelka-Munk (KM) units, smoothed (boxcar algorithm, factors between 15 and 25), and corrected for baseline shifts using the software WIN-IR Pro 3.4 (Digilab, MA, USA). When evaluating the OM composition the DRIFT signal intensities from specific functional groups have to be normalized against other absorption band in the same spectrum, e.g., against one single signal or against the sum of all signal intensities from organic functional groups [5]. Proportions of specific functional groups can also serve as a proxy for physical properties of the OM at intact surfaces. For example, the relation between C-H stretching vibrations of alkyl groups (WN 3000 - 2800 cm\(^{-1}\)) and those of C=O groups (around WN 1720 and 1610 cm\(^{-1}\)) can be used as potential wettability index (PWI) [16] of the OM.

Complementary analyses: For quantitative and more detailed analyses of organic or mineral matter at intact macropore surfaces, the outermost <1mm thick layer of the macropores can be separated from the underlying soil matrix. In the separated material, different parameters can be measured by standard laboratory techniques and can be related to the DRIFT spectra of the surface areas from where the material was taken. The OC content of the separated material can be determined easily by dry combustion elemental analysis [6]. However the identification of specific OM compounds may require more elaborative techniques such as pyrolysis field-ionization mass spectrometry (Py-FIMS) for the determination of heterocyclic nitrogen and nitriles as representative for more stable OM compounds [5]. The separation of surface material should consider different macropore types (earthworm burrows, root channels, cracks with and without clay-organic coatings) and can be carried out using knife and scalpel.
Here, the challenge is to ensure a uniform separated layer thickness that should be as small as possible to avoid dilution effects by the underlying soil matrix material. **Statistical relations:** The relationships between DRIFT spectra and related measurement data (e.g., OC content, OM compounds) can be statistically analyzed by partial least squares regressions (PLSR) [13]. As one non-commercial product, the software R [17] can be used with the module PLS (SIMPLS, cross-validation: leave-one-out) to build a calibration model from a set of DRIFT mapping spectra and corresponding measured values. This model can be used to predict values for intact sample surfaces by using spectra from DRIFT mapping. The number of components used in a PLSR calibration model depends on the lowest predicted root-mean-square error (RMSEP) for the respective components. The score and loading values can be plotted for the components that explain the variance of the data. By combining DRIFT spectra and corresponding measurement data via PLSR, a detailed analysis of most responsible spectral regions may become feasible and thereby, dominant functional groups can be identified.

**TEST RESULTS**
The DRIFT mapping technique was applied for describing the mm-scale, two-dimensional distribution of (i) the potential wettability of the OM as one important physical effect of the OM composition [4] (Fig. 2b), (ii) the proportions of relatively stable OM compounds [5] (Fig. 2c), and (iii) the OC content along intact macro pore surfaces [6].

The OM at earthworm burrow walls was characterized by a mix of relatively labile aliphatic-C-rich and more stable lignin and alkyl-aromatic compounds whereas the OM of coated cracks and pinholes was dominated by relatively stable heterocyclic N and nitriles, and high-molecular aromatic compounds (benzonitrile and naphthalene). This more recalcitrant OM originated from the combustion of biomass and, in case of the till-derived Luvisol, from diesel exhaust particulates. The OM composition of pore walls reflected the differences between biopores (i.e., topsoil and plant residual, worm activity) and cracks (i.e., solutes and colloids, rapid percolation). The information of Py-FI mass spectra enabled the assignment of OM functional groups also from spectral regions of overlapping infrared signal intensities to specific OM compound classes [18]. Strong relationships between NCOMP obtained by Py-FIMS and DRIFT signals from clay minerals suggested stabilization mechanisms between the OM and clay minerals [19, 20] in coatings and pinholes which may reflect long-term humification processes. These results were underlined by increased OC contents in coated cracks [6]. At coatings along cracks and earthworm burrows which contained increased proportions of aliphatic C-H groups, reduced infiltration rates of water droplets could be proven [21, 22]. A lower wettability of macro pore surfaces could increase preferential flow because mass transfer (i.e., the water exchange between macro pore and matrix) is reduced compared to full wettable surface properties.

**CONCLUSIONS**
1. The combination of DRIFT mapping spectra from intact macro pore surfaces and complementary laboratory data from element analysis (OC content) and Py-FI mass spectra (OM compounds) via PLSR was found useful to predict the mm-scale spatial distribution of OC and OM compounds at intact macro pore surfaces.
2. Applications of DRIFT mapping with respect to further physico-chemical properties such as soil mineral composition or sorption properties seem useful.
3. The amount of OM (i.e., OC content) as well as the mm-scale distribution of the OM composition at macro pore surfaces in structured subsoils reflects preferential flow, transport, and stabilization of OM along the surfaces of flow pathways.
4. The distribution of OM compounds and OC at macro pores and its potential physical, chemical, and microbial effects should be separately considered for each macro pore-type when modeling and interpreting preferential flow and turnover processes in soils.
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Chapter I/31: IMPACT OF LANDSCAPE EVOLUTION ON THE POREWATER COMPOSITION OF CLAY ROCKS

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ABSTRACT. In Switzerland, the Opalinus Clay formation has been selected as the first-priority host rock for a deep geological repository for both low- and intermediate-level and high-level radioactive waste. An extensive site and host rock investigation programme has been carried out during the past 30 years in Northern Switzerland. The hydraulic properties of the Opalinus Clay can be described as follows: Below a near-surface decompaction zone with elevated hydraulic conductivity (up to $10^{-4}$ m/s), the hydraulic conductivity is very low ($\sim 10^{-13}$ m/s) and diffusion is the dominant transport mechanism, with advection playing a secondary role. Faults in the Opalinus Clay do not represent preferential flowpaths, which is attributed to an efficient self-sealing mechanism. The spatial distribution of the chloride content of the porewater and groundwater in the Opalinus Clay and in surrounding aquifers in the Mont Terri Underground Rock Laboratory can be explained based on a large-scale diffusion model in combination with a plausible tectonic and landscape evolution history.