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INSIGHTS FROM PROTEIN-SPIKED ARTIFICIAL SOILS INTO THE VALUE OF MATRIX-ASSISTED LASER DESORPTION/IONIZATION MASS SPECTROMETRY BASED SOIL PROTEOMICS AS TO INTERPRET ARCHAEOLOGICAL SITES

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Anthropogenic activities are known to leave chemical traces in the soil, primarily in the form of organic molecules released from occupation waste. Recent studies indicate that lipids, fatty acids and waxes can survive in soils for long periods of time and show the potential of these residues as archaeological biomarkers. Although some of these biomarkers can be traced back to their origin, the information yield is often limited, because many organic molecules in the soil have multiple sources, become mineralized or are heavily degraded. Proteinaceous biomarkers on the other hand hold specific information about anthropogenic action on the soil, but are generally believed to be very susceptible to degradation especially on archaeological time scales.

Although soils are one of the most abundant archaeological artefacts, investigation of soil proteins is quite limited. Studies on recent soils nevertheless suggest that proteins can be strongly retained by means of adsorption onto clay minerals, encapsulation by refractory organic matter, protein complexation or various combinations of these processes. Soil composition and resulting characteristics (e.g. pH, cat/anion-exchange capacity) are thus of great importance for the long-term preservation of proteins and choice of method to extract and identify proteins. Previous soil proteomic studies have focused mainly on protein extraction using strong acids or bases, chaotropic agents and phosphate buffers, whereas quantification and identification were assessed using protein assays (i.e. Bradford assay) and immunological methods respectively. Although these approaches give an indication of protein concentration and type, they are often biased by the presence of co-extracted non-Proteinaceous substances.

In this study, retention experiments with bovine serum albumin (BSA) and heat treated BSA were carried out with four protein extractants (hydrofluoric acid, guanidine-HCl, citrate and phosphoric acid/bicarbonate) and eight artificial soils containing different amounts of quartz sand, clay minerals (bentonite and kaolinite) and organic matter (humic acid and glucose). Also, matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS)

based soil proteomics were applied to both artificial and archaeological soils in order to i) study how co-extracted soil constituents affect protein detection and identification and ii) assess the value of such an approach for the interpretation of archaeological sites.

Results from this study indicate that levels of extracted proteins from soils are a function of both extractant and soil type and that the protein domains that are involved in absorption processes are highly dependent on soil type. In turn, this affects the efficiency of the applied proteomic approach, because of the limited amounts and different kinds of protein fragments that are available for SDS-PAGE separation, proteolysis, MALDI-MS analysis and protein identification. However, from most artificial soil extracts abundant proteinaceous signals could be obtained as to successfully identify BSA and this shows the potential of soil proteomics as an advanced method for archaeological prospection and site interpretation. In contrast to these findings, extraction experiments with archaeological soils implied that proteinaceous signals in these soils are often quantitatively and qualitatively insufficient for protein identification. This is probably due to the low concentration and degradative state of proteins in archaeological soils.