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## Microstructure studies reveal conditions for attenuation processes in aged tar-oil contaminated soil

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The microstructure determines the conditions for biogeochemical processes in aged tar-oil contaminated soil. Such porous media are complex materials with non-aqueous phase liquids as additional factors affecting soil formation. These non-aqueous phase liquids are predominantly composed of tar oils, i.e. high molecular weight hydrocarbons (HC) and their degradation products. Microstructural investigations of such soils are quite limited, and little is known about degradation pathways and processes in such systems.

We present a case study on the microstructure of a tar-oil contaminated soil with specific focus on the spatial distribution patterns of mineral phases, petroleum and non-petroleum organic matter (OM). Thin sections were prepared from samples from different depths from a soil profile at a tar-oil contaminated site. They were investigated using light- and digital microscopy, scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDX) and FTIR microscopy.

The first 20 cm of the soil profile were visually affected by tar oil. The soil profile featured four superimposed layers (A, B, C1, C2) with distinct boundaries, characterized by severe difference in total petroleum HC (TPH) and total C (TC) content, as well as significant variety in the microstructure. The top layer (A, 0-7 cm) was highly porous with remnants of plant tissue and OM. It contained 28 mg g<sup>-1</sup> TPH and 270 mg g<sup>-1</sup> TC. The second layer (B, 7-15 cm below the surface) was the most contaminated, with up to 90 mg g<sup>-1</sup> TPH and 395 mg g<sup>-1</sup> TC. It consisted of large (1-2 cm) oil-bearing aggregates harboring isolated macropores (up to 10-50  $\mu$ m in size). In some pores, we detected Fe minerals – siderite. The third layer, (C1, 15-22 cm below the surface) had again a high porosity, but contained significantly less TPH (16 mg g<sup>-1</sup>) and TC (193 mg g<sup>-1</sup>). We observed accumulation of a disperse Fe phase (presumably hematite) along macropores and root channels. The deepest layer (C2, 22-30 cm below surface) macroscopically showed no evidence of tar contamination. However, FTIR microscopy and SEM-EDX revealed that some macropores (including root channels) were coated with HC.

In layer B, TPH comprised up to 23 % of TC; in layers A and C1 this proportion was 10 % and 8 %, respectively. Microbial biomass was significantly larger in contaminated layers than in an uncontaminated control soil (0.4-0.5 mg  $\rm g^{-1}$  and 0.1 mg  $\rm g^{-1}$ , respectively). We assume that OM input, high porosity and free water inflow supported favorable conditions for oxic degradation of tar-oil in the layers A and C1. Accumulation of Fe along macropores and root channels in layer C1 might reveal hotspots of oxic attenuation. The presence of siderite in isolated pores in layer B indicated the existence of anoxic conditions for tar-oil transformation within oil bearing aggregates.