

## Natural attenuation of aged tar-oil in soils: A case study from a former gas production site

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Contamination of soils with tar oil occurred on many industrial sites in Europe. The main source of such contamination has been former manufactured gas plants (MGP). As many of them were destroyed during the World War II or abandoned in the second half of the XXth century, the contamination is depleted in volatile and degradable hydrocarbons (HC) but enriched in the heavy oil fractions due to aging processes.

We studied a small tar-oil spill in a former MGP reservoir basin. The tar-oil had a total petroleum hydrocarbon (TPH) content of 245 mg/g. At the margin of the spill, vegetation has started to overgrow and intensively root the tar-oil layer. This zone comprised the uppermost 5-7 cm of our profile and contained 28 mg/g of TPH (A-layer). The layer below the root zone (7-15 cm) was the most contaminated, with 90 mg/g TPH (B-layer). The layer underneath (15-22 cm) had smaller concentrations of 16 mg/g TPH (C-layer). Further down in the profile (D-layer) we found only slightly higher TPH content than in the control samples (1,4 mg/g vs 0,6 mg/g). The polycyclic aromatic hydrocarbons analysis showed the same distribution throughout all layers with highest contents of the PAHs with 4-6 condensed aromatic rings.

Direct cell count and extraction of microbial biomass showed that the highly contaminated soil layers A and B had 2-3 times more bacteria than the control soils. CARD-FISH analysis revealed that in samples from layers A and B Archaea were more abundant (12% opposing to 6-7% in control soil). Analysis of bacteria (tested for Alpha-, Beta-, Gamma- and Epsilonproteobacteria and Actinobacteria) showed the dominance of Alphaproteobacteria in the layer A and C both beneath and above the most contaminated layer B. The primers covered the whole microbial consortia in these two layers, leaving almost no unidentified cells. In the most contaminated layer B Alphaproteobacteria amounted only to 20% of the microbial consortium, and almost 40% of the cells remained unidentified, suggesting the presence of other microorganisms using high-molecular weight HC as carbon source. All contaminated layers were found to be enriched in total Fe and both dithionite-extractable and oxalate-extractable Fe. Besides, siderite crystals were identified using FTIR microscopy. The presence of secondary crystalline and poorly crystalline Fe(III)-oxides and secondary Fe(II)-carbonates in the same horizons suggests simultaneous occurrence of oxic and anoxic zones within the porous system of the contaminated layers.

Although HC pollution is often considered to inhibit microbial activity in soil, in our study the layers with highest TPH-amounts were the most "alive". We assume that aging processes (the sum of volatilization, dissolution, microbial degradation, chemical oxidation, polymerization and migration) and eventually a long-term microbial adaption to the HC carbon source resulted in the development of a microbial consortium, capable of transforming high-molecular weight HC. Presumably, iron-compounds in the tar oil act as an electron acceptor and trigger HC degradation. However, to unravel natural attenuation processes and degradation pathways it seems mandatory to take into account the soil structure and spatial distribution of microbes.