CHEMICAL ANALYSIS OF SOIL POLLUTING LUBRICANT OILS PRIOR TO DESIGN A SOIL REHABILITATION PROCEDURE

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Abstract
Excessive consumption of petroleum products carries the risk that these toxic chemicals enter and accumulate in the environment hazarding natural habitats or human health. Areas being close to vehicle traffic or where handling and maintenance operations of vehicles take place are considered to be particularly vulnerable, thus, we aimed at investigating a railway marshalling yard polluted by used lubricant oils (ULOs). Quantitative determination of total petrol hydrocarbons in the polluted soil revealed a high level of pollution. Apart from the presence of open-chain or branched paraffins and aromatics, Fourier transform infrared spectroscopy identified intermediers from the microbial degradative pathways of hydrocarbons. Occurence of metabolically active microorganisms even in this highly ULO-contaminated soil indicates that biological rehabilitation techniques can be preferable over more invasive and expensive physico-chemical methods to meet the soil standard.

Introduction
Lubricating oils (LOs) are widely used as friction-reducing, cooling and anti-corrosion agents on mechanical moving parts of motorized vehicles, which undergo a great variety of physicochemical changes during normal operation [1]. Used lubricating oils are complex chemicals consisting of a hydrocarbon mixture with varied carbon counts and diverse structures, additives and a considerable level of such harmful compounds as polychlorinated and polyaromatic hydrocarbons (PCBs and PAHs) or heavy metals [2-4]. Since ULOs can strongly bind to soil particles, persist in soil and cause changes in its physical, chemical and biological properties [5], contamination usually results in narrowing the soil spectra for later uses.

Experimental
Areas being close to vehicle traffic or where handling and maintenance operations of vehicles take place are considered to be particularly vulnerable, since the probability of contamination inevitably increases in these places [6]. ULOs, leaking from locomotives and polluting the soil, have been a long-standing environmental problem at a railway marshalling yard near Szeged, Hungary. We aimed at determining the level of total petrol hydrocarbons (TPH) in the polluted soil and elucidating changes in chemical composition of ULO exposed to natural weathering processes. Fourier transform infrared spectroscopy (FTIR) was applied to compare chemical properties of spent ULO to fresh MK8 locomotive LO. Determination of pollution level and chemical properties of the pollutant are essential for designing appropriate environmental soil rehebilitation processes.

Results and discussion

Soil samples were collected from the upper layer of soil along a transect on the ULO-polluted train track. TPH levels in samples A-F (Fig. 1.) exceeded the pollution limit of 100 mg TPH/kg soil set out in Government Decree 6/2009 (IV. 14.) [7].

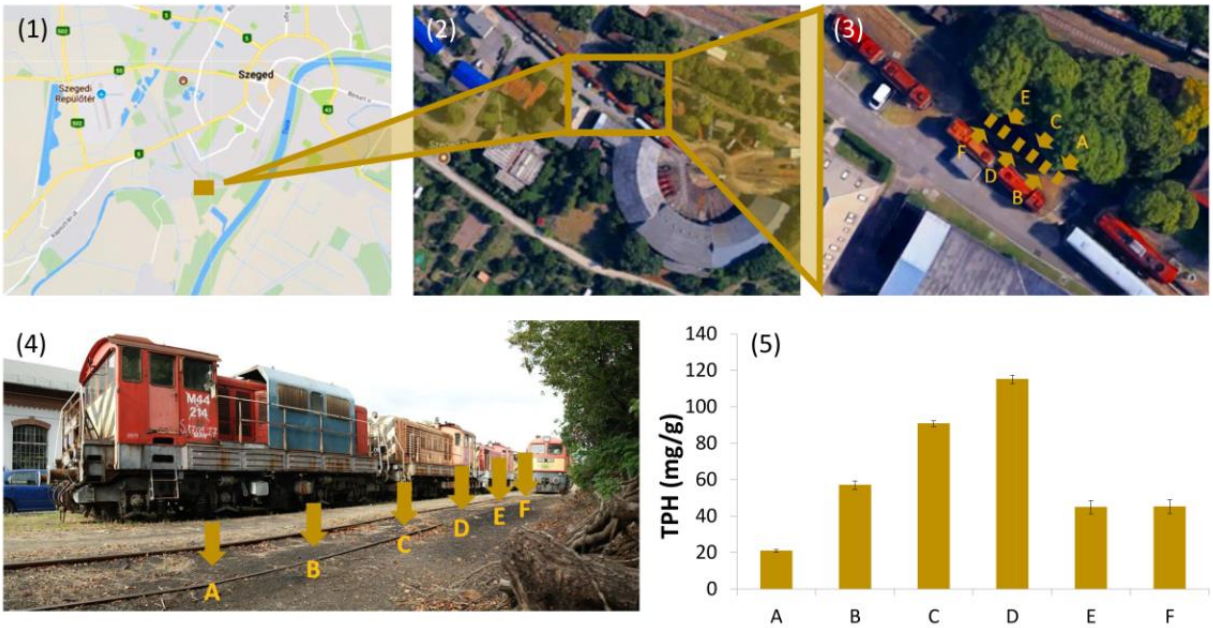

Figure 1. Sampling site: 1-2) ULO-polluted area of a railway marshalling yard near Szeged, 3-4) soil sampling points and 5) TPH levels in ULO-contaminated soil samples (A-B).

Comparison of FTIR spectra of spent ULO and fresh MK8 LO (Fig. 2.) revealed that LOs primarily composed of open-chain and branched paraffins [8-10]. Absorbance bands of C-H stretching vibrations in spent ULO are a bit shifted indicating disordered oil structure and shortened hydrocarbon chains possibly due to microbial ULO-degradation in soil. Alcohols and carboxylic acids are also intermediers in the degradative pathways of hydrocarbons [1, 8, 11]. Bands corresponding to the presence of esters, ethers and amines [9, 12] further proves that metabolically active microorganisms can be found in polluted soils despite the high level of ULO-contamination. Metal-containing additives of LOs (zinc dialkyl dithiophosphates - ZDDPs) detergents (sulfonates, phenolates and carboxylates) and antifoams were also present according to the absorbtion bands of their P-O-C, P=S and Si-H bonds [12-14]. Increased concentration of aromatics was also detected in spent ULO compared to the FTIR spectrum of fresh LO [12].

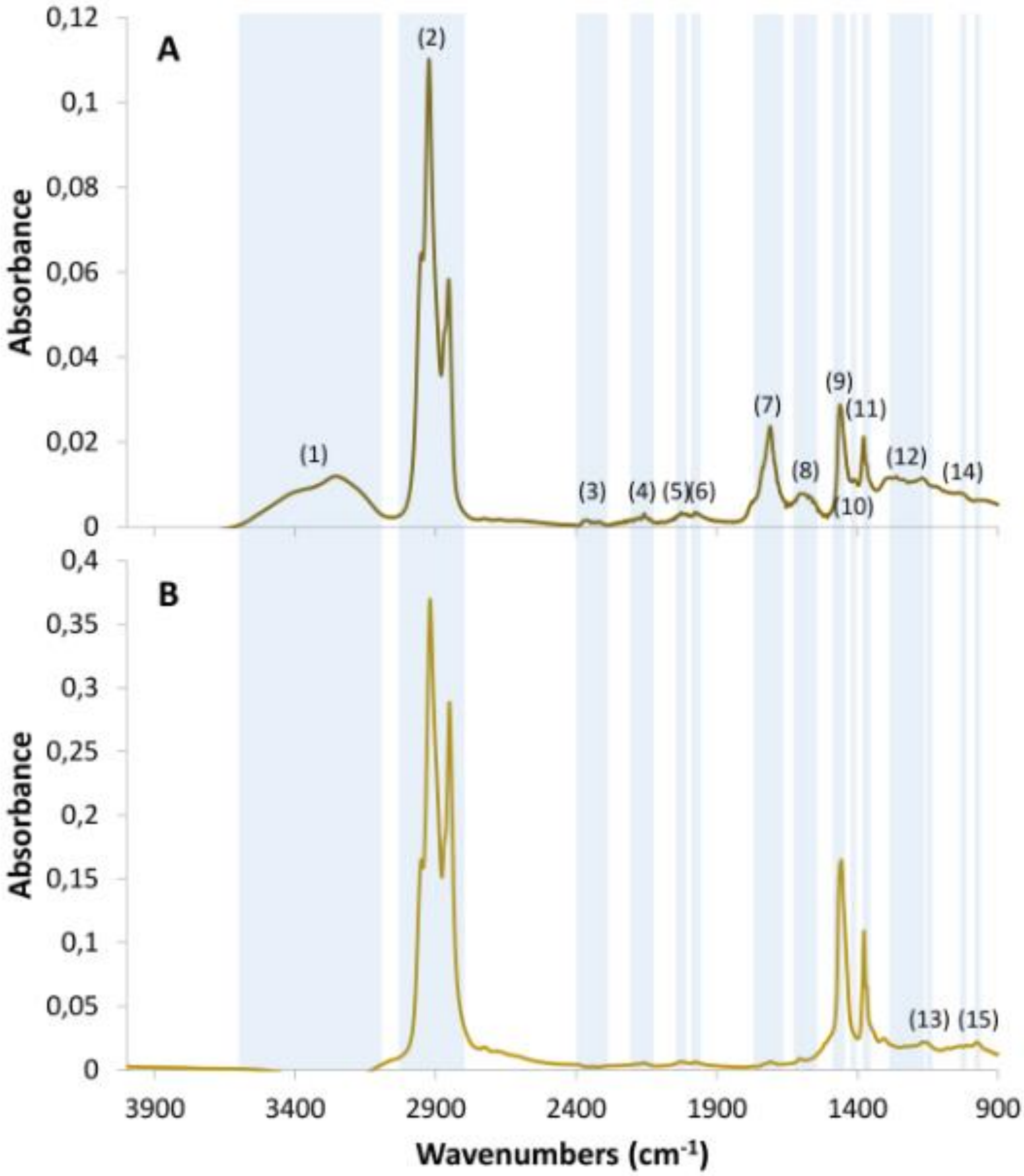

Figure 2. FTIR spectra of MK8 lubricanting oil: A) spent ULO and B) fresh LO. Absorbance bands: (1) O-H stretching in alcohols; (2) C-H stretching in hydrocarbons; (3) NH2+ deformation and NH+ stretching in amines; (4) Si-H stretching; (5) N=C=S stretching in isothiocyanates; (6) C-H bending in aromatics; (7) C=O stretching in esters, ketones and carboxylic acids; (8) C-C stretching in aromatic rings; (9) C-H bending in hydrocarbons; (10) S=O stretching in sulfates and sulfonates; (11) C- H branching vibration in hydrocarbons; (12) C-O-C stretching in esters and ethers; (13) sulfonate salts, methacrylates; (14) C-N stretching in amines; (15) P-O-C and P=S bonds in zinc dialkyl dithiophosphates (ZDDPs).

Conclusion

Detection of biomolecules and intermediers from ULO-biodegradation indicate the presence of metabolically active microorganisms even in this highly ULO-contaminated soil, hence biological rehabilitation techniques can be preferable over more invasive and expensive physico-chemical methods to meet soil standards.

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