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Sorption behaviour of an n-alkane in soil and its influence on bioavailability for remediation application

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The biological remediation of petroleum hydrocarbon contaminated geosorbents is considered as a beneficial and promising tool although limitations in the effective clean up of soils and sediments still impede success rates. Petroleum hydrocarbon products consist of complex mixtures of compounds and the influence that inherent processes in soil have on biodegradation of constituent compounds, including migration, uptake and release, and the concomitant affect on bioavailability, is still largely inconclusive. Residual hydrocarbon fractions which remained undegraded were observed in previous studies investigating the bioremediation of geosorbents contaminated with petroleum products. It was reported that total petroleum hydrocarbons undergo rapid biodegradation during initial stages but the rate of degradation reduces with time to reach asymptotic levels. This was explained by the fact that pollution by complex mixtures comprise of a biodegradable fraction and a fraction that is either toxic, recalcitrant or unavailable to microorganisms. Limited studies have been done on defining the fraction remaining in soil after biodegradation rates declined particularly with respect to petroleum contamination, and also identifying the type of constituent compounds in petroleum products that show reduced bioavailability. Greater insight into processes which result in reduced availability of specific petroleum constituent compounds in soil is likely to improve our understanding of the transport and migration of these contaminants. Moreover, evaluating their behaviour in different soils could assist in the prediction of the pollutants' fate in remediation efforts.

The complexity and variability of petroleum hydrocarbons make it difficult to identify the fraction that is readily degraded and the fraction which remains in the soil. With this in mind, the sorption behaviour of a specific petroleum hydrocarbon constituent compound, the aliphatic pentadecane ($n-$C15), was assessed in eight soils during the

present study. Batch equilibrium isotherms were setup to investigate adsorption and desorption behaviour and to assess the measure of isotherm nonlinearity and hysteresis which may result from different organic carbon (OC) content in soils. The data was fit to the Freundlich equation and the isotherm exponent (N) for adsorption and three subsequent desorption steps was used to calculate an index which denotes hysteresis and degree of difficulty of pentadecane molecules to desorb from the soil matrices. Through the examination of pentadecane adsorption and desorption, it was shown that sorption is nonlinear and hysteric for these soils. Isotherm nonlinearity, partitioning coefficients and degree of sorption-desorption hysteresis provided an indication that the geochemistry of soil organic matter determines binding and release of the compound. A poor correlation was found between Freundlich partitioning coefficient (K_F) and OC content which reveal that the structural conformation of the organic fraction plays a pivotal role in governing sorption. Sorption capacity of two soils (TOC 2.3 and 1.4 %, respectively) was higher by a factor of between 1.5 and 3.5 compared to two other soils though they have higher OC contents (TOC 5.5 and 4.5 %). All desorption isotherms for all soils showed hysteresis with lower index values indicating reduced desorption. This shows that bioavailability is a factor that should be considered in biodegradation studies which involves alkanes present in mixtures such as petroleum products when the potential for soil remediation applications is evaluated.