PURPOSE: The speciation of soil organic pollutants is of great importance for risk assessment and contaminant remediation, however, only few studies have attempted to develop a speciation scheme for a facilitated risk assessment. This paper postulates a pragmatic speciation scheme for the fractionation of soil polycyclic aromatic hydrocarbons (PAHs) that could correlate with their bioavailabilities, and the aim was to develop a reliable sequential ultrasonic extraction scheme that could differentiate PAHs into four fractions with different environmental relevance. We also investigated the key factors to the fraction distribution of PAHs, as well as the relationship between bioavailability of PAHs and their fractions. MATERIALS AND METHODS: Four representative PAHs were spiked into two soils and the distribution of PAH fractions was measured over a period of 90 to 210 days. The reliability of the sequential ultrasonic extraction method was cross-examined by an isotope experiment. The key factors to the fraction distribution, including aging time and properties of soil and PAH, were tested using ultrasonic extraction. The correlation between four fractionated PAHs and their bioavailabilities was assessed with a semipermeable membrane device (SPMD)-assisted desorption assay that mimics the bioconcentration of PAHs. RESULTS AND DISCUSSION: Soil PAHs were speciated into water-soluble-, organic acid-soluble-, organically bound-, and residual fractions via sequential ultrasonic extraction. The water-soluble- and organic acid-soluble fractions, which approximated the total PAHs estimated by SPMD, corresponded to the most bioavailable portions. The latter ones decreased significantly during aging. In contrast, the residual fraction, which limits the effectiveness of remediation, increased during aging following methanolic saponification. The concentrations of water-soluble-, organic acid-soluble-, and organically bound fractions are negatively correlated with the soil organic matter content and the partition coefficient between octanol and water (K_ow) of pollutants CONCLUSIONS: The bioavailability of soil PAHs can be mimicked by a sequential chemical extraction protocol developed in this study. This speciation scheme can be readily used for studying the environmental fate and risk of PAHs, providing us with better rationales in selecting remediation strategies of soil contaminated with PAHs based bioavailability.