Effects of Non-Aqueous Phase Liquid (NAPL) on Biodegradation of PAHs in Spilled Oil on Tidal Flat

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Polycyclic aromatic hydrocarbons (PAHs) like Benzo(a)Pyrene and Dibenz(a,h)anthrathene are known to be carcinogen or endocrine disruptor and one of the most important oil fractions that may cause significant environmental impacts in case of oil spills. In the case of the *Nakhodka oil* spill, 1997, the Sea of Japan, 50% of three or larger-rings PAHs remained for more than 21 months after the spill. These biodegradations are significantly slower than those dissolved in water.

Oil is composed of a large amount of organic matrices called non-aqueous phase liquid (NAPL) like resins and asphaltenes and PAHs are dissolved in NAPL. As the biodegradation of PAHs are known to take place through solubilization of PAHs from NAPL into water, the rate of PAHs dissolution may influence on their biodegradation rates.

Tidal flats are regarded as one of the most important coastal ecosystem and various human impacts on these ecosystems like oil spills and reclamation are one of the largest environmental concerns in Japan. NAPL in the spilled and stranded oils on tidal flats are known to be penetrated into the sediment of the tidal flats by tidal action. Some parts of penetrated NAPL remains in the sediment and PAHs in it damage tidal flat ecosystem. The purpose of this study is to clarify the effects of NAPL on the biodegradation of PAHs in stranded oil on tidal flats with special emphasis on the relationship between their dissolution rates of PAHs into water and persistency of NAPL in tidal flats.

Dissolution fluxes of PAHs from NAPL into water were determined to estimate biodegradation rates of PAHs in NAPL. Biodegradation of PAH in NAPL in tidal flat sediment was determined using tidal flat sediment slurry reactors. Two types of reactors to simulate tidal flat ecosystems were used; one is a tidal system with seawater inflow and outflow to evaluate the effects of the wash out of NAPL with tidal action and the other is a closed system without inflow and outflow of seawater. Table 1 shows first order rate constants for NAPL washout and biodegradation. The washout of NAPL by outflow of seawater was 8 times and 4 times as high as biodegradation for crude oil and fuel oil C, respectively. Therefore, washout is an important factor for the decrease in NAPL in tidal flat.

Biodegradation rates of PAHs were estimated from their dissolution flux using a numerical model assuming that the dissolution of PAHs from NAPL into water is the limiting step for the biodegradation of PAHs. The good agreement between the observed and the estimated biodegradations supports the assumption. The biodegradation of PAHs is slow for the closed system compared to the tidal system. This result indicates that the washout in NAPL accelerates biodegradation of PAHs in NAPL. Therefore, PAHs in fuel oil C is residual compared to that in crude oil, because slow decrease of NAPL for fuel oil C.