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## How does pore size distributions affect the accumulation and release rates of a PAH in porous media of sediments and soils?

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In areas contaminated by the petroleum industry, persistent compounds such as polycyclic aromatic hydrocarbons (PAH) are often accumulated in the porous matrixes of sediments and soils (S&S), implicating risks to ecosystems and human health since these contaminants are released over time to interstitial and surrounding water. Pore size distributions (PSD) and PAH binding strengths to sorption sites on S&S are characteristics that affect such accumulation and release. Sorption, desorption and diffusion are among the critical processes that control the availability of PAH, and it is therefore crucial to evaluate these processes in order to understand and predict transport and fate of these contaminants in S&S, and for selecting effective remediation procedures. Four S&S samples were obtained from previously contaminated sites, air-dried, and sieved (mesh 200), and organic matter (OM) was reduced in subsamples by hydrogen peroxide treatment, resulting in eight different porous media. Surface areas and PSD were determined (Autosorb IQ2MP, Florida), and OM were estimated by calcination (ASTM, 1993). Benzo(a)pyrene (BaP) was selected as study PAH and adsorption experiments were carried out in the dark with S&S suspended in NaCl ( $I=0.047$  M) solutions, by adding five different concentrations of BaP with  $^{14}\text{C}$ -BaP as radioactive tracer, between  $2.59$  and  $12.6 \times 10^{-4}$  mmolBaP/gS&S, according to TG 106 Guideline (OECD, 2000). Reactors were fed with  $\text{CO}_2$ -free air to keep suspensions oxygenated and allow carrying  $^{14}\text{CO}_2$  and stable  $\text{CO}_2$ , produced by mineralization of BaP and OM, respectively, to alkaline traps, where  $\text{CO}_2$  production was measured by changes in electrical conductivity. Supernatant aliquots in the reactors and alkaline traps were obtained and  $^{14}\text{C}$  was measured in a liquid scintillation counter (Beckman Counter LS6500). At the end of the BaP adsorption experiments (14 d),  $6.5 \text{ cm}^2$  polyoxymethylene (POM) was added as a passive sampler, desorbing BaP from S&S. POM-accumulated BaP was extracted with acetone and sonication (EPA, 2007).  $^{14}\text{C}$  was quantified in the extracts as described above.

In the case of samples with complete organic matter, sorption at 14 days varies between 91.5 and 95.8%, while in the samples with reduced organic matter a variation between 78.7 and 89.9% was observed. Desorption velocities were much slower than adsorption rates, finding values between 2.0 and 6.0 % in 14 days and between 2.2 and 11.1% in 43 days. Using these values it is estimated that the time required to desorb BaP varies between 644 and 8,290 days. This difference between rates of adsorption and desorption should be considered when planning remediation actions for contaminated sites.

Two different time dependencies were observed in adsorption and desorption kinetics: a fast step considered to be due to diffusion of the BaP to the external surface, macro and mesopores, and a slow step, considered as diffusion of BaP into the micropores capillaries. Sorption equilibrium constant (KL), sorption sites and kinetic constants were experimentally obtained and a two-step conceptual model that describes the effect of the dynamics in porous media on the reactive transport of BaP in S&S with different PSD was developed.

### References

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OECD (Organisation for Economic Cooperation and Development) (2000). OECD Guideline for the testing of chemicals. Adsorption –Desorption using a batch equilibrium method.

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