

Technical University of Denmark



## Dynamic passive dosing for studying microbial PAH degradation: a comparison of experimental and model results

Smith, K. E. C.; Rein, Arno; Trapp, Stefan; Gosewinkel Karlson, U.

*Published in:*  
Abstract Book

*Publication date:*  
2012

*Document Version*  
Publisher's PDF, also known as Version of record

[Link back to DTU Orbit](#)

### *Citation (APA):*

Smith, K. E. C., Rein, A., Trapp, S., & Gosewinkel Karlson, U. (2012). Dynamic passive dosing for studying microbial PAH degradation: a comparison of experimental and model results. In Abstract Book: 6th SETAC World Congress/SETAC Europe 22nd Annual Meeting (pp. 347). Society of Environmental Toxicology and Chemistry.

**DTU Library**  
Technical Information Center of Denmark

---

### **General rights**

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

influence of charge and molecular structure on the sorption process. Representative emerging contaminants were selected, covering hormones, pharmaceuticals, personal care products, and pesticides. Batch sorption studies were conducted with natural DOM-containing water samples obtained from Finland, United Kingdom, and the Netherlands and by using polyacrylate passive samplers to determine aqueous contaminant concentrations. The DOM samples were characterized by chemical and physical fractionation methods. The results indicated that charge and molecular size of ionized compounds dominate sorption to both DOM and polyacrylate. Positively charged compounds showed a strong pH dependent sorption to DOM, whereas the neutral forms were the most important species responsible for sorption to polyacrylate. Negatively charged compounds showed the lowest affinity to both DOM and polyacrylate. For most neutral compounds investigated, the water phase represented a more favorable medium compared to DOM. The obtained results may increase our knowledge on the sorption of polar organic contaminants to DOM, which is currently based on only limited data.

#### TU 293

##### Binding can increase the mobility and uptake of hydrophobic organic compounds

V. Gouliarmou<sup>1</sup>, K.E.C. Smith<sup>1</sup>, L.W. de Jonge<sup>1</sup>, C. Collins<sup>2</sup>, P. Mayer<sup>1</sup>

<sup>1</sup>Aarhus University, Roskilde, Denmark

<sup>2</sup>Reading University, Reading, United Kingdom

The binding of hydrophobic organic compounds (HOCs) is usually considered to be a risk reduction process. However, if the bound form becomes mobile then it can in fact enhance uptake and risk. This phenomenon can be seen in 1) colloid facilitated transport 2) the use of chemical agents to enhance soil remediation and 3) in biology, where body fluids can enhance the release of HOCs from soil and consequently increase their bioaccessibility.

In the current work we studied the above examples using "enhanced capacity" as a new measurement endpoint. Enhanced capacity (E) has some similarities to the well-established concept of "solubility enhancement", but should not be confused with it. Solubility enhancement is determined at, and applies only to, the saturation level of the HOCs, whereas E can be determined at or below the saturation, and for defined levels of each mixture component. This means it refers to a more relevant range of environmental concentrations and mixture compositions. Passive dosing method<sup>1</sup> was applied to determine E for HOCs of 1) soil leachates collected from tile-drains of sandy clay loam and sandy loam fields of the Danish Pesticide Leaching Assessment Programme 2) sodium dodecyl sulfate and hydroxypropyl- $\beta$ -cyclodextrin that are used as chemicals in soil remediation technology and 3) artificial digestive fluids used in in-vitro test for assessing bioaccessibility of soil-bound PAHs<sup>2</sup>. The use of passive dosing circumvented artefacts associated with adding crystals of HOCs into an aqueous solution, and due to the low relative standard deviation of the method even small enhancements could be measured with high precision.

##### References:

[1]Gouliarmou, V.; Smith E.C.K.; de Jonge L.W.; Mayer, P., Measuring binding and speciation of hydrophobic organic chemicals at controlled freely dissolved concentrations and without phase separation, SUBMITTED.

[2]Tilston E.L., Gibson G.R., Collins C.D., Colon extended physiologically based extraction test (CE-PBET) increases bioaccessibility of soil-bound PAH, Environmental Science & Technology, 2011, 45, 5301-5308

#### TU 294

##### Dynamic passive dosing for studying microbial PAH degradation: a comparison of experimental and model results

K.E.C. Smith<sup>1</sup>, A.R.N.O. Rein<sup>2</sup>, S.A.J. Trapp<sup>2</sup>, U. Gosewinkel Karlson<sup>1</sup>

<sup>1</sup>Aarhus University, Roskilde, Denmark

<sup>2</sup>Technical University of Denmark, Lyngby, Denmark

Biodegradation plays a key role in PAH fate, and understanding kinetics as a function of (bio)availability is critical for elucidating their persistence. However, biodegradation mainly occurs in an aqueous environment, posing technical challenges for producing reliable kinetic data because of low PAH solubilities and sorptive losses. To overcome these, an experimental approach based on dynamic passive dosing is presented which: avoids using co-solvent for introducing the PAHs, buffers substrate depletion so biotransformation is measured within a narrow and defined concentration range and enables high compound turnover to simplify biodegradation measurements even at realistically low concentrations. The biodegradation kinetics of two PAHs by the bacterium *Sphingomonas paucimobilis* EPA505 were measured at defined dissolved concentrations ranging over 4 orders of magnitude, from 0.115 to 865  $\mu\text{g L}^{-1}$  for phenanthrene and 0.028 to 141  $\mu\text{g L}^{-1}$  for fluoranthene. Both compounds had similar biodegradation rates, and these increased in line with higher dissolved concentrations. First-order biodegradation rate constants were also similar for both, but these decreased at higher dissolved concentrations. The experimental results were compared to those obtained using different modelling approaches, including simulations based on the Best equation. These show a good agreement at the lower dissolved concentrations, whereas at higher concentrations the experimental measurements were lower than predicted, and indicate that that other factors such as PAH toxicity or essential nutrient availability play a role. Therefore, combining measurements of PAH biodegradation kinetics at defined concentrations using dynamic passive dosing, and their interpretation by modelling is a useful tool to further understand their bioavailability, biodegradation and persistence.

#### TU 295

##### Enhanced mass transfer of hydrophobic organic compounds from NAPLs into the aqueous phase by dissolved organic carbon

K.E.C. Smith<sup>1</sup>, M. Thullner<sup>2</sup>, L.Y. Wick<sup>2</sup>, H. Harms<sup>2</sup>

<sup>1</sup>Aarhus University, Roskilde, Denmark

<sup>2</sup>UFZ - Helmholtz Centre for Environmental Research, Leipzig, Germany

Hydrophobic organic compounds (HOCs) are often found as mixtures in the form of non-aqueous phase liquids (NAPLs). Due to their hydrophobic nature, the HOCs preferentially remain in the NAPL, with slow mass fluxes into the aqueous phase. However, since water dissolved HOCs play a key role in diffusive uptake into organisms, microorganisms using HOCs as a source of carbon and energy face a large reservoir of inaccessible food in the NAPL which is often reflected in slow bioremediation of NAPL contaminated sites. Interestingly, mobile "colloidal-like" phases can contribute to diffusive mass exchange processes between surfaces and the bulk aqueous phase, a phenomenon termed enhanced or facilitated diffusion. Therefore, this study investigated the role of dissolved organic carbon (DOC) in enhancing the mass transfer of hydrophobic organic compounds from NAPLs into the aqueous phase above that attributable to dissolved molecular diffusion alone. In controlled experiments, mass transfer rates of five NAPL-phase PAHs (log KOW 4.15 - 5.39) into the aqueous phase containing different concentrations of DOC were measured. Mass transfer rates were increased by up to a factor of four in the presence of DOC, with the greatest enhancement being observed for more hydrophobic compounds and highest DOC concentrations. These increases could not be explained by dissolved molecular diffusion alone, and point to a parallel DOC-mediated diffusive pathway. The nature of the DOC-mediated diffusion pathway as a function of the DOC concentration and PAH sorption behaviour to the DOC was investigated using diffusion-based models, and found to increase with DOC concentration and compound sorption. Therefore, for "super"hydrophobic compounds this pathway could both dominate but also increase mass transfer rates by orders of magnitude, even at environmental DOC concentrations. This has important implications for their bioremediation, as well bioconcentration and toxicity.

#### TU 296

##### On the effect of vitamins and nutrients on the solubilization of petrodiesel/biodiesel blends in water

M.H. Yassine<sup>1</sup>, M.T. Suidan<sup>2</sup>, A.D. Venosa<sup>3</sup>

<sup>1</sup>University of Cincinnati, Cincinnati, United States of America

<sup>2</sup>American University of Beirut, Beirut, Lebanon

<sup>3</sup>U.S. Environmental Protection Agency, Cincinnati oh, United States of America

The effect of mineral salts on the aqueous solubility of nonelectrolytes is largely assumed to exhibit the "salting out" or "salting in" effects in which the aqueous solubility of nonelectrolytes is decreased or increased upon the addition of salts. Pioneering investigations by Setschenow [1] and later by Carter and Hardy [2] among others, resulted in semi-empirical relationships that describe the dependence of the solubility of nonelectrolyte solutes on salts concentrations. We conducted equilibration experiments of petrodiesel/biodiesel blends (B0, B20, B40, B60, B80, and B100, where B100 is 100% biodiesel) in water in the presence and absence of standard vitamins and nutrients used for bacterial growth studies. The solubility of aromatic compounds was found to be in agreement with the salting out effect in the presence of the added nutrients. The solubility of the C10 - C21 n-alkanes, however, exhibited very odd and complex behavior and was found to be significantly enhanced ( $p < 0.0005$ ), up to 40-fold in the presence of the fatty acid methyl esters (FAMES) and the vitamins and nutrients medium, compared to FAMES and deionized water alone. A similar observation was made by Baker [3] regarding the effect of salts on solubilization of the alkanes and aromatic compounds in the presence of fatty acid soap solution. They reported that, in the presence of sodium chloride in dilute fatty acid soap solutions, the solubility of paraffin hydrocarbons is markedly higher and that of aromatic hydrocarbons is lower. Those observations are found to contribute significantly to the bioavailability of the n-alkanes in the water column. Biodegradation studies conducted in our laboratory showed significant enhancement for the microbial utilization rates of the n-alkanes in the petrodiesel/biodiesel blends, which we interpret to be due to the increase in aqueous concentrations of the n-alkanes in the presence of the FAMES and nutrients.

##### References

[1] Setschenow, J.Z. 1889. Über Die Konstitution Der Salzlösungenauf Grund Ihres Verhaltens Zu Kohlensäure. Z. Physik. Chem. 4:117-125.

[2] Carter, J.S., Hardy, R.K. 1928. The salting-out effect: influence of electrolytes on the solubility of m-cresol in water. J. Chem. Soc. 131:127-129.

[3] Baker, E. G. 1959. Origin and Migration of Oil. Science. 129:871-874.

#### TU 297

##### Photo-transformation of 2,3,7,8-TCDD in presence of natural organic matter studied by in vitro bioassay

M. Bittner<sup>1</sup>, P. Macíková<sup>1</sup>, J.P. Giesy<sup>2</sup>, L. Bláha<sup>1</sup>

<sup>1</sup>Research Centre for Toxic Compounds in the Environment (RECETOX), Brno, Czech Republic

<sup>2</sup>Department of Biomedical Veterinary Sci. and Tox. Centre, Univ. of Saskatchewan, Saskatchewan, Canada

2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) as a representative of hydrophobic organic compounds (HOCs, frequent anthropogenic environmental pollutants comprising also various pesticides), can cause many adverse effects in organisms. Activation of arylhydrocarbon receptor (AhR) can be very important mechanism of toxicity for so called "dioxin-like" HOCs. Natural organic matter (NOM), being naturally occurring compounds (up to 50 mg/L in waters), occurs together with HOCs in contaminated water. Beside other important ecological properties, NOM serves as a natural source of reactive oxygen species that are formed after NOM irradiation. Direct photolysis of HOCs is a very important way of their degradation in the aquatic environment. Nevertheless, oxygen species, formed after HS irradiation, can theoretically enhance the photochemical degradation of HOCs. In present study, we have assessed the ability of various NOM concentrations to enhance photo-degradation of TCDD. Aqueous TCDD+NOM