

## Completed projects (1999-2010)

### **Sources, transport and fate of organic contaminants in the anaerobic aquifer of the Oderbruch, Germany**

The behaviour of the three organophosphorus flame retardants and plasticizers tributyl phosphate (TBP), tris(2-chloroethyl)phosphate (TCEP) and tris(2-butoxyethyl)phosphate (TBEP) during infiltration of river water to ground water was investigated. The monitoring site was the River Oder and the adjacent Oderbruch aquifer. From March 2000 to July 2001, 76 ground water samples from monitoring wells located close to the River Oder and nine river water samples were collected. Additionally, influent and effluent samples from local waste water treatment plants and samples of rain water and roof runoff were collected. All samples were analyzed by solid-phase extraction (SPE) followed by gas chromatography-mass spectrometry (GC-MS).

TBP, TCEP and TBEP were detected at mean values of 622, 352 and 2955 ng/L, respectively, in municipal waste water effluents. These findings point to a major input of these compounds into the River Oder by municipal waste water discharge. The concentrations of TBP and TBEP decreased downstream the River Oder possibly due to aerobic degradation. TBP, TCEP and TBEP were detected in ground water influenced predominantly by bank-filtered water. This demonstrates a transport of organic compounds by river water infiltration to ground water. TBP, TCEP and TBEP were also detected in rain water, roof runoff and ground water predominantly influenced by rain water infiltration. This hints to an input of these compounds to ground water by dry and/or wet deposition after atmospheric transport. TBP, TCEP and TBEP were also detected in parts of the aquifer at 21 m depth indicating low anaerobic degradation rates.

**Partners:** Dr. Christoph Merz, **Leibniz-Centre for Agricultural Research (ZALF)**, Müncheberg, Germany

**Funding:** German Research Foundation, 1999-2002

### **Occurrence of 4-Nonylphenol in rain and snow**

The aim of this project was to study the occurrence of the endocrine disruptor 4-nonylphenol (4-NP) in rain and snow. In July and November 2001 and in January 2002, rain and snow sampling was conducted at different urban, suburban and rural areas in Germany and Belgium. The mean concentration of 4-NP in rain water and roof run off was 0.253 µg/L (n=8) with a higher mean concentration in suburban areas at 0.534 µg/L and considerable lower mean concentrations in rural and urban areas of 0.099 and 0.062 µg/L, respectively. The mean concentration of 4-NP of 0.099 µg/L (n=3) was much lower in summer rain than in winter rain of 0.346 µg/L. In snow samples, 4-NP was detected with a mean value of 0.242 µg/L (n=8). A higher mean value of 4-NP in snow at 0.478 µg/L (n=4) was found at urban sites whereas in snow from suburban areas the mean concentration of 4-NP of 0.030 µg/L (n=2) was much lower. 4-NP was never detected above its determination limit in snow samples from rural areas.

**Partners:** Dr. Christoph Merz, **Leibniz-Centre for Agricultural Research (ZALF)**, Müncheberg, Germany

**Funding:** German Research Foundation, 1999-2002

### **Interactions of volatile organic compounds (VOC) with non-growing and growing ice crystals: Importance of below-cloud and in-cloud scavenging for atmospheric deposition**

New experimental approaches have been developed to study the uptake of gaseous volatile organic compounds (VOC) by non-growing and growing dendritic ice crystals. First, separately grown ice crystals were exposed inside a walk-in cold chamber (WCC) to gaseous benzene and alkylated benzenes for different exposure times at -20°C. Concentrations in the melted ice were determined using solid phase microextraction (SPME) and GC-MS. Secondly, ice crystals were grown from an ambient airflow in the presence of the gaseous VOC inside the WCC for 22 hours at different temperatures. During uptake experiments, concentrations in the gas phase were controlled using glass sampling tubes packed with activated charcoal and subsequent extraction using carbon disulfide and GC-MS.

Results of the laboratory experiments with non-growing ice crystals revealed that gas uptake by ice surfaces is negligible for the atmospheric removal of benzene and alkylated benzenes. It is therefore unlikely that the occurrence of these compounds in precipitation is due to below-cloud scavenging. In contrast, uptake from the gas phase was observed for gaseous lower volatile alkylated benzenes. The uptake increased with decreasing air temperatures. Since most precipitation is formed via ice in the troposphere at low temperatures, in-cloud scavenging is an important removal process for those compounds from the atmosphere

**Partners:** Dr. Subir Mitra, Dr. Karoline Diehl, Institute for Atmospheric Physics, **Johannes-Gutenberg-University Mainz**, Germany, Prof. Dr. Stephan Borrmann, **Max-Planck-Institute for Chemistry**, Mainz, Germany

**Funding:** German Research Foundation, 2002-2007

### **Occurrence of volatile organic compounds (VOC) in snow at the High Altitude Research Station Jungfraujoch, Switzerland (3580 m asl)**

Time-resolved snow/ice samples were collected at the High Altitude Research Station Jungfraujoch (JFJ) (3580 m asl) in the Swiss Alps during the two international field campaigns CLACE 4 and CLACE 5 (CLOUD and Aerosol Characterization Experiment) in 2005 and 2006, respectively. The time spans between sampling were dependent on the occurrence of snow events. The number of precipitation-free days prior to sampling were estimated via cloud events identified using a Particulate Volume Monitor (PVM-100, Gerber Scientific) by the Paul Scherrer Institute during CLACE 4 and by the Leibniz-Institute for Tropospheric Research during CLACE 5. Snow/ice crystals were collected during single snow events using a custom-built collector (stainless steel) with a sampling area of 0.2 m<sup>2</sup>. The collector was installed at the measurement platform on the research station Sphinx at JFJ to ensure it was in the clouds during snowfall. Snow/ice samples were collected using a custom-made device (stainless steel) from the first few centimeters of the snow surface during snowfall and pressed into 10 mL brown glass vials. Sample vials were filled up to the septa, giving volumes of melted snow/ice samples between 1.7 and 6.7 mL. Melted snow/ice samples were analyzed by solid phase dynamic extraction (SPDE) and GC-MS. The results were examined with reference to the meteorological parameters, e.g. air temperature, wind direction and wind speed, which were obtained from a monitoring station of the Swiss Meteorological Institute as a part of the Swiss Air Pollution Network (NABEL) and the Global Atmospheric Watch Program (GAW).

The detection of benzene, alkylated benzenes, trichloroethylene and tetrachloroethylene in snow/ice collected directly in clouds with concentrations between 10 and 766 ng/L indicated that in-cloud scavenging plays an important role in the removal of these compounds from the atmosphere. Generally, there was a tendency for higher concentrations after longer precipitation-free periods, suggesting that higher concentrations in snow/ice may be caused by a washout effect of precipitation. High concentration variations in snow/ice samples collected at the same time at the same place highlighted the heterogeneous nature of snow/ice

**Partners:** Dr. Ernest Weingartner, **Paul-Scherrer Institut (PSI)**, Villingen, Switzerland, Dr. Paul Connolly, **University of Manchester**, UK, Dr. Stephan Mertes, **Leibniz-Institut for Tropospheric Research (IFT)**, Germany, Prof. Dr. Stephan Borrmann, **Max-Planck-Institute for Chemistry**, Mainz, Germany, Dr. Joachim Curtius, Institute for Atmospheric Physics, **Johannes-Gutenberg-University Mainz**, Germany, Prof. Dr. Stephan Weinbruch, Institute for Applied Geosciences, **Technical University of Darmstadt**, Germany

**Funding:** German Research Foundation, 2004-2006

### **Organic pollutants in snow and ice from Antarctica: long range transport and deposition processes**

Long range transport (LRT) of organic pollutants (OP) from temperate zones to the polar region is an important phenomenon demonstrating the persistence of organic chemicals in the environment. To evaluate the fate of OP in the environment interactions of chemicals with ice and snow play an important role especially in areas characterized by low temperatures. Firn samples attributed to the period between 2002 and 2005 were collected from a snow pit on the Ekstrom Shelf Ice in the Weddell Sea (70843.80S, 8825.10W). Low-volume meltwater samples (5 mL) were extracted by SPME and analyzed for polycyclic aromatic hydrocarbons (PAHs) by GC-MS.

PAH concentrations in snow were found within the range of 26–197 ng/L. The most prevailing substances were determined to be naphthalene, 1- and 2-methylnaphthalene, acenaphthylene, acenaphthene and phenanthrene, with naphthalene accounting for an overall mean of 82% of total PAH. Potential emission sources of PAHs in snow were studied using back-trajectory statistics and available emission data of combustion sources in and around Antarctica. The distance to the sources (ships and research stations) in this region was found to control the snow PAH concentrations. There was no indication for intercontinental transport or marine sources.

**Partners:** Prof. Dr. Jana Klanova, **Masaryk University**, Brno, Czech Republic, Centre for Environmental Chemistry and Ecotoxicology (RECETOX), Prof. Dr. Gerhard Lammel, **Max Planck Institute for Meteorology**, Hamburg, Germany

**Funding:** Ministry of Education, Youth and Sports of the Czech Republic, Ministry of Environment of the Czech Republic, European Commission (7th FWP R&D 226534, ArcRisk, and ERASMUS program), 2007-2009

### **Occurrence and distribution of 1,3-benzothiazole in wastewater and in river water of the Schwarzbach watershed (Germany)**

1,3-benzothiazole, a heterocyclic compound produced mainly by sunlight photolysis of 2-mercaptobenzothiazole, has been measured at 15 river sites in the Schwarzbach watershed as well as in untreated and treated wastewater samples. 1,3-benzothiazole has been detected in all analysed wastewater and river water samples. This corroborates the ubiquitous occurrence of 1,3-benzothiazole in the aqueous environment. Rather continuous 1,3-benzothiazole concentrations over a wide range of discharge indicate that dilution along the mainstream is negligible and, thus, supporting the hypothesis that paved surface runoff during rain events is an important 1,3-benzothiazole source not only for wastewater influent but also for river water. This is supported by detecting the highest 1,3-benzothiazole concentrations at sampling locations close to the dense highway network around the city of Frankfurt. Since 1,3-benzothiazole has been also detected in river water collected from locations that are clearly unaffected by wastewater effluent discharge, surface runoff must be considered as a diffuse source of 1,3-benzothiazole in river water.

**Partners:** Dr. Tillmann Gocht, Centre for Applied Geosciences, **University of Tuebingen**, Germany, Dr. Jörg Klasmeier, Institute of Environmental Systems Research, **University of**

Osnabrueck, Germany, Dr. Rolf Goetz, **Sewage Treatment Plant of the City Frankfurt am Main**, Germany.

**Funding:** Research Pool of the University of Osnabrueck, 2007-2009

### **Sorption of ortho-phenylphenol to soil**

Conflicting sorption coefficients for ortho-phenylphenol (OPP) have been reported in the literatures, which resulted in the conflicting assessments on OPP mobility in soil. To ascertain the sorption coefficient of OPP, batch experiments were performed based on OECD guideline 106, using three types of soils. SPME and GC-MS were applied for determination of OPP concentration in the liquid phase. The sorption isotherms obtained for all three soils under equilibrium conditions were described well, assuming linear sorption. The organic carbon normalized distribution coefficients ( $K_{oc}$ ) ranged from 894 to 1703 L/kg, which suggested that OPP is moderately mobile in soil. The results also showed that the  $K_{oc}$  value of OPP can be predicted precisely from the octanol-water partitioning coefficient ( $K_{ow}$ ), whereas it was underestimated by one order of magnitude when water solubility is used.

**Partners:** Prof. Dr. Till Eggers, Ecology Group, Department of Biology/Chemistry, **University of Osnabrueck**, Germany, Dr. Chunli Zheng, School of Energy and Power Engineering, **Xi'an Jiaotong University**, Xi'an, China

**Funding:** German Academic Exchange Service, 2009-2010.

## **7. Current projects (2007- present)**

### **Atmospheric deposition of organophosphate flame retardants and plasticizers to soil**

Due to their technical and physico-chemical characteristics, organophosphate flame retardants and plasticizers (OFR) are widely utilized in rubbers, textiles, upholstered furniture, lacquers, plastics, building materials and electronic equipment. The global consumption of OFR estimated to 186 000 tons in 2001, increased by almost 10% for five years and it is still growing in the last years, due to the ban of brominated diphenyl ethers (BDE) - penta-BDE and octa-BDE- in the EU. This gives cause for concern, because some OFR are persistent and have toxic effects. Individual data on the occurrence of several OFR in water and air has increased continuously over the last decade. Data on the occurrence of OFR in soils, however, are rather limited. The aim of this project is to develop analytical methods for analyzing OFR in soil and precipitation using Soxhlet Extraction, SPME and GC-MS. These methods are applied to determine concentrations of OFR in soil and precipitation collected from different sites in Germany to study OFR-pollution of soils from diffuse atmospheric sources and to identify the main deposition processes.

**Partners:** Prof. Mirjana Vojinovic Miloradov, Department of Environmental Engineering and Occupational Safety and Health, **University of Novi Sad**, Serbia

**Funding:** German Federal Environmental Foundation (DBU), 2010-2011

### **Toxicity of sediments from coasts of the Baltic Sea, the North Sea and the Mediterranean Sea**

In preliminary studies some indications have been found for the first time that the toxicity of beach sand is caused by organic contaminants like polycyclic aromatic hydrocarbons (PAHs). The aim of this project is to monitor and evaluate the chemical contamination and toxicity of sediments from coasts of the Baltic Sea, the North Sea and the Mediterranean Sea. A dataset is provided as a basis for risk assessment of beach sands in this area. During

August-October 2011 monitoring campaigns are performed where beach sand samples are collected. A combination of biotests with oyster larvae and chemical analyses based on Soxhlet extraction and GC-MS is applied to allow the determination of the bioavailable fractions of PAHs sorbed on the sediments that are causing the toxicological effects. Multivariate statistical analyses are applied to identify the sources of PAHs.

**Partners:** Dr. Francois Galgani, **Institut français de recherche pour l'exploitation de la mer** (Ifremer), Laboratoire LER/PAC, Bastia, Corsica, France

**Funding:** Institut français de recherche pour l'exploitation de la mer (Ifremer), Laboratoire LER/PAC, Bastia, Corsica, France, 2011-2012.

### **Emissions, fate and effects of organic plastic additives (OPAs) from plastic debris in landfills and the marine environment**

This project investigates the release, distribution and fate of organic plastic additives (OPAs) from polymers into water to assess the chemical impact of such contaminants on water quality and ecosystems. Leaching experiments with polymers and batch experiments with sediments are performed to provide leaching rates and distribution coefficients for different OPAs. The migrating chemicals are determined in the aqueous phase using SPME/GC-MS. The influence of different factors such as polymer type, additive polarity, weathering, pH, temperature, ionic strength and organic carbon content on leaching behaviour is studied. Exposure concentrations of OPAs in sea water are estimated by considering quantities of marine plastic debris and experimentally determined fate parameters.

In addition, microplastics are extracted from sediments collected from the Baltic Sea, the North Sea and the Mediterranean Sea and OPAs and polymers are identified using Thermodesorption-pyrolysis-GC-MS (TD-PyGC-MS). In addition, biotests (daphnia magna, fish eggs) are performed with marine plastic debris to assess the toxicity. The results of this project contribute to a Collaborative Project under the 7th Framework Programme of the EC, called ENV 2012 – 6.2.4 "Management and potential impacts of litter in the marine and coastal environment " coordinated by Ifremer, Bastia, Corsica.

**Partners:** Dr. Francois Galgani, **Institut français de recherche pour l'exploitation de la mer**

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**Funding:** Institut français de recherche pour l'exploitation de la mer (Ifremer), Laboratoire LER/PAC, Bastia, Corsica, Research Pool of the University of Osnabrueck, 2010-2012.

### **Occurrence of corrosion inhibitors in the aquatic environment: sources, fate and risk assessment of 1H-benzotriazole and tolyltriazoles**

Benzotriazoles (BT) as 1H-benzotriazole (1H-BT), 5-methyl-1H-benzotriazole (5Me-BT), and 4-methyl-1H-benzotriazole (4Me-BT) are frequently used as corrosion inhibitors in dish washer detergents and aircraft de-icing/anti-icing fluids (ADAFs). Discharge of treated municipal waste water and controlled over-runs of combined waste water sewers are potential point sources for BT in rivers. This project was established to achieve the following aims: (i) the development of an analytical method based on SPE/GC-MS for the detection of BT in river water, waste water and products. This method should be relatively simple, cheap

and quick because of numerous samples, and both tolyltriazoles-isomers (4Me-BT and 5Me-BT) should be quantified separately, (ii) the evaluation of contribution of BT-input originating from ADAFs used at Frankfurt Airport and dishwasher detergents into rivers of the catchment area of the River Schwarzbach, (iii) the determination of spatial and temporal variability of concentrations and mass flows in the River Schwarzbach and its tributaries, (iv) the assessment of persistence and eco-toxicological risk potential of BT in the aquatic environment, and (v) validation of the exposure concentrations of all three substances predicted by the GREAT-ER model (Geography-referenced Exposure Assessment Tool for European Rivers) for the selected catchment.

**Partners:** Prof. Dr. Jörg Oehlmann, Department Aquatic Ecotoxicology, Institute for Ecology, Evolution and Diversity, **Johann Wolfgang Goethe University Frankfurt**, Germany, Prof. Dr. Henner Hollert, Department of Ecosystem Analysis, Institute for Environmental Research, **RWTH Aachen University**, Germany, Prof. Dr. Michael Matthies, Dr. Jörg Klasmeier, Dr. Jürgen Berlekamp Institute of Environmental Systems Research, **University of Osnabrueck**, Germany

**Funding:** German Federal Environmental Foundation (DBU), 2007-2011.