



Institute of Hydrochemistry

**Chair for Hydrogeology,
Hydrochemistry and
Environmental Analytical
Chemistry**

Annual Report

2002



U. Pöschl, C. Haisch, R. Nießner, M. Weller, T. Baumann, U. Panne, D. Knopp

Institute of Hydrochemistry
Chair for Hydrogeology, Hydrochemistry and Environmental Analytical Chemistry
Technische Universität München
Marchioninstr. 17

D-81377 München

Editor: Dr. Thomas Baumann

Editorial

Dear Friends and Colleagues,

The year 2002 was a troubled one: Full of hope and disappointment.

Our international standing is still strong. Based on the excellent work done in the various working groups at the institute we continued to become present in the A-page of various leading journals (e.g. ES&T, or Anal. Chem.). One of the hot topics has been magnetic resonance imaging, a tool which receives increasing acceptance for direct visualization of dynamic processes in aquifer materials. (Well, the director's session in the university hospital's computer tomograph machine seems to have been very inspiring...)

The long lasting story on diesel exhaust monitoring by photoacoustic spectroscopy has seen a major breakthrough. Funded by the leading diesel car manufacturers the applicability of our PASS ("photoacoustic soot sensor") under field conditions has been demonstrated on many occasions. The perspectives for a transfer to a routine application in motor test stands (at least) within Germany are bright. Also, the microarray chip technology, tailored for the detection of allergen contact of human beings, was successfully demonstrated. We will certainly continue this way. Finally, high parallel throughput analysis might be an interesting alternative to serial high throughput analysis. Here, our expertise in developing electrooptical and mechanical hardware is our big advantage. Sometimes, even I am surprised on what our mechanical workshop created so far.

Disappointing on the other hand are the numbers of diploma students interested in studying Analytical Chemistry. The numbers dropped down to two students, and there is still no improvement to be seen. Consequently the number of Post Docs working at the institute increased. In the meantime a ratio of one-to-one is seen for PhD students and Post Docs from all around the world. On one hand, a Post Doc introduces new experience, knowledge and culture to a possibly static institute, but a long lasting scientific evolution on a time scale of about 10 years is only possible with young diploma students, pursuing their scientific love of adventure after a PhD being back at the old institute for a second qualification. Disappointing is the general research funding situation in Germany, too. After strong 10 years with about € 1 - 2 millions support per year, we experienced the first breakdown in the national funding. Already promised contracts became withdrawn by a single phone call from the ministry. Without our multinational relationships and strong funding from the German Research Society (DFG), European Union, and contributions from industry and the State of Bavaria as well, a very dark future would be at the horizon.

In the year 2002 we lost a long lasting coworker of our institute: Dr. Dagmar Weil. Already retired, she passed away by a sudden heart attack. Together with her husband she formed the highly acknowledged backbone of the organic trace analytical chemistry of the institute. We will certainly not forget her. Dr. Manfred Baumann, our senior hydrogeologist, decided to apply for early retirement. On occasion of a large festivity his merits received wider attention. Nearly no well within Bavaria (spa or mineral water), where he was not connected with. Numerous spas and health resorts rely on his expertise. In the meantime Dr. Thomas Baumann, already leading the hydrogeological research group, took over his tasks as well.

Of course, the staff of the Institute and me also experienced positive events in the year 2002. First, Dr. Ulrich Panne successfully finished his "habilitation" and



became a lecturer for “Analytical Chemistry” at the Technical University of Munich. Rewarding his achievements in laser plasma spectroscopy, he received the prestigious Karl-Martens-Prize for Analytical Chemistry from the National Institute for Material Research & Testing, Berlin, in November.

Our MRI Post Doc, Dr. Nikolaus Nestle, was granted the *venia legendi* for “Experimental Physics” at the University of Leipzig, and became appointed professor at the newly established University of Bolzano (Italy) and junior professor at Technical University of Darmstadt in December.

A honourable call to a chair for Analytical Chemistry at University of Dortmund, connected with a directorship at the Institute of Spectrochemistry & Applied Spectroscopy (ISAS) was given to Prof. Nießner. The extremely enervating negotiations took almost the whole year 2002, and it was not before early January 2003 that he finally decided to stay in Munich. The approved and successful structure, and especially the individual permanent contribution of all coworkers – the human resources of the Institute – weighted higher than a very generous offer from the State of North Rhine Westphalia.

Keeping this context, it is my great pleasure to say thanks to all who supported our work. Namely the coworkers deserve greatest honours this year.

Reinhard Nießner
Head of the Institute

1 Research

1.1 Hydrogeology

1.1.1 Applications of MRI in Hydrogeology

Funding: DFG, Ba1592/1-1

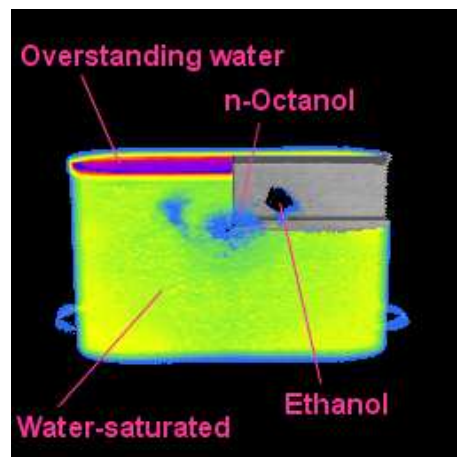
Cooperation: Department of Neuroradiology Großhadern, LMU, Department of Radiology, University of Ulm

Understanding transport of water and contaminants in the unsaturated zone and in aquifers is a key challenge in environmental risk assessment, environmental remediation and water technology. Presently, most of our knowledge in this field comes either from field data or from column experiments. On the basis of breakthrough curves for contaminants obtained in such experiments, transport, filtration (or sorption) and remobilisation for the respective contaminants are computed on the basis of models. As the actual profiles of the substance concentrations and the flow velocities of the contaminants in the column or the underground are not known in such an experiment, a direct verification of the assumptions made for modelling the processes is not possible.

Non-invasive tomographic observations of transport processes in column experiments offer the possibility to observe concentration profiles and transport properties in columns directly. In principle, two techniques are available for such experiments: MRI and X-ray techniques. In the DFG-funded project running 2001 and 2002, we have succeeded in exploring the potential of MRI in studying a range of different scenarios of water and contaminant transport and environmental remediation:

With regard to the binding of sorptive heavy metal ions in sand sediments under transient and static conditions the enrichment of ions from a dilute solution on the pore surfaces, the traces left by the propagation of a locally injected higher concentration of heavy metal ions with the water flow, the remobilization of adsorbed heavy metal ions upon changing hydrochemical conditions, and the long-term stability of adsorbed ions in sand were investigated. The amounts of heavy metal ions used in these studies were typically in the mg-range or even below. Of the distribution of these ions, 3D volume data with a spatial resolution of less than 2 mm^3 and with a temporal resolution of minutes could be acquired for sand columns with a volume of several litres. In the long-term studies, indications for slow sorption processes with much higher sorption capacities could be observed.

A second topic was the fate and impact of non-aqueous phase liquids (NAPL) in sediments. Depending on the NAPL under consideration, relaxation time contrast and diffusion contrast are available between the water and the NAPL. This is especially the case for high-viscosity NAPL. For low-viscosity NAPL such as MTBE, paramagnetic contrast agents are necessary to visualize the NAPL within the sediment. In both cases, it is possible to track the distribution of NAPL blobs with sizes in the range of several $10 \mu\text{L}$ in the sediment with a time resolution on the order of 1 min. When working with contrast agents, time resolutions on the order of 10 s could be achieved. NAPL transport phenomena were studied in saturated static and flow systems and in static unsaturated columns. The figure shows a 3D rendering of an alcohol flooding experiment in a static column in which a model contamination with n-octanol is dissolved in a density-driven ethanol flow. The sand bed in the experiment had a volume



of about 1 L and the originally injected quantity of n-octanol was about 5 mL.

As an ongoing topic, the possibilities for a direct measurement of filtration and transport of colloidal substances in sediments were assessed. Current data suggests a limit of detection of less than 100 μg superparamagnetic colloids with the experimental conditions as described above.

Direct observation of chemical profiles during a column transport experiment not only permits the identification of possible local deviations from model assumptions but also enables direct studies of the action of heterogeneity and of non-equilibrium processes in the column. These possibilities offer an interesting potential for fast laboratory-scale tests of remediation measures or for risk assessment studies on such models.

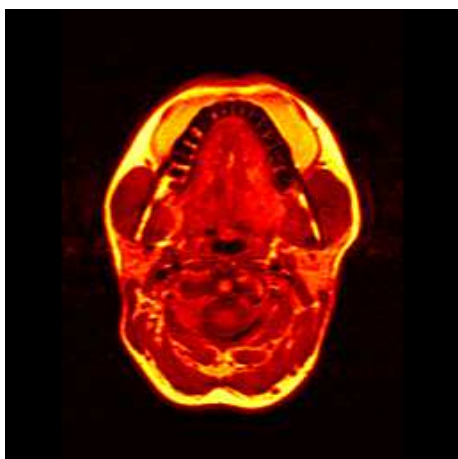
(N. Nestle, T. Baumann)

1.1.2 NMR and MRI studies on oxygen super-saturated water

Funding: IWC

Cooperation: Department of Neuroradiology Großhadern, LMU, Department of Radiology, University of Ulm

In recent years, a rising number of different table waters supersaturated with oxygen have hit the market with claims of both positive health effects and an increase in athletic performance. Presently, a rigorous scientific verification of these benefits is still an open question.



There are two main challenges for balneological research in this field, starting from the determination of oxygen content in bottled and open oxygen supersaturated table waters, the fate of oxygen supersaturated water in the body after peroral uptake in the body.

For both questions, NMR techniques can provide valuable insights. As molecular oxygen is paramagnetic, the relaxation time of water depends on the dissolved oxygen concentration. NMR relaxometry on oxygen supersaturated waters is essentially a contactless method and thus eliminates the problems with outgassing of oxygen that affect established electrochemical and wet-chemical oxygen determination techniques.

The relaxation time changes brought about by dissolved oxygen also can provide a contrast in MRI experiments. Preliminary in-vivo studies of oxygen supersaturated water in the mouth and the stomach indicate that a considerable oxygen concentration actually reaches the stomach in drinking of oxygen-supersaturated water. Oxygen losses in waters supersaturated with both CO_2 and O_2 are much faster than those in water supersaturated with oxygen only, both during storage in open vials and in the human body.

(N. Nestle)

1.1.3 Exploration of Ground Water and Mineral Water

Funding: State of Bavaria

The year 2002 saw a major change in the structure of the Hydrogeology group at the IWC. Dr. Manfred Baumann, who has been responsible for the exploration of mineral waters for many years, retired and passed his duties to Dr. Thomas Baumann, who has been heading the hydrogeology research group since 1994 and who started his career as a hydrogeologist with M. Baumann.

While we continue to provide our analytical and consulting services to spas and health resorts, the range of services is expanded in the field of geochemical modelling and tracer applications.

(*T. Baumann*)

1.1.4 Electrochemical Cleanup of Water Treatment Residues

Funding: BayFORREST F179

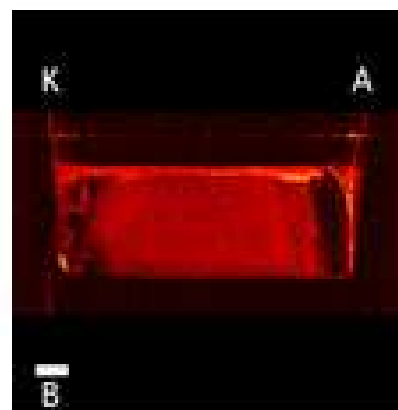
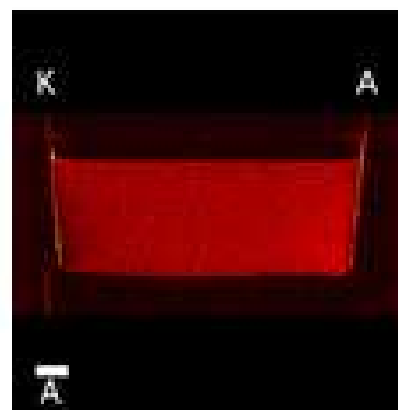
The treatment of drinking water produces 125.000 t (dry matter) of waterwork sludge in Germany each year. 50% of these sludges are deposited on landfills, 7% are fed into the sewer or directly into the the waste water treatment plants, 4% are used for cement, and brick production, 16% are used otherwise. For 23% of the waterwork sludges, the utilisation is unknown.

The concentrations of heavy metals and organic contaminants in these sludges are often too high for a discharge into a sewer or directly into the waste water treatment plants, although this kind of “recycling” would imply some advantages for the waste water treatment plants: First, an addition of metal salts for phosphate precipitation is not necessary due to the relatively high iron content in the waterwork residues. An addition of lime-milk is also generally not necessary due to the high lime concentration in the waterwork sludges and the desulphurisation of the sewage gas is not needed due to the high iron concentrations in the sludges. A consequence of the waiving of precipitants is the prevention of the salination of the recipient stream.

The purpose of this project is the geochemical and mineralogical characterisation of waterwork residues and the removal of heavy metals and organic contaminants from these residues with the aid of electrokinetic methods. After the cleaning the residues can be fed into the sewer or into sewage treatment plants. The electrokinetic technique is based on electrophoresis, electroosmosis and electrochemical processes at the electrodes. Numerous electrokinetic experiments with synthetic and real sludges were done, some of them under control of magnetic resonance imaging (MRI). The MRI pictures show the changes of the homogeneous signal in the waterworks residue after applying a DC current. Close to the cathode the structure of the residue changes. Close to the anode the signal decreases, which might be due to the transport of paramagnetic ions.

The results show that the removal of metal ions from waterwork residues by electrochemical treatment is possible, in principle. However, the matrix is much more complex than previously described applications in soil or wastewater treatment sludges. Therefore additional fundamental research is needed to assess the feasibility of electrochemical techniques for field scale applications.

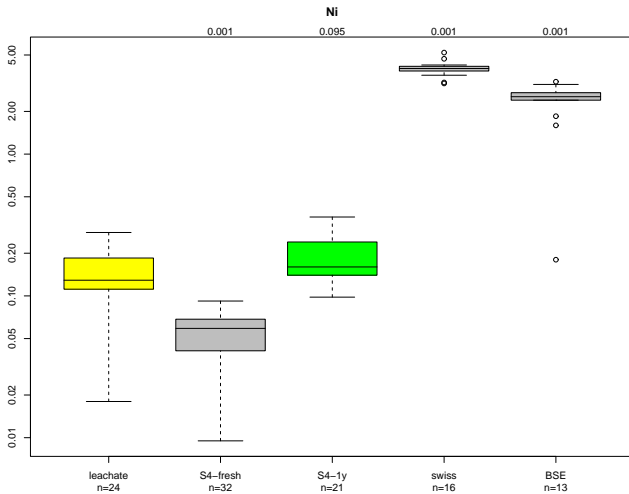
(*D. Spangenberg, T. Baumann*)



1.1.5 Statistical Methods for the Assessment of Leachate Concentrations at the Point of Compliance

Funding: BMBF 02WP0175

In order to protect the groundwater against pollution from contaminated sites, the German Guideline on Soil Protection stipulates, that the source strength of contaminants (Quellstärke) must be investigated prior to the deposition of partly hazardous material such as bottom ash from municipal solid waste incinerators.



With respect to the heavy metal content in the bottom ash, it is important to determine conclusions to the environmental impact of the bottom ash material. Several authors have described a dependency of heavy metal concentration from the pH value and the storage time. Because bottom ash is often used in road construction, it is important to assess the mobility of heavy metals in contact with water under different conditions. In order to describe the potential risk of a bottom ash material transferred into nature, it is necessary to find a proper way of extraction describing the way of leaching under natural conditions.

In the current project we could show by statistical methods (multivariate regression, factor analysis, clustering), that the heavy metal concentration in the leachate from 28 different incineration plants

all over Germany is neither influenced by any technical parameter of the incineration plant nor by the waste composition and amount. In toto, bottom ash can be described as a rather homogeneous material. There is statistical evidence that the heavy metal concentrations in three different bottom ash disposals can be approximated with the concentration in the leachate from the DEV-S4 extraction test performed with bottom ash, stored for one year prior to the test. The results from the other elution tests such as the soil saturation extract, the Swiss elution test as well as the DEV-S4 with 'younger' bottom ashes seems to overestimate the dissolvable heavy metal content in the bottom ash material. The figure shows the Ni²⁺ concentrations obtained with the different elution tests.

Available data suggests an exponential decrease of leachate concentrations with time which is very similar to the observed exothermal reactions in the MSWI bottom ash material. This knowledge gives us the possibility to predict the heavy metal concentration in the S4 extract at any time of bottom ash aging. The underlying hypothesis is, that the carbonization of the bottom ash, which was measured independently, not only reduces the availability of reactive phases in the bottom ash, thus leading to a decrease of the heat production. These coatings also reduce the availability of the metal ions, thus leading to reduced leachate concentrations.

(R. Klein)

1.1.6 In Situ Monitoring for Soil and Water by Infrared Sensing

Funding: EU EVK1-CT-1999-00042

Cooperation: Fraunhofer-Institut für Physikalische Messtechnik, Freiburg; Technische Universität, Wien; Universität für Bodenkultur, Wien; Tel Aviv University; Université de Rennes; CSIC, Barcelona

From landfills emanates a high latent and sometimes very real potential for environmental hazards, since many of these landfills are presently not encapsulated according to with state of the art technologies. This is caused by nonexistent flexible membrane linings, missing mineral base linings or the lack of seepage collecting and treatment systems. Despite of numerous efforts for the reduction and prevention of waste, the production in Europe still increases. Therefore nearly 60% of domestic waste and 68% of hazardous waste are still deposited in landfills. One can assume that ground- and surface water in the surrounding of landfills, is exposed to the risk of contaminations for a long time. Consequently there are increased requirements for a continuous control and surveying system of landfill contaminations. But not only landfills, also abandoned waste sites need to be screened and monitored for possible release of organic matter.

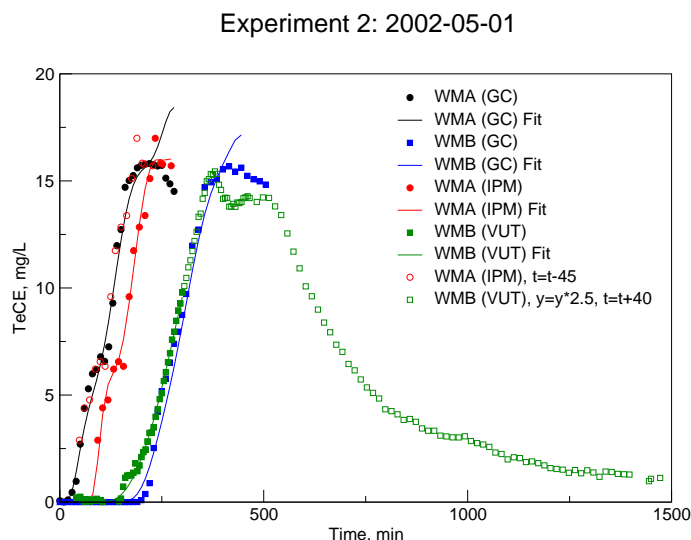
Within the scope of the IMSIS project (In Situ Monitoring of Landfill Related Contaminants in Soil and Water by Infrared Sensing) a fibre-optic evanescent wave sensor system for the detection of organic pollutants (BTEX, PAH, etc.) in groundwater and seepage is developed. Besides, the IMSIS system could be used for the screening of landfills and abandoned sites.

The accuracy, durability, and the response times of the IMSIS sensor were investigated with laboratory and pilot scale tests. A typical breakthrough curve as obtained with the different sensor systems and by conventional GC analysis is shown in the figure. It has to be noted, that only the sensor systems were able to give information on the breakthrough on-line, whereas GC-analysis took more than a month to complete all measurements.

The IMSIS system is to be used for short- to medium-term surveillance of groundwater monitoring wells, or be fixed for long-term surveillance. In addition, the system is to be upgraded at existing sites and to be installed at newly built landfills in Europe.

Particularly, at the planning of clean-ups and the critical phase of decontaminations, a flexible field measuring system is useful for a fast and steady contribution of analytical data.

(M. Alte)

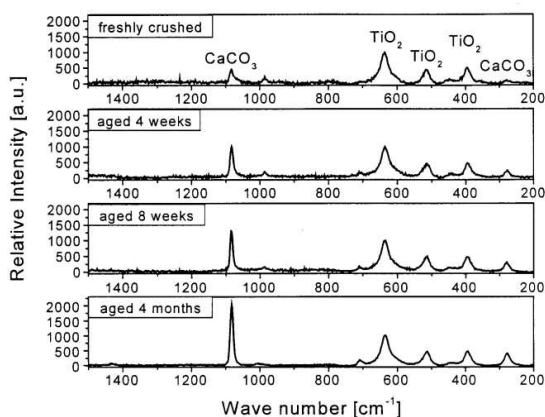


1.2 Hydrochemistry

1.2.1 Photocatalytic Atrazine Degradation by Synthetic Minerals, Atmospheric Aerosols and Soil Particles

Funding: BayFORUV C2

Photocatalyst-modified cements are discussed for various applications in building and environmental technology ranging from self-cleaning surfaces to solar powered remediation devices for polluted waters. In this project the photocatalytic atrazine degradation by white Portland cement samples modified with different semiconducting oxides (TiO_2 in form of Degussa P25, Hombikat 100 UV, anatase Jenapharm, and ZnO) was used as a model reaction to investigate a possible application of modified cements for the degradation of pollutants on building surfaces. The cement mixtures were also characterised with respect to hydration kinetics and compressive strength which are relevant for possible construction applications.



to defined ageing conditions and carbonation was followed directly by laser Raman spectroscopy (see figure). Photocatalytic activity decreases during ageing of the hardened cement pastes. However, aged cement modified with Degussa P25 or Hombikat 100 UV exhibited at least three fold degradation efficiency compared to unmodified cement. Taking into account the sufficient radiation over a long time in the environment, degradation of harmful substances by modified cement samples could contribute considerably to the abiotic degradation of pollutants in the environment.

(M. Lackhoff)

Particle suspensions containing 1 $\mu\text{g/L}$ atrazine were irradiated with a sun simulator, and the atrazine degradation was monitored by ELISA (enzyme-linked immunosorbent assay). The atrazine degradation followed a first order kinetic and the obtained rate coefficients were compared with the degradation rate by unmodified cement samples.

A significant enhancement of the photocatalytic activity due to the addition of 10 wt% TiO_2 in the form of Degussa P25 and Hombikat 100 UV to Portland cement was observed, whereas addition of ZnO and coarse grained anatase showed no effect. The primary crystal particle size of the semiconductor seems to have significant influence on the photocatalytic efficiency of the modified samples. Additionally, modified cements were subjected

1.3 Bioanalytics I

1.3.1 Automated Immunoassay System for Continuous Air Safety Control (AISAC) and its Application to Air Pollution and Aero-allergen Monitoring

Funding: EU IC15-CT-98-0322

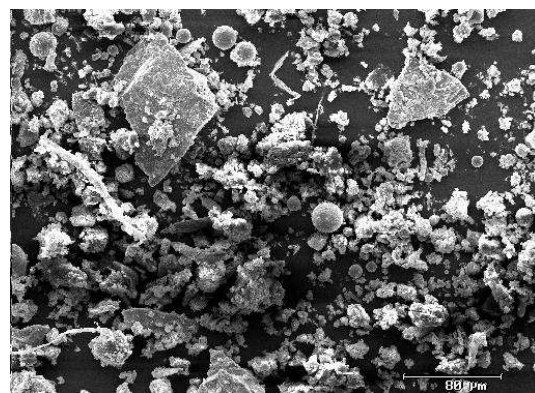
Cooperation: Institute Pasteur (Paris, France), University Pècs (Pècs, Hungary), Academy of Sciences (Prague, Czech Republic), EXBIO Praha (Prague, Czech Republic)

In recent years, an increased prevalence of allergic conditions has been observed in developed countries. In particular, the ability of combustion products to modulate the immune system has now been established. The rapid growth in road traffic in our cities has given rise to new pollutants and new concerns. Among the pollutants which are suspicious of causing an increase in allergic airway diseases are diesel exhaust particles of special interest because of their widespread occurrence.

These particles consist mainly of a non-extractable core with adsorbed polycyclic aromatic hydrocarbons (PAHs) and other organic substances. Studies have shown that fine particles associated with air pollutants can interact with pollen, possibly modifying their release of allergens. However, the concentration of particle associated organic compounds is low, composition rather unknown and their determination requires very sensitive methods. Moreover, these methods should be as cheap as possible to allow routine analysis of many samples, applicable in-situ to allow quasi-continuous detection and quantification of dust and pollen extracts by automated equipments in the future. Until now, very limited experience exists on the use of immunological methods for air samples.

In this project a new monoclonal antibody with broad specificity against PAHs on the base of a new benzo(a)pyrene immunogen has been prepared and an ELISA developed. Six traffic dust samples (tunnel dust) were collected at Prague and provided by our Czech partner Dr. Kasicka. Samples were extracted and PAHs determined by HPLC and ELISA and analysed by Scanning Electron Microscopy/ Energy Dispersive X-Ray Analysis (SEM/EDX). Additionally, one dust sample extract was fractionated according to Lewtas et al. (Mutat. Res. 19, 1998, pp 91-105) and the resulting seven fractions of different polarity measured by ELISA. These fractions were also delivered to our French partner Dr. Peltre and used for in vivo toxicological experiments with mice.

(T. Scharnweber, D. Matschulat)





1.3.2 Determination of Sulfonylurea Herbicides Using Combined Immunoaffinity Extraction-Liquid Chromatography-MS

Funding: DFG Kn 348/8-1

Cooperation: Fraunhofer Institute of Molecular Biology and Applied Ecology (Schmalenberg)

In residue analysis, a high degree of molecular selectivity can be achieved with affinity extractions, e.g. with immobilized antibodies (immunoaffinity extraction, immunoextraction, IE). Several supporting matrices have been chosen for the preparation of immunoadsorbents. One of the emerging techniques is the encapsulation of antibodies in porous silicate glass by the sol-gel technology. Corresponding supports have been shown to be relatively inert while preserving the biological activity of the encapsulated protein. Recently, we have reported some applications of corresponding adsorbents for the enrichment of small analytes, mainly PAHs and derivatives, from real samples.

In this project, antibodies were prepared against sulfonylurea herbicides using a complete molecule or only different structural parts as haptens. Antibodies with broadest specificity were immobilized in sol-gel glasses. Recovery experiments have shown that up to 15 compounds could be enriched from a mixture of 26 different sulfonylurea herbicides. For most of the compounds, recovery exceeded 60%.

(P. Degelmann)

1.3.3 Preparation of Monoclonal Antibodies with High Selectivity for Benzo[a]pyrene

Funding: BMBF 02WU0290

Many PAHs are carcinogenic and they are, therefore, of significant concern as environmental contaminants. They can be found in air, precipitation, soil, water, sediment, and even in food. The main sources are combustion of fuel, coal and crude oil treatment, waste incineration, and exhaust gas from motor vehicles. In the new European Community Directive for Drinking Water (Guideline 98/83/EC) a limit value of 10 ng/L was set for benzo[a]pyrene (BaP), one of the most potent carcinogenic PAHs. Traditional analysis includes extraction of water sample with cyclohexane, followed by drying with anhydrous sodium sulphate, concentration by rotary evaporation and N₂-flow, redissolution in acetonitrile and, finally, HPLC analysis with fluorescence detection. This method has required sensitivity, but is time-consuming and needs large amounts of organic solvents.

Availability of a rather selective antibody against BaP and corresponding immunoassay would facilitate analysis clearly. In the past, a few PAH ELISAs became known. Both polyclonal and monoclonal antibodies have been prepared using weakly toxic 3- and 4-ringed PAH derivatives for immunogen preparation. Resulting antibodies exhibited relatively broad selectivity. In this project, new BaP-derivatives were synthesized which have several alkanolic acid functions at different positions of the molecule. These derivatives were coupled to different proteins for use as immunogens or coating antigens.

(D. Matschulat, A. Deng)

1.3.4 Development of an ELISA for Diclofenac

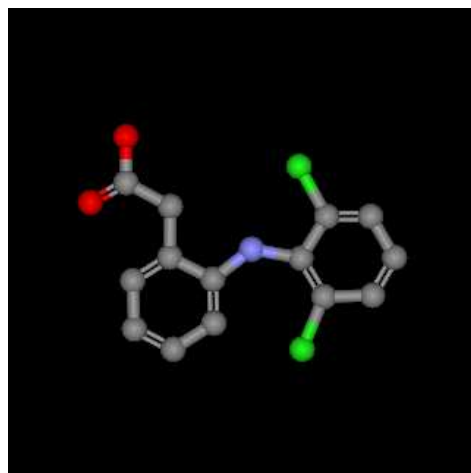
Funding: IWC/TUM and JKU Linz

Cooperation: Institute of Chemistry, Department of Analytical Chemistry, Johannes-Kepler-University (Linz, Austria), Bavarian Water Management Agency (Munich)

Within the last years a number of investigations have been reported which clearly demonstrate the widespread occurrence of therapeutic agents in the environment, notably in the aquatic compartment at low ppt or ppb (ng - $\mu\text{g/L}$) concentrations, thus establishing these compounds as a new class of priority pollutants. The pharmaceuticals and their metabolites may originate from both human and veterinary usage and can be released directly after passing through waste water treatment plants, sludge dispersion on fields, and by other sources such as landfill leachates and non-point discharges from agricultural runoff, mainly. Less is known on the long-term effects of low-level exposure of such compounds to both aquatic ecosystems and humans i.e. the possibility of chronic effects that may not become apparent for many years. However, because of the potential of a wide range of xenobiotic chemicals to interact and disrupt the endocrine systems of animals and humans, the presence of microcontaminants in the aquatic environment is of increasing public concern.

Diclofenac, beside clofibrac acid and ibuprofen, belongs to the most frequently detected pharmaceutically active compounds in the water-cycle. It is considerable stable under normal environmental conditions. Average concentrations in the low ppb range were detected in influents and effluents of municipal waste water treatment plants (WTPs) and surface waters in Austria, Brazil, Germany, Greece, Spain, Switzerland and the U.S. Both gas and liquid chromatography combined with MS(-MS) detector were applied for the analysis of diclofenac at ppt or ppb concentrations after preliminary polymer-based or octadecylsilica solid-phase extraction from water samples. The preparation of antibodies against diclofenac was not reported so far. In this project, a highly sensitive and specific indirect competitive enzyme-linked immunosorbent assay (ELISA) was developed. The assay was applied for the determination of diclofenac in tap and surface water samples, as well as waste water collected at 20 waste water treatment plants (WTPs) in Austria and Germany.

(A. Deng)



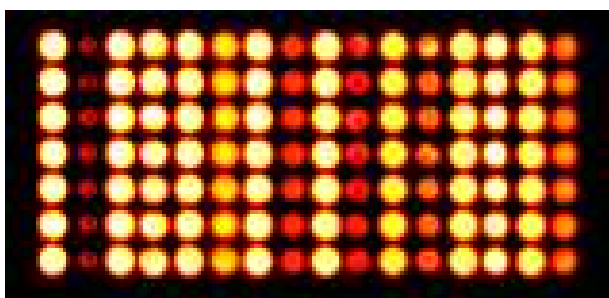
1.4 Bioanalytics II

1.4.1 Development of a Biosensor for the Parallel Detection of Antibiotics in Milk

Funding: Forschungskreis der Ernährungsindustrie, FEI

Cooperation: LMU Munich (Prof. Märtlbauer)

The presence of antibiotic residues in milk due to improper use can lead to allergic reactions and the harm of the intestinal flora. There is also concern about increasing bacterial resistance to antibiotics. In the dairy industry, contaminated milk can result in the loss of cultured products (yoghurt and cheese) due to the inhibition of starter cultures and inflict severe economic loss.



For consumer protection, regulatory authorities have established residue limits (MRL) for several antibiotics in bovine milk (EC Regulation 2377/90). Microbial inhibition (agar diffusion) assays are commonly used as screening tests. One disadvantage of these methods is the duration of about three hours. Usually the results are obtained, when the milk is already in production. For this reason dairies use quick tests which can detect the mostly used β -lactam-antibiotics before the milk is pumped out of the dairy van to avoid troubles with fermentation steps

in the milk processing. Other antibiotic groups than the β -lactam antibiotics can not be determined with these tests. Furthermore, the dairy has to dispose the whole milk of a dairy van in case of a positive test result which entails costs for the processing in a bioreactor and the disprofit of the value of the milk. To avoid the contamination of the already collected milk a sensor is necessary, which enables the rapid detection of all relevant antibiotics before the milk is pumped into the dairy van.

The basis for this sensor is the PASA-system (Parallel Affinity Sensor Array) in which an indirect ELISA format is transferred on a biochip. Analyte molecules are immobilized as haptens in an array of spots on a biochip with a spot density of 4 spots/mm². The glass chip is silanized, to obtain reactive epoxy groups on the surface to which hapten protein conjugates can bind. The spots are created by a noncontact spotting system with a piezo tip. The diameter of the spots is about 250 μ m. The disposable chip is integrated in a flow cell of about 100 μ l volume, where all incubations and reactions are carried out. At present the parallel detection of the following analytes is possible in whole milk (detection limits and MRLs in brackets): streptomycin (2 μ g/L, MRL: 200 μ g/L), penicillin G (4 μ g/L, MRL: 4 μ g/L), cloxacillin (0.5 μ g/L, MRL: 30 μ g/L), sulfadiazine (8 μ g/L, MRL: 100 μ g/L), sulfamethazine (5 μ g/L, MRL: 100 μ g/L), erythromycin (1 μ g/L, MRL: 40 μ g/L) and gentamicin (11 μ g/L, MRL: 200 μ g/L). Most analytes can be detected far below the respective MRL. For penicillin G the detection limit is exactly at the MRL. The test duration is less than 5 minutes. There is no sample preparation necessary.

(B. Knecht)

1.4.2 Development of Fast Immunological and LC-ESI-TOF-MS Methods for the Analysis of Cyanotoxins (Microcystins) in Drinking and Surface Water

Funding: BMBF 02WU9848/9

Cooperation: AWQC Adelaide, Australia (Prof. Bursill)

The most frequently found cyanotoxins during freshwater blooms of cyanobacteria (also known as blue-green algae) are the microcystins. These cyclic heptapeptides can

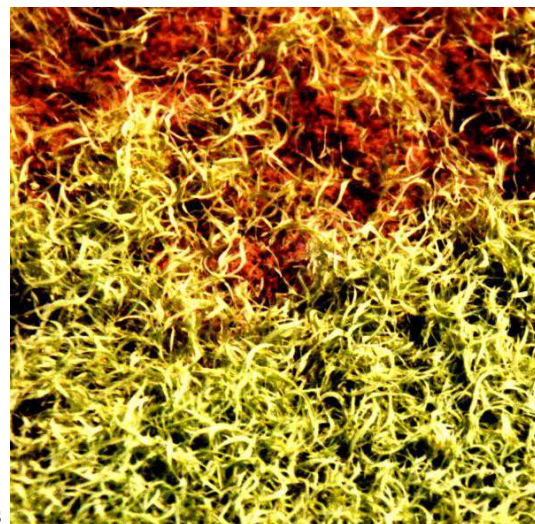
cause acute and chronic liver damage and intestine injury when ingested with drinking water or during bathing from contaminated surface water. They are also suspected to have tumor promoting activity. Common to nearly all the microcystins is the unusual amino acid Adda ((2S, 3S, 8S, 9S)-3-amino-9-methoxy-2,6,8-trimethyl-10-phenyldeca-4,6-dienoic acid). Adda is also found in the cyanotoxin nodularin - a closely related cyclic pentapeptide found in marine blooms. The World Health Organization (WHO) proposed a provisional guideline value of 1 $\mu\text{g}/\text{L}$ for the best known microcystin-LR in drinking water.

Two monoclonal antibodies for detection of microcystins and nodularin were recently generated in this project. The antibody against Adda moiety of the toxins exhibits good cross-reactivity to a range of microcystins whereas the microcystin-LR antibody particularly detects microcystins that show an arginine next to Adda amino acid in the cyclic peptide. Both antibodies exhibit a high affinity to the desired analytes.

For the large scale production of antibody the recently isolated Adda-antibody producing hybridoma cells had to be re-fused with myeloma cells. This generated viable antibody producing cells that were interleukin independent. Consequently antibody production could be started on a larger scale than before. The ELISAs were applied for the measurement of surface water samples and cyanobacteria containing algal food samples.

The microcystin-LR antibody was applied for the enrichment of microcystins. Different materials as well as immobilization methods for the generation of microcystin-immunoaffinity columns were tested. The cartridges and immobilization materials were selected in order to minimize antibody consumption. The system was tested for its applicability for online enrichment of toxins and direct analysis using electrospray ionization mass spectrometry with time-of-flight mass analyser. This device offers the opportunity to separate and detect the different toxins according to their molecular mass without chromatographic separation of the analytes prior to mass spectrometry. The results showed the high selectivity of the immunoaffinity cartridge and its applicability for elimination of matrix compounds interfering with mass spectrometry.

(I. Schaupt, M. Kiening, A. Zeck)



1.4.3 Rapid immunological methods for the detection of traces of peanuts and tree nuts in complex food matrices

Funding: EU QLRT-2000-01151 Cooperation: IFA Tulln, Austria (Prof. Krska); RIKILT, The Netherlands (Dr. Haasnoot); CSL, UK (Dr. Banks); r-Biopharm, Germany (Dr. Schmitt); UNIMI, Italy (Prof. Restani); VU, Belgium; CMHT, UK (Dr. Wilson)

Rising prevalence of allergies is a major health problem and especially concerns industrialized countries. In particular, intolerances against certain food ingredients may cause severe adverse reactions in sensitized persons. Peanut and tree nut (e.g. hazelnut) proteins both are representatives of the most important food allergens. Epidemiologic studies show that nearly half a percent of the population is suffering of adverse reactions to these allergens. In some cases incorporation of even trace amounts of peanuts or tree nuts caused lethal anaphylaxis.

The only effective measure for these patients is strict avoidance of foodstuffs containing respective ingredients. However, so called "hidden allergens" are causing unpredictable responses. The current European regulation is based on the principle that the consumer knows the composition of compound ingredients. It is therefore not obligatory to label components of compound ingredients that make up less than 25% of the final product. Therefore, fast analytical methods are required for the screening of trace amounts of potentially allergenic proteins in food samples. Enzyme-linked immunosorbent assays (ELISA) are the method of choice for such applications.



The major goal of this project is to develop rapid assays for the determination of trace amounts of peanuts and hazelnuts in complex food matrices. In the first step different laboratory immunoassays will be optimized. Up to now we reached detection limits for peanuts in the 1 mg/kg range in various food matrices. Also first screening investigations on commercial available food samples started.

One of the further tasks will be to transform these assays into rapid easy-to-use formats, for instance homogeneous dipsticks using the enzyme channeling technique and lateral flow assays. We will also have to develop methods for the simple extraction of different food matrices. After validation of our test formats we will screen suspected foodstuffs from different EU member states for

the presence of hidden peanut and hazelnut proteins.
(M. Kiening)

1.5 Laser Spectroscopy I

1.5.1 Microanalysis Using the Laser-Induced Plasma Spectroscopy (LIPS) and VUV-Echelle Spectrograph

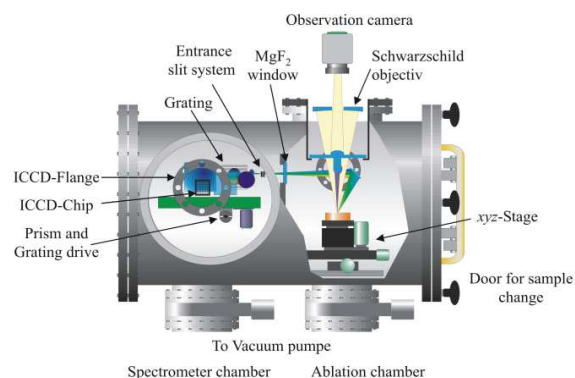
Funding: DFG Pa 716/2-1

Cooperation: ISAS, Berlin

Laser-induced plasma spectroscopy (LIPS) is a powerful tool for the multi-element analysis of a huge variety of solid, liquid, and gaseous samples of industrial relevance. For LIPS an intense, pulsed laser beam (typically a Nd:YAG or excimer laser) is focused on the sample of interest, resulting in an evaporation, atomization, and partial ionization of the sample in an expanding plasma cloud. After a delay of some hundred nanoseconds to discriminate against the recombination background, the elemental composition of the sample can be determined via the spectrally and temporally resolved detection of the characteristic atomic and ionic emissions. Due to the minimum sample preparation, the low cost for a single measurement, and the potential for an extensive automation, LIPS is an attractive approach to process analysis.

The objective of this work to extend the range of elements, which can be analyzed by LIBS, via observation of atomic emission in the VUV range. This permits not only a multielement analysis of metals, but also access to emission lines of metalloids such as S, P, N, O, C, and As. Two experimental set-ups for VUV-LIPS are presented: A set-up for bulk analysis based on conventional Czerny-Turner monochromator and a new echelle spectrograph for high spectral resolution ($> 10\,000$) in the spectral range 150-300 nm.

Applying an appropriate beam shaping ("micro focusing"), LIPS allows a fast spatially resolved elemental characterization of surfaces with a typical resolution of $10\ \mu\text{m}$. Using a UV laser beam ($\lambda = 266\ \text{nm}$) for plasma ignition, fractionization effects can be minimized and a quantitative analysis can be performed. Analysis of the spectra from the single pulses permit a depth- and spatially resolved investigation of a sample.
(I. Radivojevic)



Micro-LIPS system with VUV-Echelle spectrometer

1.5.2 Investigation of the Colloidal Transport in Biological Sewage Plants Using AF⁴ and ICP-MS

Funding: DFG Pa716/4-1

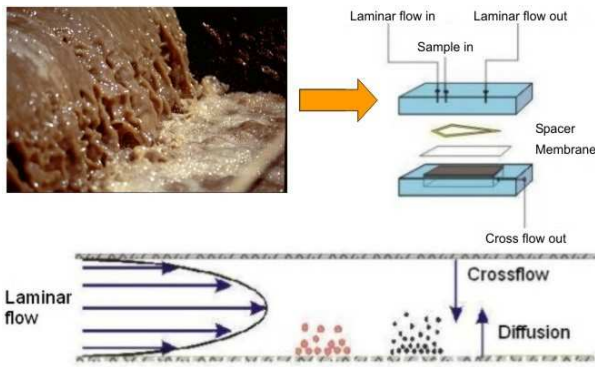
Cooperation: Institute of Water Quality Control and Waste Management, TUM (Prof. Wilderer)

The aim of this work is the characterization of colloids in biological sewage plants. At present only little knowledge of the colloidal freight in such plants and their influence on the cleaning capacity exists. In addition to an element mass balance of the spatial and temporal variance of the particle concentration in technical plants, investigations on the location and the modification of colloids within biofilms are carried out. The mass balance is methodically based on the inductively coupled plasma mass spectrometry (ICP-MS). The colloids are size-segregated prior to ICP-MS analysis via an online coupling with an asymmetrical flow field-flow fractionation (AF⁴). AF⁴ permits a

fast size-selective separation of colloids under very gentle conditions. The separation takes place in a separation channel, in which a laminar flow is formed due to the small channel height. Perpendicularly to it, a cross flow is generated, which drives the colloidal particles toward the bottom of the channel. Due to their higher diffusion coefficient, smaller particles diffuse back into the channel faster than larger particles and therefore leave the channel earlier. Using an appropriate calibration, the diffusion coefficients can be calculated from the measured retention times. Their knowledge enables the combination of the retention time with the molecular weight and the particle diameter. First, methods for the separation from sewage plant colloids were developed. For calibration, monodisperse polystyrene sulfonate standards (PSS) were utilized. Afterwards numerous samples were fractionated both from different sewage plants and from different places and depths of the same plant and compared with one another.

Further experiments were done on the microscopic interactions with biofilms in a laboratory reactor and the macroscopic colloidal transport in technical plants with natural and/or artificial tracer colloids. At present investigations at a biofilm reactor with monodisperse silicate particles are accomplished. The results show that the employed technique is suitable to detect colloids in complex matrices quantitatively and to receive information about their location and interactions with biofilms.

Several spherical heavy metal phosphate colloids with narrow size distribution have been synthesized by a slow increase of pH in solutions which contain soluble heavy metal salts and phosphoric acid. According to this method, now monodisperse lanthanoide phosphate particles are synthesized which are to be used as tracer colloids in the



future.
(H. Prestel)

1.6 Laser Spectroscopy II

1.6.1 Development of a Photoacoustic Sensor System for Time-resolved Soot Measurement in Diesel Exhaust

Funding: VFI, Frankfurt

Motor vehicles like cars and heavy duty trucks are major sources of air pollution. Particulate mass emitted by diesel engines consists mostly of carbonaceous material. The influence of soot particles on human health as well as global and local climate is well established by now and led to recent regulations demanding a reduction of particle emission in diesel exhaust up to 90 % within the next years. This is not only a challenging task for car manufacturers to design a new generation of low emitting engines and new particle filter systems, it also brings the classical analytic methods to their limits.

The measurement of elemental and organic carbon is conventionally accomplished by particle collection on filters, followed by thermochemical or thermogravimetric detection methods. Wet chemical analysis and combustion require well equipped laboratories and time consuming sample preparation. Due to the integration on a filter, a time-resolved analysis is not possible. To meet the new emission regulations a new generation of measurement instruments for process monitoring are needed. Requirements for such systems are high sensitivity combined with high selectivity for elemental carbon. Their implementation will be only possible if time-resolved soot detection with sufficient sensitivity can be realised.

The highest particle emissions from diesel engines are generated during load changes. Within such load changes the emitted soot concentrations can rise several orders of magnitude for a period of few seconds to decrease immediately afterwards. Process studies afford a fast time response with a sampling rate in the range of 1 Hz. Mobile systems with a certain simplicity and economic efficiency are generally preferred. The presented photoacoustic sensor system is optimised for a highly sensitive and fast on-line and in situ quantification of soot.

The system combines a time resolution of 1 s (sampling rate 3 Hz) with an aerosol mass sensitivity better than $10 \mu\text{g}/\text{m}^3$. The system consists of two photoacoustic cells, which are operated in a differential mode to avoid cross sensitivities to any molecular absorption. The cells were built as acoustical resonators to increase sensitivity. A diode laser with a wavelength of $>810 \text{ nm}$ and an output power of $>1 \text{ W}$ was employed for excitation. To avoid condensation of water, the cells are heated to $50 \text{ }^\circ\text{C}$. The whole system is incorporated into a 19"-rack.

The design is rugged for field applications at an engine test site to withstand external acoustic noise, temperature fluctuations, and dust contamination. The overall performance and figures of merit were established under laboratory conditions with soot aerosols generated by a spark discharge aerosol generator. Meanwhile, the system is routinely used for engine development at engine test sites. At the site, the system was calibrated by recording several stationary cycles. The time resolution was validated by on-line measurements of transient cycles. Throughout all experiments, reference analysis was performed via a thermochemical standard procedure, i.e. a

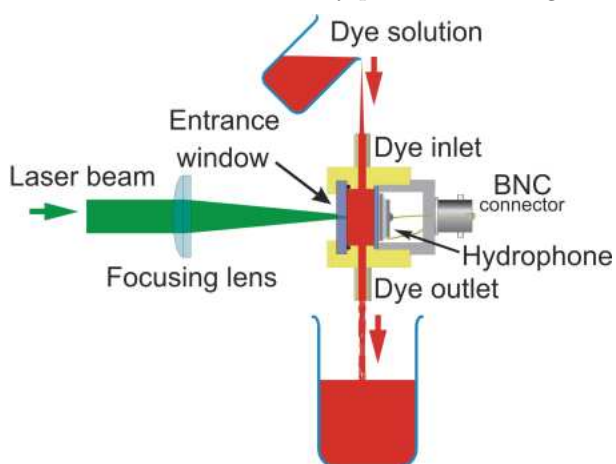


German standard reference method (VDI guideline 2465, sheet 1).
(H. Beck, C. Haisch)

1.6.2 On-line Monitoring of Opaque Liquids by Photoacoustic Spectroscopy

Funding: IWC TUM Cooperation: Deutsches Textilforschungszentrum Nord-West (DTNW), Krefeld

The dyeing of textiles is performed with highly concentrated dye solutions with concentrations from 50 mg/L up to 40 g/L. For process optimization and control of the wastewater, an on-line monitoring of the dye concentration is needed. Optical transmission measurements allow the determination of the dye concentration in a relatively small range. Samples with concentrations in the upper ppm and g/L range have to be diluted before the measurement due to their optical opacity. Additionally, light scattering particles have a strong effect on the transmitted light intensity. Photoacoustic spectroscopy allows the determination of concentrations in condensed matter over several orders of magnitude. Furthermore, scattering particles do not generate any photoacoustic signal.



Therefore, a photoacoustic sensor system for on-line monitoring of highly concentrated and optical opaque samples was developed. Pulsed photoacoustic spectroscopy is based on the absorption of short laser pulses inside condensed matter where non-radiative relaxation processes convert the absorbed energy into heat. Due to the thermal expansion of the medium, a pressure wave is generated which can be detected by piezoelectric transducers. After normalization with regard to laser pulse energy and temperature, the amplitude of the photoacoustic signal depends linearly on the optical absorption coefficient of the sample and the concentration of the absorbing compound. Here, hydrophones for detection of laser induced pressure waves in water and aqueous solutions were developed. A 25 μm thick piezoelectric poly(vinylidene fluoride) (PVDF) film allows the detection of acoustic waves with frequencies up to a few 100 MHz. By use of suitable coupling materials, high acoustic transmission from the liquid sample to the piezoelectric detector could be achieved. The acoustic transmission factor of the hydrophone was 82%. Hydrophones were integrated into a sensor cuvette and a flow cell for stationary and continuous measurements, respectively. For excitation of photoacoustic signals, different laser systems with diverse properties were used. A Nd:YAG laser on an optical bench was used to characterize the sensors and to develop a strategy for data evaluation. The results were transferred to measurements with a dye laser which was pumped by a XeCl excimer laser. The laser system allowed measurements at different wavelengths. Finally, a compact and transportable sensor system could be set up by use of a nitrogen laser. The sensor systems were calibrated with different textile dyes at various laser wavelengths and laser pulse energies from 100 μJ to 1 mJ. The dye concentration could be determined in a range of approximately 100 mg/L to 30 g/L without any dilution or other sample preparations, although the generation of different acoustic waveforms led to a non-linear calibration curve. In continuous measurements, the signal was not affected by the flow velocity. Changes of the dye concentration could be monitored on-line with a time-resolution of a few seconds. In a small stirring tank reactor, the dye concentration could be monitored

during addition of a textile dye and during its dilution by addition of water. The plot of concentration versus time was in good agreement with the theoretically calculated trend.

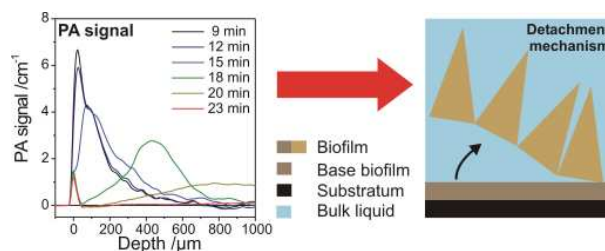
(*T. Schmid, C. Helmbrecht*)

1.6.3 Biofilm Monitoring by Photoacoustic Spectroscopy (PAS)

Funding: DFG Ni 261/14-1

Biofilms are aggregates of microorganisms which occur at aqueous interfaces. Biofilms attached to solid surfaces can be found in natural and engineered water systems. The unwanted deposition of biofilms in technical processes is termed biofouling. Biofouling reduces the water quality and increases the frictional resistance in tubes. In wastewater treatment plants, biofilms are used for removal of organic pollutants. For improvement of anti-fouling strategies and for process optimization in wastewater treatments plants, an analytical technique for on-line monitoring of biofilms is needed. A new technique for on-line and in situ monitoring of biofilms based on photoacoustic spectroscopy (PAS) has been developed. PAS is based on the absorption of electromagnetic radiation inside a sample. By non-radiative relaxation processes, the absorbed energy is converted into heat and due to the thermal expansion of the medium, pressure waves are generated, which can be detected by piezoelectric transducers. If short laser pulses are used for excitation, a depth-resolved investigation of layered samples can be performed by measurement of the time delay between laser pulse and detection of the pressure waves.

The photoacoustic sensor heads used in this study consist of a 25 μm thick wide-band piezoelectric poly(vinylidene) fluoride (PVDF) film which was coupled to a transparent prism by a conductive epoxy. The piezoelectric film was integrated into a BNC socket to eliminate electromagnetic interference. The sample is irradiated through one side and the base of the prism. In this way, an indirect detection scheme has been realized, i.e. excitation and detection of pressure waves are performed from the same side of the sample. The characterization of the sensor heads was performed with biofilm models consisting of agar-agar hydrogels. The sensor system allows the depth-resolved analysis of aqueous samples (aqueous solutions, hydrogels and biological tissues) with a depth resolution of about 10 μm and a detection limit for the absorption coefficient of 0.02/cm at a laser pulse energy of $E_0 = 1$ mJ. First experiments with a biofilm growing directly on the sensor surface showed the potential of PAS in the field of nondestructive biofilm monitoring. By photoacoustic absorption measurements in the visible spectral range (Nd:YAG laser at $\lambda = 532$ nm), growth and detachment of biofilms which were associated with the sensor surface could be monitored depth-resolved. Important changes in the biofilm due to changes in pH-value, flow conditions, particulates etc. could be detected for the first time in a depth-resolved fashion by photoacoustic measurements at three different positions inside a flow channel. The investigation of biofilm models with well-defined thickness revealed a possibility for biofilm thickness measurements by depth-resolved photoacoustic spectroscopy. The minimum of the photoacoustic signal profile reflects the interface region between biofilm and liquid bulk phase. The photoacoustic thickness measurements were validated by confocal laser scanning microscopy (CLSM) using



real biofilms grown on glass slides. The result of the photoacoustic thickness measurement was in good agreement with the independent microscopic imaging technique. An optical parametric oscillator (OPO) which is pumped by a Nd:YAG laser allows the generation of short laser pulses in the wavelength range from 410 nm to 2550 nm. By means of this tunable laser system, photoacoustic absorption spectra of biofilms were determined. Absorption bands of main components such as pigments, water and carbohydrates could be identified in the Vis and NIR spectra. Depth-resolved measurements revealed the possibility to investigate the distribution of chemical compounds inside the biofilm system. The photoacoustic monitoring technique was used for an extensive investigation of the effectiveness of various biocides. The effect of hydrogen peroxide on biofilms was compared with diverse isothiazolinone biocides. Biofilm removal by the oxidant hydrogen peroxide was the most effective way to remove biofilms from solid surfaces. Most of the adsorbed biomass was removed within a few minutes. The changes in signal shape and biofilm thickness indicated that sloughing off of relatively large areas of the biofilm lead to the fast biofilm detachment (see figure).
(*T. Schmid*)

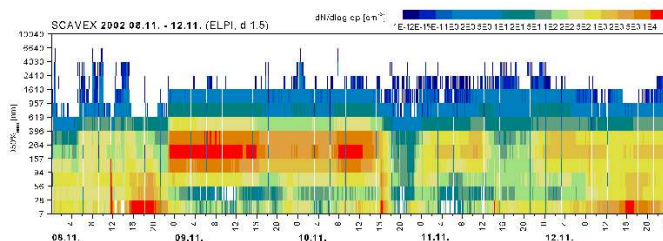
1.7 Aerosol Research

1.7.1 Schneefernerhaus Aerosol and Reactive Nitrogen Experiment (SCAVEX)

Funding: BayStMLU Cooperation: Vienna University of Technology (Institute of Analytical Chemistry), Paul Scherrer Institute (Atmospheric Chemistry Laboratory), University of Clermont Ferrand (Institute of Physical Meteorology), University of Innsbruck (Institute of Ion Physics), German Aerospace Center (DLR, Institute of Atmospheric Physics), German Weather Service (DWD, Observatory Hohenpeissenberg), Max-Planck-Institute of Nuclear Physics (Institute of Atmospheric Physics)

To allow an accurate assessment of the influence of aerosols on atmospheric chemistry and climate, a thorough physical and chemical analysis of atmospheric aerosols is required, including the characterisation and quantification of organic particle components. The SCAVEX aerosol measurement program at the Schneefernerhaus observatory (UFS) on Mt. Zugspitze is aimed at an extensive physical and chemical characterisation of air particulate matter in the high alpine environment, where either boundary layer air or free tropospheric air prevail under different meteorological conditions.

A couple of intensive measurement campaigns have been performed at the Schneefernerhaus observatory in April and November 2002, applying a wide range of aerosol measurement instrumentation (CPC, SMPS, ELPI, PM_{2.5}-HV-FS, PASS). A sampler for water vapor condensation nuclei has been built and characterised under laboratory conditions and will be deployed in future campaigns. Analytical techniques for various classes of organic particle components, in particular for polycyclic aromatic compounds and biopolymers have been developed and applied to the collected filter samples.



Depending on the meteorological situation, the observed total particle number concentrations varied typically from a few hundred up to a few thousand particles per cubic centimetre. At low particle concentrations, i.e. under clean conditions such as free tropospheric air, the number size distributions exhibited a maximum in the accumulation mode (particle diameter 100 nm). At high particle concentrations different size distribution patterns were observed, on some occasions a strong nucleation mode (particle diameter 20 nm) dominated the total number concentration, in others also the accumulation mode was enhanced. An example for the high variability of aerosol number concentration and size distribution is shown in the attached figure.

Also the mass concentration and chemical composition of air particulate matter sampled on filters exhibited a high variability and pronounced seasonal trends. A detailed interpretation of the aerosol measurement results in combination with trace gas and meteorological data is under way.

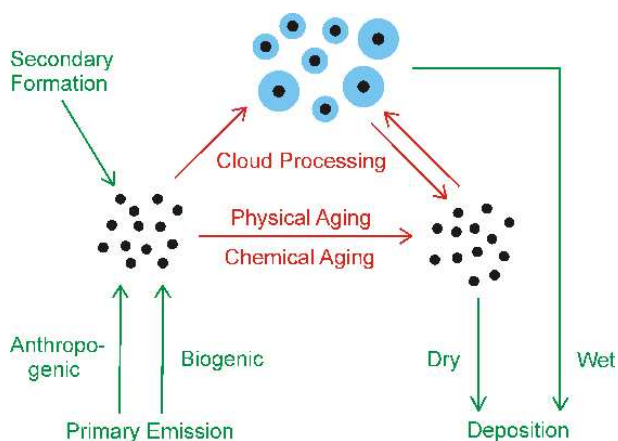
(K. Krause, A. Messerer, A. Zerrath)

1.7.2 Carbonaceous Aerosol Components: Chemical Composition, Reactivity and Hygroscopicity (CARBAERO)

Funding: BMBF AFO 2000 07ATC05

The influence of aerosols on atmospheric chemistry and physics, climate and human health is one of the central topics in today's environmental research. Besides the aerosol particles' size distribution their chemical composition is the primary parameter governing heterogeneous and multiphase chemical reactions in the atmosphere, formation of clouds and precipitation, radiative climate forcing effects, and health effects of aerosols. Several studies have shown that carbonaceous components are major constituents of tropospheric aerosols (10-50 % mass fraction), that black carbon is the main light absorber in air particulate matter, and that organics can strongly affect the physicochemical particle properties. The actual composition of atmospheric particles is, however, spatially and temporally highly variable, and in particular carbonaceous components have been characterized only sparsely and incompletely up to now.

Therefore the central aim of the CARBAERO project is to characterize the molecular structures and abundances, reactivity and water vapor interactions of carbonaceous aerosol components. The investigations are focused primarily on aromatic compounds, macromolecules (biopolymers and humic-like substances), and elemental carbon, and the following key questions are addressed: What are the effects of carbonaceous aerosol components on the physico-chemical properties of atmospheric particles, on their interaction with reactive trace gases, water vapour, clouds, and precipitation, and thus on their influence on climate and public health, and how is the composition of carbonaceous aerosol components changed by chemical aging (reaction products and kinetics), and how can these processes be efficiently described in atmospheric models?



In the year 2002 research activities have been pursued and scientific results have been achieved in the following areas:

- Development and optimization of analytical methods for the determination of polycyclic aromatics, carbohydrates, proteins, and humic-like substances in atmospheric aerosol samples (extraction schemes, chromatographic and spectrometric methods, enzymatic assays).
- Field measurement campaigns at urban/suburban, rural/alpine and high alpine locations (Munich, Hohenpeiussenberg, Zugspitze): observation of characteristic differences in the physical properties (particle number and mass concentration and size distribution) and chemical composition (TC/EC, PAH, proteins, amino acids).
- Aerosol flow tube experiments on the interaction of spark-discharge soot particles (with/without PAH-coating) with reactive trace gases (O_3 , NO_2) and water vapor: reaction kinetics and products.
- Investigation of the hygroscopic growth and microphysical restructuring of aerosol particles with complex chemical composition upon interaction with water vapor (HTDMA-experiments with mixtures of biopolymers, salts, etc.)

- Development of a kinetic model framework for aerosol surface chemistry and gas-particle interactions.

(T. Franze, E. Mikhailov, U. Schaller, C. Schauer, A. Zerrath)

1.7.3 Development of a Filterless Catalytic System for the Continuous Oxidation of Soot Particles for Heavy Duty Vehicles (PM-KAT)

Funding: Bayer. Forschungstiftung

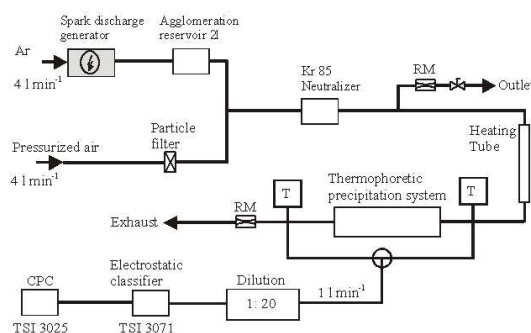
Cooperation: MAN Nutzfahrzeuge AG, Nürnberg; Oberland-Mangold, Garmisch-Partenkirchen; Fritz-Haber-Institute, Department of Inorganic Chemistry, Berlin; Max-Planck-Institute for Polymer Research, Mainz.

Since conventional soot particle filter systems exhibit a significant increase in exhaust gas back pressure and are easily clogged by engine oil ashes, current research activities are focused on the development of filterless soot particle deposition structures. First experiments confirmed the high potential of newly developed structures for efficient particle deposition. Detailed studies of the involved processes including thermophoresis are currently under way and will be used to optimize the design and operating conditions. The reaction mechanisms and kinetics of soot particle oxidation by nitrogen oxides are also investigated for different deposition structures and types of soot under a wide range of experimental conditions relevant for modern diesel engine exhaust systems.

A test gas bench suitable for the investigation of soot particle deposition and oxidation in specially designed flat bed reactor systems has been constructed. With a cross section of 10×6 mm these reactors provide a high flexibility concerning the type of deposition structure, their length (74.5 to 290 mm), temperature conditions (25 to 450°C), model gas composition and flow velocity under laboratory scale conditions. Simulated hourly space velocities range between 10,000 and 100,000 h^{-1} . Model soot aerosols are produced by spark discharge generator. For the measurement of the size distribution of the soot aerosol before and after the deposition device a SMPS system consisting of an electrostatic classifier and a condensation particle counter is applied. Complex heat control devices have been implemented to ensure isothermal sampling conditions at all sampling points to minimize potential measurement artefacts due to thermophoretic sampling losses.

To characterize the effect of thermophoresis on the deposition of agglomerated sub-micrometer soot particles, a plate-to-plate deposition system has been developed and implemented in the model gas test bench (attached figure). The oxidation of deposited soot particles by nitrogen oxides is investigated under conditions typical for modern diesel engine exhaust treatment systems (temperature, space velocity, and gas composition). The reaction products and kinetics are measured by FTIR spectroscopy and complementary analytical techniques. The experiments with spark discharge soot are complemented by experiments with particles composed of well defined polycyclic aromatic hydrocarbons (e.g. hexabenzocoronene) and with real diesel soot particles sampled at engine test benches.

(D. Rothe, A. Messerer, C. Adelhelm)



2 Publications of Present Members of the IWC

2.1 Journal articles (reviewed)

- T. Baumann, R. Petsch, G. Fesl and R. Niessner; Flow and Diffusion Measurements in Natural Porous Media Using Magnetic Resonance Imaging. *J. Environ. Qual.* 31 (2002) 470-476
- T. Baumann, S. Müller and R. Niessner; Transport of Heavy Metals and PCP in the Presence of Colloids in a Heterogeneous Calceous Gravel and a Homogeneous Quartz Sand - Tank Experiments. *Water Research* 36 (2002) 1213-1223
- E. Fernvik, T. Scharnweber, D. Knopp, R. Niessner, B. Vargaftig and G. Peltre; Effects of Fractions of Air Polluted Urban Dust on TH2-cytokines, IgE Levels and Bronchial Hyperresponsiveness in Mice. *Journal of Toxicology and Environmental Health Part A* 65 (2002) 1025-1045
- H. Fink, U. Panne and R. Niessner; Process Analysis of Recycled Thermoplasts from Consumer Electronics by Laser-induced Plasma Spectroscopy (LIPS). *Anal. Chem.* 74 (2002) 4334-4342
- C. Haisch and R. Niessner; Light and Sound - Photoacoustic Spectroscopy. *Spectroscopy Europe* 14 (2002) 10-15
- L. Kleiber, H. Fink, R. Niessner and U. Panne; Strategies for the Analysis of Coal by Laser-Ablation Inductively Coupled Plasma Mass Spectrometry. *Anal. Bioanal. Chem.* 374 (2002) 109-114
- M. Lackhoff and R. Niessner; Photocatalytic Atrazine Degradation by Synthetic Mineral, Atmospheric Aerosols and Soil Particles. *Environ. Sci. Technol.* 36 (2002) 5342-5347
- T. Letzel, C. Schauer, U. Pöschl und R. Nießner; Strömungsrohr mit mobilem Probenahmekopf: Kompaktes Reaktionssystem für toxische und korrosive Gase und Aerosole. *Chemie Ingenieur Technik* 74 (2002) 1148-1151
- G. Nachtwei, A. Manlescu, N. Nestle, H. Kunzel, Ferromagnetism in a Quantum Hall System due to Exchange Enhancement in a GaInAs Quantum Well, *Physica E*, 12, 20-23, 2002.
- N. Nestle, T. Baumann and R. Niessner; From Radiology to "Patient Earth": Magnetic Resonance Imaging in Environmental Science. *Environ. Sci. Technol.* 36 (2002) 154A -160A
- N. Nestle, T. Baumann und R. Nießner; Patient Grundwasser: Kernspintomographie in der Hydrogeologie. *Nachrichten aus der Chemie* 50 (2002) 946-952
- N. Nestle, A. Quadan, P. Galvosas, W. Suss, J. Karger, PFG NMR and Internal Magnetic Field Gradients in Plant-Based Materials, *Magn. Res. Img.*, 20, 67-73, 2002.
- N. Nestle, P. Galvosas, J. Karger, K. Friedemann, K. C. Zimmermann, M. Dakkouri, NMR Measurements of Cement Hydration as Affected by Eluants, *GDCh-Monographie*, 24, 98-102, 2002.
- N. Nestle, C. Zimmermann, M. Dakkouri, J. Karger, Transient High Concentrations of Chain Anions in Hydrating Cement - Indications From Proton Spin Relaxation Measurements, *J Physics D*, 35, 166-171, 2002.

-
- R. Nießner, J. Broekaert, J.W. Einax, H. Emons, W. Engewald, K. Heumann, H. Hutter, D. Knopp, R. Krska, U. Panne, U. Pyell, R. Salzer, W. Stöcklein, N. Trautmann, M. Weller; *Trendbericht Analytische Chemie. Nachrichten aus der Chemie* 50 (2002) 455-461 und 485-487
- U. Panne, R. Düsing and R. Niessner (2002) Time Resolved Excitation Emission (TEE) Spectra: A New Screening Tool Based on Multidimensional Fluorescence Spectroscopy. In: *Field Screening Europe 2001*, edited by W. Breh et al., Kluwer Academic, Dordrecht, p. 169-174
- U. Panne, R. Neuhauser, C. Haisch, H. Fink and R. Niessner; Remote Analysis of a Mineral Melt by Laser-induced Plasma-Spectroscopy (LIPS). *Appl. Spectrosc.* 56 (2002) 375-380
- U. Panne, R. Düsing, R. Niessner, Time-resolved Excitation Emission (TEE) Spectra: A New Screening Tool Based on Multidimensional Fluorescence Spectroscopy, in *Field Screening Europe 2001*, W. Breh, J. Gottlieb, H. Hötzl, F. Kern, T. Liesch, R. Niessner Kluwer Academic Publishers, 169-174, 2002.
- U. Panne, *Spectrochemical Analysis with Lasers, Analytical and Bioanalytical Chemistry*, 372, 23-25, 2002.
- U. Pöschl, Formation and Decomposition of Hazardous Chemical Components Contained in Atmospheric Aerosol Particles, *Journal of Aerosol Medicine*, 15, 203-212, 2002.
- T. Scharnweber, M. Fisher, M. Suchanek, D. Knopp and R. Niessner (2002) Immunological Detection of Polycyclic Aromatic Hydrocarbons (PAHs) in Airborne Aerosols. In: *Field Screening Europe 2001*, edited by W. Breh et al., Kluwer Academic, Dordrecht, p. 233-238
- T. Schmid, U. Panne, C. Haisch, M. Hausner and R. Niessner; A New Photoacoustic Technique for Depth-Resolved In-Situ Monitoring of Biofilms. *Environ Sci. Technol.* 36 (2002) 4135-4141
- C. Stalikas, D. Knopp and R. Niessner; Sol-Gel Glass Immunosorbent-Based Determination of s-Triazines in Water and Soil Samples Using Gas Chromatography with Nitrogen Phosphorous Detection System. *Environ. Sci. Technol.* 36 (2002) 3372-3377
- M. G. Weller; *Algengifte im Wasser, Nachrichten aus Chemie* 50 (2002) 700-705.
- J. Yakovleva, D. Knopp, R. Niessner and S. Eremin: Development of a Polarization Fluoroimmunoassay for the Herbicide Metsulfuron-methyl. *Food & Agricultural Immunology* 14 (2002) 217-229
- J. Zhang and R. Niessner; Simultaneous Determination of Trace Ni²⁺ and Zn²⁺ in Water by Using Fluorescence-based Flow Injection Analysis. *Fenxi Shiyanshy* 21 (2002) 1-4
- Q.-Z. Zhu, P. Degelmann, R. Niessner and D. Knopp; Selective Trace Analysis of Sulfonylurea Herbicides in Water and Soil Samples Based on SPE Using a MIP. *Environ. Sci. Technol.* 36 (2002) 5411-5420
- Q.-Z. Zhu, K. Haupt, D. Knopp and R. Niessner; A Molecularly Imprinted Polymer for Metsulfuron-methyl and its Binding Characteristics for Sulfonylurea Herbicides. *Anal. Chim. Acta* 468 (2002) 217-227

2.2 Monograph

W. Breh, J. Gottlieb, H. Hötzl, F. Kern, T. Liesch and R. Niessner (2002) *Field Screening Europe 2001*. Kluwer Academic Publishers, Dordrecht

2.3 Conference Presentations

2.3.1 Oral Presentations

- T. Baumann, N. Nestle & R. Niessner, Quantifizierung des Transports von Kolloiden, Schwermetallen und NAPLs in porösen Medien mit Hilfe der Kernspintomographie, FH-DGG Tagung, 9.-11.5.2002, Greifswald.
- T. Baumann, Visualisation of Colloid Transport Processes with Magnetic Resonance Imaging and in Etched Silicon Micromodels, Colloids and Colloid-Facilitated Transport, 19.-20.9.2002, Foulum, DK.
- R. Klein, T. Baumann & R. Niessner, Elutionen an frischen und gealterten Schlacken, Wasserchemische Gesellschaft, 6.-8.5.2002, Eichstätt.
- R. Klein, T. Baumann, N. Nestle & R. Niessner, Prediction of the Thermal Stress Imposed on the Liner Systems of Solid Waste Landfills, Thermal Treated Solid Waste Residues, 21.-22.3.2002, Wien.
- R. Niessner, A. Zerrath, K. Krause, T. Franze, U. Pöschl, Analysis of Biopolymers in Atmospheric Aerosols, 6th Intern. Aerosol Conference, 8.-13.9.2002, Taipeh, Japan.
- U. Panne, Möglichkeiten der Laserspektroskopie in der Prozess- und Umweltanalytik, GDCh-Vortrag, 08.04.2002, Universität Hamburg.
- U. Panne, Trends in Chemical Analysis of Bioaerosols, Bioaerosols: A View from Different Perspectives, International Workshop, 02.07-03.07.2002, FTU Karlsruhe.
- T. Schmid, U. Panne, C. Haisch, R. Niessner, Biofilm Monitoring by Photoacoustic Spectroscopy (PAS), International Specialised Conference on Biofilm Monitoring, 10.03-20.03.2002, Porto, Portugal.
- T. Schmid, U. Panne, C. Haisch, R. Niessner, Process Analysis of Biofilms by Photoacoustic Spectroscopy, Euroanalysis XII, 8.09.-13.09.2002, Dortmund, Germany.
- U. Panne, I. Radivojevic, C. Haisch, R. Niessner, H. Becker-Ross, S. Florek, Development of a VUV-LIPS System, FACCS 2002, 13.10-17.10.2002, Providence, RI, USA.
- U. Panne, T. Schmid, C. Haisch, R. Niessner, Biofilm Monitoring by Photoacoustic Spectroscopy, FACCS 2002, 13.10-17.10.2002, Providence, RI, USA.
- U. Panne, Spektrochemische Prozessanalytik mit Lasern-Trends und Applikationen, Symposium Prozessanalytik, Wacker, 22.10-24.10.2002, Burghausen, Germany.
- U. Panne, Die Anwendung der Laser-Plasma-Spektroskopie in der Prozessanalytik, Preisträger-Kolloquium Adolf-Martens-Preis, Bundesanstalt für Materialwissenschaften und-prüfung, 30.10.2002, Berlin, Germany.
- U. Pöschl, Analysis and Reactivity of Carbonaceous Aerosol Components, EGS XXVII General Assembly 2002, 21.4.-26.4.2002, Nice.
- Q.-Z. Zhu, P. Degelmann, M. Schedl, D. Knopp, R. Niessner, Enrichment and Analysis of Sulfonylurea Herbicides using Molecularly Imprinted Polymers (MIPs) and Immunoaffinity Supports, 6th Sino-German Symposium on Chromatography, 26.-30.04.2002, München.

2.3.2 Poster Presentations

- M. Alte, T. Baumann, R. Niessner, B. Mizaikoff, W. Konz, J. Lucas, A. Katzir, N. Fleischmann & J. M. Bayona, In situ Versuche mit einem IR-spektroskopischen Sensorsystem zum Dauermonitoring von deponierelevanten organischen Schadstoffen auf Deponien und Altlastenflächen, FH-DGG Tagung, 9.-11.5.2002, Greifswald.
- M. Alte, T. Baumann, R. Niessner, B. Mizaikoff, W. Konz, J. Lucas, A. Katzir, N. Fleischmann & J. M. Bayona, Die in situ Messung deponierelevanter organischer Schadstoffe mit einem IR-spektroskopischen Sensorsystem, Wasserchemische Gesellschaft, 6.-8.5.2002, Eichstätt.
- H. Beck, C. Haisch and R. Niessner, A Photoacoustic Sensor System for Quantification of Soot Aerosols, 6th Intern. Aerosol Conference, 08.-13.09.2002, Taipei, Japan.
- P. Degelmann, Q.-Z. Zhu, D. Knopp, R. Niessner, Comparison of Molecularly Imprinted Polymers (MIPs) and Sol-Gel-Generated Immunoaffinity Columns (SGG-IAC) for the Enrichment and Analysis of Sulfonylurea Herbicides, Jahrestagung der Wasserchemischen Gesellschaft, 6.-8.5.2002, Eichstätt.
- R. Forkel, I. Barnes, H. Geiger, R. von Kuhlmann, U. Pöschl, Validation of Chemical Mechanisms to Describe the Degradation of Isoprene and alpha-Pinene for Incorporation in 3-D Chemistry-Transport Models (VALCHEM), AFO2000 Statusseminar, 7.10.-9.10.2002, Schliersee.
- T. Franze, R. Niessner, U. Pöschl, Protein Analysis in Aerosol Samples, Euroanalysis 12, 8.9.-13.9.2002, Dortmund.
- T. Franze, R. Niessner, U. Pöschl, Analysis of Proteins in Atmospheric Aerosols, Bioaerosols: A View From Different Perspectives, 1.7.-2.7.2002, Karlsruhe.
- C. Haskard, I. Schaupt, M. G. Weller: Enzyme Linked Immunosorbent Assay for the Detection of Cyclic Peptide Toxins and Their Fragments, 10th International Conference on Harmful Algae, 21.-25.10.2002, St. Pete Beach, Florida USA.
- R. Klein, T. Baumann & R. Niessner, MSWI Bottom Ash Elution, GRACOS International Workshop, 21.-22.5.2001, Tübingen.
- R. Klein, T. Baumann & R. Niessner, Energiebilanz einer Deponie aus Schlacken der Hausmüllverbrennung, FH-DGG Tagung, 9.-11.5.2002, Greifswald.
- B. Knecht, M. G. Weller, R. Nießner: Development of a Biosensor for the Rapid Detection of Antibiotics in Milk, 4th International Symposium on Hormone and Veterinary Drug Residue Analysis, 4.-7.6.2002, Antwerpen.
- K. Krause, A. Zerrath, R. Niessner, U. Pöschl, Chemical Analysis of Carbohydrates in Atmospheric Aerosols, Bioaerosols: A View From Different Perspectives, 1.7.-2.7.2002, Karlsruhe.
- K. Krause, T. Franze, A. Zerrath, R. Niessner, U. Pöschl, Chemical Analysis of Biopolymers in Atmospheric Aerosols, EGS XXVII General Assembly 2002, 21.4.-26.4.2002, Nice.
- K. Krause, T. Franze, A. Zerrath, R. Niessner, U. Pöschl, Chemical Analysis of Biopolymers in Atmospheric Aerosols, EUROTRAC Symposium 2002, 11.3.-15.3.2002, Garmisch-Partenkirchen.
- A. Messerer, U. Pöschl, R. Niessner, Thermophoretic Deposition of Soot Particles under Heavy Duty Vehicle Exhaust Gas Conditions, Fluid-Particle Interactions VI, 25.8.-30.8.2002, Barga.

-
- A. Messerer, U. Pöschl, R. Niessner, Thermophoretic Deposition for the Continuous Removal of Diesel Particulate Matter, 6th International ETH-Conference on Nanoparticle Measurement, 18.8.-21.8.2002, Zürich.
- R. Niessner, T. Schmid and U. Panne, On-line Monitoring of Biofilm Growth and Detachment by Photoacoustic Spectroscopy, XII. Intern. Conf. on Photoacoustic and Photothermal Phenomena, 24.-27.06.2002, Toronto.
- U. Pöschl, T. Franze, K. Krause, E. Mikhailov, C. Schauer, A. Zerrath, Carbonaceous Aerosol Components: Chemical Composition, Reactivity and Hygroscopicity (CARBAERO), AFO2000 Statusseminar, 7.10.-9.10.2002, Schliersee.
- U. Pöschl, T. Franze, K. Krause, E. Mikhailov, C. Schauer, A. Zerrath, Carbonaceous Aerosol Components: Chemical Composition, Reactivity and Hygroscopicity, Atmospheric Chemistry Within the Earth System: From Regional Pollution to Global Climate Change (IGAC, CACGP), Iraklion, 18.9.-25.9.2002.
- A. Sadezky, S. Kamm, U. Pöschl and R. Niessner, Raman Spectroscopy for the Characterisation of Soot Particles, EUROTRAC Symposium 2002, 11.3.-15.3.2002, Garmisch-Partenkirchen.
- P. Sazelova, D. Koval, V. Kasicka, F. Kilar, D. Knopp, G. Peltre, Analysis of Water Extracts from the Airborne Dust Samples by Capillary Isotachopheresis, 13th International Symposium on Capillary Electroseparation Techniques, 1.-4. 9. 2002, Helsinki, Finland.
- C. Schauer, K. Krause, R. Niessner, U. Pöschl, Analysis of Polycyclic Aromatic Hydrocarbons (PAH) and Nitro-PAH in Aerosol Samples, International Symposium on Chromatography, 8.9.-13.9.2002, Leipzig.
- C. Schauer, R. Niessner, U. Pöschl, Polycyclic Aromatic Aerosol Components: Chemical Analysis and Reactivity, EGS XXVII General Assembly 2002, 21.4.-26.4.2002, Nice.
- C. Schauer, R. Niessner, U. Pöschl, Polycyclic Aromatic Aerosol Components: Chemical Analysis and Reactivity, EUROTRAC Symposium 2002, 11.3.-15.3.2002, Garmisch-Partenkirchen.
- I. Schaupt, M. G. Weller, R. Nießner: LC-ESI-TOF-MS in Verbindung mit Immunoaffinitätsanreicherung für den Nachweis von Microcystinen in Trink- und Oberflächenwasser, Jahrestagung Wasserchemische Gesellschaft, 6.-8.5.2002, Eichstätt.
- T. Schmid, U. Panne, C. Haisch, R. Niessner: Biofilm Monitoring by Photoacoustic Spectroscopy (PAS), International Specialised Conference on Biofilm Monitoring, 17.-20.3.2002, Porto, Portugal.
- T. Schmid, U. Panne, C. Haisch, R. Niessner: Process Analysis of Biofilms by Photoacoustic Spectroscopy, Euroanalysis XII, 8.-13.9.2002, Dortmund.
- T. Schmid, U. Panne, C. Haisch, R. Nießner: Untersuchung von Biofilmen mittels Photoakustischer Spektroskopie (PAS), Jahrestagung der Wasserchemischen Gesellschaft 2002, 6.5-8.5.2002, Eichstätt.
- T. Schmid, U. Panne, C. Haisch, R. Nießner: Untersuchung von Biofilmen mittels Photoakustischer Spektroskopie (PAS), GVC/DECHEMA-Jahrestagungen 2002, 11.6-13.6.2002, Wiesbaden.
- T. Schmid, U. Panne, R. Niessner: On-line Monitoring of Biofilm Growth and Detachment by Photoacoustic Spectroscopy, 12th International Conference on Photoacoustic and Photothermal Phenomena, 24.6-27.6.2002, Toronto, Canada.

-
- T. Schmid, C. Helmbrecht, C. Haisch, U. Panne, R. Niessner: On-line Monitoring of Opaque Liquids by Photoacoustic Spectroscopy, Euroanalysis XII, 8.9.-13.9.2002, Dortmund.
- D. Spangenberg, A. Reisinger, T. Baumann & R. Niessner, Elektrokinetische Behandlung von Wasserwerksrueckstaenden, Wasserchemische Gesellschaft, 6.-8.5.2002, Eichstätt.
- J. Uecker, M. Hanke, S. Kamm, B. Umann, F. Arnold, U. Pöschl, R. Niessner, Measurements of Gas-phase H₂SO₄, HO, SO₂ and Aerosol Size Distributions on Mt. Zugspitze at the Schneefernerhaus: Estimation of Sources and Sinks of Sulfuric Acid, AFO2000 Statusseminar, 7.10.-9.10.2002, Schliersee.
- J. Uecker, M. Hanke, S. Kamm, B. Umann, F. Arnold, U. Pöschl, R. Niessner, Measurement of Gas-phase H₂SO₄, OH SO₂ and Aerosol Size Distribution on Mount Zugspitze at the Schneefernerhaus: Estimation of Sources and Sinks of Sulfuric Acid, EGS XXVII General Assembly 2002, 21.4.-26.4.2002, Nice.
- R. von Kuhlmann, M. G. Lawrence, U. Pöschl, P. J. Crutzen, Sensitivities in Modeling Isoprene in a 3-D Global Chemistry-Transport Model, AFO2000 Statusseminar, 7.10.-9.10.2002, Schliersee.
- C. Wersching, M. G. Weller, R. Nießner: Indirekter, kompetitiver Enzym-Immunoassay für das Herbizid Glufosinat, Jahrestagung Wasserchemische Gesellschaft, 6.-8.5.2002, Eichstätt.
- A. Zerrath, K. Krause, R. Niessner, U. Pöschl, Analysis of Carbohydrates in Air Particulate Matter, Euroanalysis 12, 8.9.-13.9.2002, Dortmund.
- A. Zerrath, K. Krause, T. Franze, R. Niessner, U. Pöschl, Analysis of Biopolymers in Atmospheric Aerosols, 6th International Aerosol Conference, 8.9.-13.9.2002, Taipeh.
- A. Zerrath, K. Krause, T. Franze, C. Schauer, A. Messerer, S. Kamm, R. Niessner, U. Pöschl, Physical and Chemical Characterisation of Alpine Aerosols at the GAW Observatory Schneefernerhaus on Mount Zugspitze, EGS XXVII General Assembly 2002, 21.4.-26.4.2002, Nice.
- A. Zerrath, K. Krause, T. Franze, C. Schauer, A. Messerer, S. Kamm, R. Niessner, U. Pöschl, Physical and Chemical Characterisation of Alpine Aerosols at the GAW Observatory Schneefernerhaus on Mount Zugspitze, EUROTRAC Symposium 2002, 11.3.-15.3. 2002, Garmisch-Partenkirchen.

2.3.3 Invited Lectures

- D. Knopp, Preparation and Application of Molecularly Imprinted Polymers (MIPs) and Natural Antibodies for the Enrichment of Sulfonylurea Herbicides in Environmental Samples, 7th International Symposium on Advances in Analytical Separation Science, 3.-5.6. 2002, Pörschach, Austria
- D. Knopp, Immunologische Analytik im Umweltbereich, 6.6.2002, Johannes Kepler Universität Linz, Institut für Chemie, Bereich Analytische Chemie
- R. Nießner, Laser & Antikörper: Starke Partner der Analytischen Chemie. Institutskolloquium, 15.01.2002, Institut für Spektrochemie und Angewandte Spektroskopie, Dortmund
- R. Nießner, Laser & Antikörper: Starke Partner der Analytischen Chemie, Fachbereich Chemie, 04.02.2002, Universität Leipzig

-
- R. Nießner, Laser & Antikörper: Starke Partner der Analytischen Chemie, GDCh-Kolloquium, 17.04.2002, Universität Marburg
- R. Nießner, Laser Spectroscopy and Antibodies: Strong Partners for Analytical Chemistry, Lecture, Department of Optics & Quantum Electronics, 15.05.2002, University of Szeged
- R. Nießner, Laser Spectroscopy and Antibodies: Strong Partners for Analytical Chemistry, Lecture, Department of Chemical Information Technology, 16.05.2002, Budapest-University of Technology & Economics
- R. Nießner, Laserlight or Antibodies: Two Strong Partners for Analysts, Kolloquium, 11.06.2002, ETH Zürich
- R. Nießner, Laser-based Detection Techniques for Environmental Analysis, International Symp. on the Environment and Analytical Chemistry, 17. - 21.06.2002, University Plymouth
- R. Nießner, Laser & Antikörper: Starke Partner der Analytischen Chemie, 26. Clemens-Winkler-Kolloquium, 24.10.2002, Bergakademie Technische Universität Freiberg
- R. Nießner, Laserlight and Antibodies: Two Strong Partners for Analysts, 10as Jornadas de Análisis Instrumental, Barcelona, 26.-29.11.2002, Expoquimia Barcelona
- U. Pöschl, Carbonaceous Aerosol Components: Chemical Composition and Reactivity Labor für Radio- und Umweltchemie, Paul Scherrer Institut, 18.1.2002, Villigen.
- U. Pöschl, Analyse, Reaktivität und ökologische Effekte organischer Aerosolkomponenten, Lehrstuhl für Hydrologie, Universität Bayreuth, 6.6.2002, Bayreuth.
- U. Pöschl, Physikalisch-chemische Eigenschaften kohlenstoffhaltiger Aerosolkomponenten, Institut für Physikalische und Theoretische Chemie, Technische Universität Wien, 12.6.2002, Wien.
- U. Pöschl, Physical and Chemical Characterisation of Alpine Aerosols at the GAW Observatory Schneefernerhaus on Mount Zugspitze, ETH Zürich, Institut für Atmosphären- und Klimaforschung, 24.6.2002, Zürich.
- U. Pöschl, Aerosolcharakterisierung am Observatorium Schneefernerhaus/Zugspitze, Institut für Meteorol. und Klimaforsch., Forschungszentrum Karlsruhe, 25.6.2002, Karlsruhe.
- U. Pöschl, Erdatmosphäre und Klima: Naturwissenschaftliche, gesellschaftliche und technische Perspektiven, Verein Deutscher Ingenieure (VDI), 26.6.2002, München.
- U. Pöschl, Carbonaceous Aerosol Components: Chemical Composition and Reactivity, 224th American Chemical Society National Meeting, 21.8.2002, Boston.
- U. Pöschl, Aerosol Measurements at the Schneefernerhaus Observatory on Mount Zugspitze, Swiss Academy of Natural Sciences, Workshop on Atmospheric Research in the Alps, 20.9.2002, Davos.
- M. G. Weller, Multidimensional Analysis of Cyanobacterial Toxins, Analytica 2002, 25.4.2002, München.
- M. G. Weller, B. Knecht, R. Nießner, E. Märtilbauer, A. Strasser, R. Dietrich, K. Zaadhof, Biosensor zum Antibiotikachweis, 75. Tagung des Wissenschaftlichen Rates der AiF, 28.11.2002, Magdeburg.

2.3.4 Scientific Committee

- R. Nießner: Jahrestagung 2002 der Wasserchemischen Gesellschaft, Eichstätt, 06.-08.05.2002 (Scientific Programme Committee)
- R. Nießner: Workshop, Karlsruhe Forschungszentrum, 02.-03.07.2002, Bioaerosols: A View from Different Perspectives (Scientific committee)
- R. Nießner: 10th International Symposium on Field-Flow Fractionation, Amsterdam, 02.-05.07.2002 (Scientific Programme Committee)

2.4 Hydrogeological Consulting

Mineralisation control analyses Bad Füssing, Bad Birnbach, Gundremmingen, Straubing, Kellberg, Bad Wimpfen, Bad Tölz, Bad Griesbach, Bad Rodach, Sibyllenbad, Kondrau, Bayreuth, Radenska (SLO)

Hydrogeological and hydrochemical expertises (mineral water, spa water) Bad Gögging, Bad Brückenau, Siegsdorf, Kondrau

2.5 Diploma Theses

- Cand.geol. Marcus Bock: Tracerversuche zur Bestimmung des Wasser- und Stoffhaushaltes der MVA-Schlackedeponie Großmehring.
- Cand.chem. Michael Elsässer: Anwendung eines elektrischen Niederdruckimpaktors zur Aerosolcharakterisierung und Untersuchung von Cellulose-Partikeln.
- Cand.chem. Lillian Kleiber: Laserablation an heterogenen Feststoffproben.
- Cand.ing. Marcus Donié: Zeitaufgelöste laserinduzierte Fluoreszenzspektroskopie von Benzo[a]pyren auf Rußaerosolen (FH München).

2.6 PhD Theses

- Dipl.-Ing. Larissa Beier: Entwicklung, Bau und Anwendung der Lichtwellen-Multiplexer für faseroptisch geführte Sensorsysteme
- Dipl.-Chem. Rüdiger Düsing: Multidimensionale Fluoreszenzspektroskopie in der Umweltanalytik
- Dipl.-Chem. Andreas Exner: Einsatz der asymmetrischen Fluß-Feldflußfraktionierung in der Hydro-Kolloidanalytik unter Verwendung Thermischer-Linsen-Spektroskopie und anderer spektroskopischer Methoden zur Detektion
- Dipl.-Chem. Lutz Krämer: Mikrostruktur ultrafeiner Aerosolpartikel und Photoakustische Detektion von Rußaerosolen
- Dipl.-Min. Claudia Speiser: Exothermer Stoffumsatz in MVA-Schlackendeponien: Mineralogische und geochemische Charakterisierung von Müllverbrennungsschlacken, Stoff- und Wärmebilanz
- Dipl.-Chem. Anne Zeck: Entwicklung von immunanalytischen, chromatographischen und massenspektrometrischen Methoden zur Bestimmung cyanobakterieller Hepatotoxine (Microcystine und Nodularine)

2.7 Habilitation Thesis

Dr. Michael G. Weller: Immunchemische Methoden in der Umweltanalytik

3 Teaching, Colloquia, and Other Activities

3.1 Classes

Chemie gelöster und ungelöster Wasserinhaltsstoffe, Teil 1: Wasserkreislauf und Gleichgewichte	Nießner
Chemie gelöster und ungelöster Wasserinhaltsstoffe, Teil 2: Hydrokolloide, micellare Systeme und photochemische Umsetzungen	Nießner
Umweltanalytik, Teil 1: Grundlagen der instrumentellen Analytik von Wasserinhaltsstoffen	Nießner
Umweltanalytik, Teil 2: Charakterisierung von Luftinhaltsstoffen (Gase und Aerosole)	Nießner
Umweltanalytik, Teil 3: Organische Spurenanalytik an Umweltmatrices	Nießner
Massenspektrometrie in der Umweltanalytik	Weller, Nießner
Biochemische und molekularbiologische Analyseverfahren in der Umweltanalytik	Knopp
Die Mineral-, Thermal- und Heilwässer in Bayern und ihr hydrogeol. Rahmen	M. Baumann, Nießner
Einführung in das hydrogeologische Praktikum I, II, III	M. Baumann, Nießner
Brunnenbau und Bohrtechnik	M. Baumann, Nießner
Hydrogeologie I und II	T. Baumann, Frisch (Lehrauftrag)
Ausbreitung von Schadstoffen im Untergrund	T. Baumann
Ausgewählte Kapitel und Übungen zur Hydrogeologie	T. Baumann
Erkundung und Sanierung von Grundwasserschadensfällen	T. Baumann
Modellierung der Grundwasserströmung und des Stofftransports	T. Baumann
Hydrochemische Modellierung	T. Baumann
Chemie und Technologie des Trink- und Betriebswassers I (Wasser und Umwelt)	Knopp
Chemische Charakterisierung von Umweltmatrices (Gase)	Nießner
Statistische Methoden in der Umweltanalytik	Panne
Umweltmeßtechnik mit spektroskopischen Methoden	Panne
Analytische Methoden für Gase und Aerosole	Pöschl
Gasmesstechnik	Pöschl
Atmosphärenchemie und Klimaforschung (TU Wien)	Pöschl

3.2 Lab Courses and Seminars

Vertiefungsfach Analytische Chemie, Teil 1 Organische Spurenanalytik	Nießner, Weller, Panne
Teil 2 Methoden der Strukturaufklärung und Instrumentellen Analytik	Nießner und Mitarbeiter, Dozenten in Garching
Wasserchemisches Praktikum I: Wasseranalyse	Panne, Weller, Nießner
Wasserchemisches Praktikum II: Wassertechnologie	Panne, Nießner
Praktikum Umweltmesstechnik	Pöschl
Hydrogeologisches Praktikum I: Gesteinsphysikalische Methoden	T. Baumann, Nießner
Hydrogeologisches Praktikum II: Hydrochemische Methoden	T. Baumann, Nießner
Hydrogeologisches Praktikum III: Geländeübungen mit Kurs	T. Baumann, Nießner
Geochemisches Praktikum (Univ. Konstanz)	T. Baumann
Hydrogeologische und hydrochemische Exkursionen	T. Baumann, Nießner
Hydrogeologisches, hydrochemisches und umweltanalytisches Seminar	T. Baumann, Nießner

3.3 Institute Colloquia

- Prof. Dr. Klaus Kümmerer, Institut für Umweltmedizin, Universität Freiburg: Chromatographische Methoden zur Analyse von Arzneimitteln und ihren Wirkungen in unterschiedlichen Matrices (16.1.2002)
- Prof. Dr.-Ing. Klaus K. Unger, Institut für Anorganische Chemie und Analytische Chemie, Universität Mainz: Multidimensionale HPLC für die Proteomanalytik (21.1.2002)
- Prof. Dr. Gunther Wittstock, Department of Chemistry, Carl von Ossietzky Universität Oldenburg: Ortsaufgelöste elektrochemische Analytik mit Rastersondenmethoden: Prinzipien und Anwendungen (29.1.2002)
- Dr. Ingrid Chorus, Umweltbundesamt Berlin: Verbreitung, Bedeutung und Bestimmung von Cyanobakterien-Toxinen (18.2.2002)
- Prof. Charles J. Werth, Dept. of Civil and Environmental Engineering, University of Illinois at Urbana-Champaign: Evaluation of a halo-respiration enhancing redox transition zone technology for dense nonaqueous phase liquid remediation (26.2.2002)
- Dr. Uwe Schlosser, Deutsches Textilforschungszentrum Nord-West e.V., Gerhard-Mercator-Universität Duisburg: Einsatzmöglichkeiten der photoakustischen und photothermischen Messtechniken in der Textilveredelung (27.2.2002)
- Dr. Hugo Hämmerle, NMI Naturwissenschaftliches und Medizinisches Institut an der Universität Tübingen: Aspekte der Zell-Chip-Kopplung in der Neuro-Sensorik (14.3.2002)
- Dipl.-Ing. Frank Dehn, MFPA Gesellschaft für Materialforschung und Prüfungsanstalt für das Bauwesen, Leipzig: Photokatalytisch aktiver Beton als Baustoff und für die Wassertechnologie: Systemkonzepte und analytische Kontrolle (26.3.2002)
- Dr. Hans Senn, Pharma Forschung, Hoffmann-La Roche AG, Basel: NMR-Miniaturisierung und -Hochdurchsatz für Qualitätskontrolle und Screening in der Pharmaindustrie (12.4.2002)

-
- Prof. Dr. Christian Huber, Instrumentelle Analytik - Umweltanalytik, Universität des Saarlandes, Saarbrücken: Hochauflösende Trennungen von Biopolymeren in monolithischen Kapillarsäulen: Optimierung der Trennsysteme und Kopplung mit der Massenspektrometrie (15.4.2002)
- Prof. Dr. Koen Janssens, University of Antwerp, Belgium: Synchrotron μ -XRF with Possibilities for Speciation in the Solid State (23.4.2002)
- Dr. Nicolas H. Bings, Institut für Analytische Chemie, Universität Leipzig: Die Flugzeitmassenspektrometrie mit dem induktiv gekoppelten Plasma: Grundlagen und Anwendungen in der Elementanalytik (13.5.2002)
- Dr. Marco Stampanoni, Institute of Biomedical Engineering, University of Zurich and ETHZ: Synchrotron Based X-Ray Tomographic Microscopy: From the Detector to Applications (14.6.2002)
- PD Dr. Volker Deckert, Institut für Angewandte Photophysik, TU Dresden: Molecular Analysis at the Edge - Spectroscopy in the Near Field (9.7.2002)
- Prof. Dr. Josef Pelzl, Institut für Experimentalphysik III Festkörperspektroskopie, Ruhr-Universität Bochum: Möglichkeiten und Anwendungen der photothermischen Mikroskopie (23.7.2002)
- Prof. Dr. Klaus Günther, Institut für Chemie und Dynamik der Geosphäre Institut III: Phytosphäre, Forschungszentrum Jülich: Hormonell-aktive Metabolite der Alkylphenolethoxylate (EDMAPEs) in Lebensmitteln und Umwelt - eine vielschichtige Herausforderung für die Analytische Chemie (27.8.2002)
- Prof. Kiyokatsu Jinno, School of Materials Science, Toyohashi University of Technology, Japan: Miniaturized Separation System with Fiber-Packed Capillaries as the Medium (5.9.2002)
- Prof. Noam Weisbrod, Department of Environmental Hydrology und Microbiology, Ben-Gurion University of the Negev: Fracture Flow in the Vadose Zone: Impact of Particle Release (17.9.2002)
- Dr. Christoph Hauger, Fa. Zeiss, Oberkochen: Medizinische Anwendungen der Optischen Kohärenz-Tomographie (11.10.2002)
- Prof. Dr. Christof M. Niemeyer, Fachbereich Chemie, Biologisch-Chemische Mikrostrukturtechnik, Universität Dortmund: Halbsynthetische DNA-Protein-Konjugate: Neue Werkzeuge für Bioanalytik und molekulare Nanotechnologie (11.11.2002)
- Prof. Dr. Peter C. Hauser, Department of Chemistry, University of Basel: Electrochemical Detection Techniques in Conventional and On-Chip Capillary Electrophoresis (25.11.2002)
- PD Dr. Albrecht Seidel, Biochemisches Institut für Umweltcarcinogene, Großhansdorf: Human-Biomonitoring carcinogener aromatischer Verbindungen (2.12.2002)

3.4 External Tasks and Memberships

Prof. Dr. Reinhard Nießner

BayFORUV	Board of Directors
BayFORREST	Member
Fachbereich IV Meßtechnik der VDI/DIN-Kommission Reinhaltung der Luft	Advisory Board Member
Bayer. Fachausschuß für Kurorte, Erholungsorte und Heilbrunnen	Member
DECHEMA Commission "Chemische Grundlagen und Anwendungen der Sensortechnik"	Member (from 11/2002)
DFG-Senatskommission für Wasserforschung	Member (from 11/2002)
Beratergremium für Altstoffe (BUA) der GDCh	Member (until 12/2002)
Heinrich-Emanuel-Merck-Award	Jury Head
ISPAC-Award for Polycyclic Aromatic Hydrocarbon Research	Jury Member
Institut für Abfallforschung, Augsburg	Advisory Board Member
Hydrochemical Society within the GDCh	Board of Directors
Association for Aerosol Research	Board of Directors
Analytical Chemistry	Associated Editor
Analytical and Bioanalytical Chemistry	Editorial Board Member
Microchimica Acta	Editorial Board Member
Römpp Lexika	Editorial Board Member
Fresenius' Environmental Bulletin	Advisory Board Member
Analytical Sciences	Advisory Board Member
Analyst	Advisory Board Member

PD Dr. Dietmar Knopp

BayFORREST	Member
KRdL-3/7/04, "Luftgetragene Mikroorganismen und Viren", im VDI/DIN	Member
Vom Wasser	Editorial Board Member

Dr. Ulrich Pöschl

Atmospheric Chemistry and Physics	Chief Executive Editor
-----------------------------------	------------------------

4 Equipment

4.1 Hydrogeology

Two pilot scale tanks with flow lengths of up to 10 m allow transport experiments in a controlled environment while preserving almost natural conditions. Apart from studies on the transport behaviour of contaminants and colloids, these facilities are used for testing sensor prototypes and serve as a test bed for numerical models.

Three field sites equipped with more than 100 monitoring wells and carefully hydrogeologically and hydrochemically characterized are available for field scale propagation studies.

Additionally three landfill monitoring sites, one municipal solid waste landfill, one MSWI bottom ash landfill, and one mixed waste landfill are run by the institute.

4.2 Environmental Analytical Chemistry

4.2.1 Laser

- 4 He/Ne-laser
- 6 Nd-YAG-laser
- 1 CO₂-laser
- 3 Dye-laser (tuneable with frequency doubler)
- 5 N₂-laser
- 8 Tuneable diodelaser (600-1670 nm; ca. 100 mW CW)
- 1 Laserdiodearray with 10 diodes (0.8 μm - 1.8 μm)
- 1 Laserdiode with external resonator
- 1 Optical parameter oscillator (410 nm - 2.1 μm)

4.2.2 Optoelectronics/Spectrometer

- 1 Rowland spectrometer
- 1 Echelle spectrometer
- 1 FTIR-Spectrometer, Perkin Elmer 1600
- 1 Fluorescence spectrometer, Perkin Elmer LS-50
- 1 Fluorescence spectrometer, Shimadzu RF 540
- 1 UV/VIS spectrometer, Beckman DU 650
- 1 Boxcar integrator
- 4 Digital storage oscilloscopes (400 MHz, 500 MHz)
- 3 Optical multichannel analysators with monochromators, time-resolving
- 3 Intensified CCD cameras
- 1 Wavemeter

4.2.3 Chromatography

- 7 GCs with FID, NPD, ECD, TEA and AED
- 1 GC/MS, block-injection and autosampler
- 1 High-resolution GC/MS, VG Autospec
- 1 LC-Orthogonal-ESI-TOF-MS, Micromass
- 1 Lyophilizer
- 1 Asymmetrical Field-flow-fractionation system
- 1 SFE-System with modifier, Suprex
- 2 Concentrators for dynamic headspace analysis
- 1 High-speed counter-current-distribution chromatographic system
- 3 HPLC, UV/VIS array detector, programmable fluorescence detector
- 2 HPLC
- 1 Capillary electrophoresis system
- 1 Ion chromatograph, Dionex 4500 i
- 1 Ion chromatograph, Dionex BioLC (Photodiode Array Detector, Electrochemical Detector)

-
- 1 AMD system for HPDC with UV, VIS and fluorescence scanner
 - 1 LC system, ECONO
 - 1 Preparative HPLC

4.2.4 Dioxin Laboratory

- 3 High security labs with locks, separate activated carbon filter and high-performance particle filter systems

4.2.5 Bioanalytics

- 2 Fluorescence reader systems, time-resolving
- 3 Photometric reader systems
- 1 Chip spotter system, GESIM

4.2.6 Element Analytics

- 1 TXRF, Atomika EXTRA II a
- 1 Flame-Photometer, Eppendorf ELEX 6361
- 2 AAS systems with flame atomization, electrothermal atomization, hydrid system, Perkin-Elmer PE 3300, ELAN 4100
- 1 ICP-MS, Perkin-Elmer ELAN 6100

4.2.7 SEM/Microscopy

- 1 SEM/EDX system
- 2 Polarisation microscopes for phase analysis
- 1 Image analysis software for automated image processing
- 1 Inert gas glovebox
- 1 Laser Raman microscope, Renishaw (514 nm, 633 nm, 780 nm)
- 1 Zetaphoremeter, SEPHY

4.2.8 Sum Parameters

- 2 Coulostat for C quantification, Coulomat 702
- 1 DOC analysator, UNOR 6 N
- 1 TOC analysator, TOCOR 2
- 1 AOX/TOX, Sigma

4.2.9 Aerosol Research

- 1 Aerosol chamber (1 m³)
- 1 Aerosol flow tube (10 L)
- 1 Ozone analyzer (UV absorption)
- 1 NO/NO₂ analyser (Chemiluminescence)
- 2 Aerodynamic particle sizers (0.5-25 μm)
- 1 Berner impactor (9 stages, 50 nm - 16 μm)
- 1 Electrical low-pressure impactor (12 stages, 30 nm - 10 μm)
- 2 Low-Volume filter samplers (PM 10, PM2.5)
- 1 High-Volume filter sampler (PM 2.5)
- 2 Differential mobility particle sizer systems (10-1000 nm)
- 2 Diffusion batteries (5-300 nm)
- 5 Condensation nucleus counters
- 3 Electrostatic classifiers (10-1000 nm)
- 2 Spark-discharge soot aerosol generators (polydisperse ultrafine carbon aerosol)
- 1 Berglund-Liu aerosol generator (monodisperse aerosols, 0.8-50 μm)
- 1 Floating bed aerosol generator (powder dispersion)
- 1 Brush aerosol generator (powder dispersion)

5 Staff 2002

Univ.-Prof. Dr. Reinhard Nießner
Dr. Manfred Baumann (until 4/02)
Dr. Thomas Baumann
Dr. Christoph Haisch
Dr. Ralf Klein
PD Dr. Dietmar Knopp
Dr. Kerstin Krause (until 11/02)
Dr. Nikolaus Nestle (until 12/02)
PD Dr. Ulrich Panne
Dr. Ulrich Pöschl
Dr. Harald Prestel
PD Dr. Michael Weller

Birgit Apel
Günter Dollinger
Roswitha Glunz
Karin Koller
Gisela Lang
Joachim Langer
Ramona Leube
Susanne Mahler
Christine Sternkopf
Christa Stopp
Sebastian Wiesemann

Hatice Hazir
Mira Kolar

PhD Students

Dipl.-Geol. Matthias Alte
Dipl.-Chem. Harald Beck (until 9/02)
Dipl.-Chem. Petra Degelmann
Dipl.-Chem. Barbara Fall (until 9/02)
Dipl.-Chem. Herbert Fink (until 5/02)
Dipl.-Chem. Thomas Franze
Leb.-Chem. Martin Kiening (from 3/02)
Dipl.-Chem. Bertram Knecht
Dipl.-Chem. Marion Lackhoff (until 12/02)
Dipl.-Chem. Diana Matschulat (from 2/02)
Dipl.-Ing. Armin Messerer
Dipl.-Phys. Igor Radivojevic
Dipl.-Chem. Ulrike Schaller (from 11/02)
Dipl.-Chem. Christian Schauer
Dipl.-Leb. Isabel Schaupt
Dipl.-Chem. Thomas Schmid
Dipl.-Geol. Dagmar Spangenberg
Dipl.-Chem. Axel Zerrath

External PhD Students

Dipl.-Chem. Michael Harris (OMG AG, Hanau)
Dipl.-Biol. Thomas Meindl (GSF)
Dipl.-Chem. Dieter Rothe (MAN)
Apothekerin Ellen Bitterle (GSF)

Diploma Students

Christoph Adelhelm (from 12/02)
Josef Fischer (from 8/02)

Guests and Research Fellows

Arpit Ahuja, India (5/02 - 7/02)
Eugenia Bucur Eriksson (4/02 - 6/02)
Dr. Anping Deng, Sichuan University, Chengdu/China
Dr. Evgene Mikhailov, State University, Petersburg/Russia (3/02 - 5/02)
Xavier Prieto-Mollar, Uni Barcelona/Spainien (until 7/02)
Anna Raszka (7/02 - 8/02)
Viktoriya Rupp (from 9/02)
Elena Salenius, Finnland (4/02 - 5/02)
Prof. Dr. Atsushi Yarai, Osaka Sangyo University, Osaka/Japan (from 8/02)
Dr. Qing-Zhi Zhu, Xiamen University/China (until 5/02)

Student Assistants

Owen Fenton, M. A. (from 12/02)
Dipl.-Biol. Iris Vomberg (8/02)
Dipl.-Chem. Anne Zeck (until 8/02)
Clemens Helmbrecht
Steven Kanngießner (from 10/02)
Andreas Keilbach
Jochen Knefel (from 10/02)
Peter Schock (from 9/02)