

## Ecotoxicology

### V3

#### **Examination of the effect of humic acids on metal content and toxicity of leachates from coal fly ash samples using the availability test NEN 7341 and a battery of bioassays**

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Coal fly ash is a major by-product that is produced by coal incineration process for power production. Although there are several ways for fly ash recycling such as cement industry, soil stabilization or control of acid mine drainage, the vast majority of generated fly ash is disposed off as solid waste. Several leaching tests have been developed for the evaluation of the environmental hazard that solid wastes may pose, due to the leaching of heavy metals from solid to liquid phase. The availability test NEN 7341 is defined as a leaching test for the evaluation of the maximum quantity of the inorganic constituents that may be released into aquatic phase under aggressive leaching conditions. Furthermore, bioavailability and toxicity of heavy metals is dependent on various physicochemical parameters such as particle size, various interactive effects, pH, hardness and complexation with organic matter (humic or fulvic acids). In the present work the availability and the toxicity of heavy metals that leached from six coal fly ash samples were examined by use of the NEN 7371 leaching test together with a battery of bioassays. The effect of humic acids on the availability and the toxicity of heavy metals was examined by the addition of 25 and 50 mg/L of humic acids in the leaching medium. The toxicity of the produced leachates was evaluated using a battery of toxicity tests including the photobacterium *Vibrio fischeri* (Microtox test), as well as the algae *Pseudokirchneriella subcapitata* and the crustacean *Daphnia magna* (Toxkits microbiotests). Physicochemical analyses showed that the presence of humic acids in the leaching medium caused a decrease of Cu concentration in the leachates of all fly ashes tested, while the concentration of other heavy metals such as Cr, Zn and Ni was not significantly affected. Furthermore, the concentration of the most soluble major constituents such as Ca, Mg and Na was significantly decreased by the presence of humic acids in the leaching medium, indicating strong complex formation ability between these constituents and humic acids. This may inhibit the detoxification capacity of humic acids, since the presence of Ca, Mg and Na in the leachate may compete the complex formation between humic acids and heavy metals. The leachates of all fly ashes tested were specifically toxic for *P. subcapitata*, indicating a growth inhibition varying from 40 to 95 %, while the toxic effects on *D. magna* and *V. fischeri* were lower. Moreover, the presence of humic acids in the leaching medium did not significantly affect the toxicity of the leachates in most cases.

**Keywords:** availability test; fly ash; leaching; bioassays; humic acids

### V4

#### **Design of sustainable chemical products: A multidisciplinary approach model: Ionic liquids**

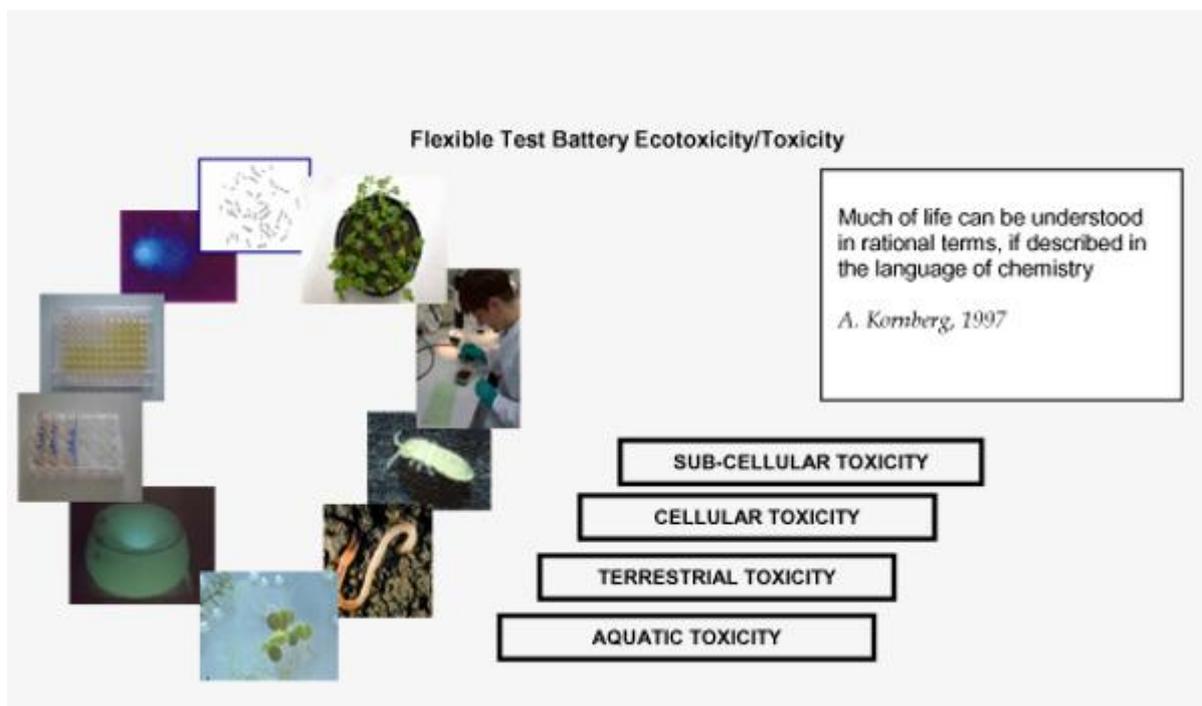
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Our inter- and transdisciplinary strategy to design sustainable chemical products ( here ionic liquids - ILs ) was published recently <sup>2,3</sup>. The strategy is aimed at the design of products with high process efficiency, acceptable costs and a toxic potential for man and the environment as low as possible without losing the wanted technological properties. In short: our strategy is based on the following tools:

- i) a work sharing open minded cooperation between academia, industry and small and medium enterprises,
- ii) a T-SAR (Thinking in terms of structure-activity-relations<sup>4</sup>) guided selection of Ionic Liquid's-

structures and substructures (“Testkit”),  
 iii) a flexible (eco-) toxicological test battery on different levels of biological complexity,  
 iv) T-SAR based theoretical assessment of presumable transformation products (“metabolites”),  
 v) metabolite identification in different biological systems,  
 vi) membrane uptake and membrane interactions, vii) evaluation of qualitative and quantitative structure-activity- relations (T-SAR/QSAR), and a multidimensional risk analysis (release, spatiotemporal range, bioaccumulation, biological activity and uncertainty).<sup>5)</sup>  
 We have divided ionic liquids structures into the following substructures: head group (positively charged moiety), side chains and anions. We shall report on the state of knowledge obtained by systematic structure-activity-relation studies on the impact of these substructures (alerts) on the (eco)-toxicity of ILs.  
 Taking the need for a sustainable development as pointed out in Agenda 21, chapter 19, and the principles of Green Chemistry (4th and 10th principle) as the starting point, this report will summarize our strategy and discuss the current status in hazard and risk assessment of Ionic Liquids established by the “Ionic Liquid Network”<sup>1)</sup>. coordinated at the University of Bremen.



[Fig 1]

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<sup>2)</sup> B. Jastorff, R. Störmann, J. Ranke, K. Mölter, F. Stock, B. Oberheitmann, W. Hoffmann, J. Hoffmann, M. Nüchter, B. Ondruschka and J. Filser (2003), How hazardous are ionic liquids? *Green Chemistry* 5, 136 - 146

<sup>3)</sup> B. Jastorff, J. Ranke, K. Mölter, P. Behrend, U. Bottin-Weber, J. Filser, A. Heimers, B. Ondruschka, M. Schäfer, A. Stark, P. Stepnowski, F. Stock, R. Störmann, S. Stolte, U. Welz-Biermann, S. Ziegert and J. Thoeming (2005), Progress in evaluation of risk potential of ionic liquids- basis for an eco-design of sustainable products, *Green Chemistry* 7, 362 - 372

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<sup>5)</sup> J. Ranke and B. Jastorff, *Environ. Sci. Pollut. Res.* (2000), 7, 105-114

## V5

### How might selenium counteract the effects of mercury toxicity in stream fish tissue across the Western USA?

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The ability of selenium (Se) to moderate mercury (Hg) toxicity needs to be considered when assessing risks associated with fish tissue Hg exposure. Mercury concentrations that ordinarily produce toxic effects in animals are counteracted when Se co-occurs with Hg and Se:Hg molar ratios >1. We analyzed whole body Se and Hg concentrations in 468 fish from 137 sites across 12 western U.S. states. The fish samples were evaluated relative to current tissue based water quality Hg criteria for wildlife (0.1 µg Hg/g) and humans (0.3 µg Hg/g) and relative to presumed protections when Se:Hg molar ratios >1. A large proportion (56%) of our total fish sample exceeded the wildlife Hg criterion while a smaller but significant proportion (14%) exceeded the human consumption criterion. However, 97.5% of the total fish sample contained more Se than Hg (molar ratio >1) leaving ~2.5% with molar excesses of Hg that are expected to pose Hg toxicity risks. All but one of the fish with Se:Hg <1, were of the same genus: *Ptychocheilus* (pikeminnow). Literature describing Se protection against Hg toxicity and our findings that the molar ratio of Se:Hg in fish of the western United States is only rarely <1, suggests that a limited number of freshwater fish, from a limited number of species, might pose Hg toxicity problems for wildlife or human consumers. Selenium should be factored into the Hg fish tissue based water quality criterion.

## Ecotoxicology

### V6

#### Bioaccumulation and heat shock proteins in marine mussels (*Mytilus galloprovincialis*) exposed to zinc pyrithione

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**Aims:** We investigated the biological fate and the effects of the organic biocide zinc pyrithione (ZPT) in comparison to inorganic Zn on the marine mussel *Mytilus galloprovincialis*, commonly widespread on hard bottoms of confined habitats such as harbours and marinas, where ZPT may be released in consequence of the use of antifouling paints and also become a source of Zn contamination. In particular, our aim was to highlight the pattern of accumulation of Zn both in his organic and inorganic form in the gills and in the digestive gland of the mussels and to assess in what measure a short term exposure to ZPT at sublethal doses could lead to the activation of repair mechanisms as highlighted by an increased expression of the early stress indicators hsp27, hsp60 and hsp70.

ZPT has been introduced as a replacement for organotin compounds, which have recently been banned from antifouling treatments, but it has received little attention due to the lack of sufficient analytical methods for its determination in environmental matrices. ZPT is marketed as being an environmentally neutral, non-persistent compound based on the fact that it easily photolyses and rapidly degrades when exposed to direct sunlight ( $t_{1/2} < 1$  hour). Few studies have examined the toxicity of ZPT to marine non-target organisms. ZPT resulted very toxic to the crustacean *Nitocra spinipes*, with LC50 varying between 180 and 340 µg/l, underlining that ZPT can potentially be highly toxic towards marine organisms other than the fouling ones.

To minimize oxidative damage and to cope with stressors, eukaryotic cells utilize a variety of protective mechanisms, including the expression of an assortment of proteins which are collectively referred to as "stress proteins". HSPs showed to be a useful biomarker, in particular to detect early effects due to low level- or short term-exposures. Because of his ubiquity the marine mussel *M. galloprovincialis* is widely used as a sentinel organism for the assessment of pollution in coastal environments. Monitoring their wellness is extremely important when harmful xenobiotic compounds are suspected to reach non-target species, as a consequence of submarine maintenance works or

aquaculture-related treatments.

**Methods:** Mussels sampled from a quay of the harbour of S.Stefano, Argentario (Italy), were exposed to 0.1 mg/l Zn and to 0.48 mg/l ZPT (with Zn at 0.1 mg/l) up to 7 days with solutions being renewed every 48 hours. A control group of mussels kept in a contaminant-free medium was set up as well. All experiments were conducted in 38‰ aerated artificial seawater medium (Reef Crystals) at 15°C, with a 12:12 light-dark cycle. The experiments started after a 7 days-acclimation in laboratory conditions, similar to those found at the sampling site, and the mussels were not fed either during maintenance or experimental periods.

After 2 and 7 days of Zn and ZPT exposure, mortality was assessed and pools of 3 specimens were collected from each experimental group. The specimens were dissected, with gills and digestive gland being removed and separately stored at -80°C until chemical and biochemical analyses.

Total tissue Zn was assessed by AAS after drying tissues at 60°C for 12 hours and total HNO<sub>3</sub> bomb digestion in microwave, in order to detect any difference in the bioaccumulation pathways among the experimental groups and between the considered tissues.

For ZPT determination, tissues were homogenized with dichloromethane and centrifuged in order to extract ZPT. An aliquot of the supernatant (500 µl), diluted when necessary, was treated with 300 µl of Cu sulphate aqueous solution (0.5 M) and shaken with magnetic stirring for 5 min in order to obtain the quantitative conversion of the zinc chelate into the correspondent copper pyrithione (CuPT), which is expected not to damage the analytical HPLC system. Subsequently the residues were digested with HNO<sub>3</sub>, in order to release the remaining Zn not ZPT bound, which concentration was detected by AAS. The obtained organic layers were subjected to reversed phase HPLC analyses on a Purospher RP-18e (125 x 4 mm; 5 µm) column equipped with a precolumn Purospher RP-18e (4 x 4 mm; 5 mm). The analyses were performed at 35°C with a mobile phase of methanol/water under gradient elution and the eluate was monitored at 240 nm by UV detection. No interfering peaks due to the biological matrix were observed.

Concerning calibration curves, working standard solutions were prepared by appropriate dilution of a copper pyrithione stock solution. The obtained solutions were processed in triplicate (10 µl) under the same HPLC conditions used for the biological samples; the peak area ratio of copper pyrithione was plotted versus the concentration of the analyte and a linear curve was obtained with a correlation coefficient  $r = 0,995$ . The peak areas of CuPT found in the biological samples were compared to the calculated calibration curve in order to quantify the correspondent content in ZPT.

To assess ZPT behavior in artificial seawater a 48 hours experiment was also set up. Seawater containing 0.48 mg/l ZPT was exposed to light, to insuffled oxygen, or both. Water samples were collected after 0, ½, 1, 6, 12, 24 and 48 hours and treated following the same procedure used for the biological samples.

To detect hsp expression, frozen tissues from pools of 3 individuals each were homogenised on ice in protease inhibitor cocktail and then centrifuged (13000g, 10min, room temperature). Supernatants were diluted in sample buffer and boiled for 5 min. 30 µg of protein were loaded in each lane, separated by electrophoresis in a 12% SDS-polyacrylamide gel and electrophoretically transferred to PVDF membranes. Immunoreactive bands were visualized using a NBT/BCIP detection system (Roche). Immunoblot images were acquired using a HP Scanjet 2300c digital scanner with default settings and analysed with ImageJ analysis software.

**Results:** The ZPT concentration detected in the experimental medium showed to decrease slowly during the considered time, even in presence of light, allowing to conclude that after several hours ZPT is still greatly available for intake, in disagreement with what is reported by many Authors.

All individuals of the control and Zn-exposed groups were alive up to 7 days, while 10% and 35% mortality was observed after 2 and 7 days, respectively, within the ZPT groups.

ZPT exposed mussels showed similar levels in total Zn contents and a similar trend in comparison to Zn exposed ones. Both in the gills and in the digestive gland a clear accumulation was measured, with Zn levels almost two-fold after 48 hours and three-fold after 7 days in comparison to the control group. Gills showed higher Zn concentrations than the gland.

ZPT resulted present at low concentration in the control and Zn-exposed mussels. Individuals exposed to ZPT showed a clear accumulation of the organic compound in their tissues already after 2 days, with values almost doubled after 7 days. The analysis of the residues highlighted that in the ZPT exposed group, as in the Zn one, Zn not ZPT bound increases over time.

Exposure of mussels to 0.1 mg/l of inorganic zinc did not cause statistically significant differences in any of the HSPs tested levels between the control and test animals. On the contrary, after exposure to 0.48 mg/l ZPT a considerably increased level of hsp27, hsp60 and hsp70 was recorded both after 2 and 7 days.

**Conclusions:** The tested procedure proved efficient and very sensitive in detecting ZPT levels in seawater and biological samples.

ZPT showed to be persistent in the seawater so that it is easily available for intake. A basal concentration of ZPT could be detected in the specimens of the control group, indicating that ZPT availability in the sampling site is already high enough to determine a detectable accumulation in *M. galloprovincialis*. After 2 days of ZPT exposure, bioaccumulation in mussels is already remarkable, even in the liver. Our results showed that, at the tested concentrations, ZPT has a clear effect on *Mytilus*, as shown by an increased hsp90 expression.

The outcome of this short-term experiment suggests that ZPT could comprise a risk for aquatic non-target organisms, especially in harbours where the water exchange is limited and where the increasing level of pollutants deriving from the anthropogenic activities is already posing an unexpected threat.

## Ecotoxicology

V7

### Estimation of pristane and phytane for assessing biogenic and petrogenic contributions in the analysis of hydrocarbons from marine sediments by gas chromatography

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In this paper, a procedure for the quantitative estimation of pristane and phytane amounts in the hydrocarbon contents of marine sediments is reported. The pristane to phytane ratio is a parameter for the estimation of biogenic and petrogenic contributions in the hydrocarbon content of marine sediments, useful for assessing the presence of contamination from petroleum products. However, the gas chromatographic determination of these two hydrocarbons can be hardly performed due to the presence of overlapped peaks which do not allow accurate quantifications of these two hydrocarbons. We propose to overcome the problem of accurate pristane and phytane determination in GC analysis by using a mathematic procedure based on a new deconvolution technique; this procedure allows the reconstruction of the gas-chromatographic profiles and the calculation of pristane and phytane area, so reducing the uncertainty depending on the presence of neighbour and strong overlapped peaks of other hydrocarbons. The proposed method has been applied to the evaluation of petrogenic and biogenic hydrocarbon contents in the monitoring of off shore platforms in Adriatic sea.

## Environmental Health

V8

### China's sustainable development in environment and health

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Currently, the situation of water, air and soil pollution in China is serious. More than 50% of China's large lakes are eutrophic. In 2007, the water quality at nearly 50% of 407 monitored sections in 197 rivers is considered Grade IV or worse in a five-class grading system, indicating heavy pollution [1]. As a result of air pollution, acid rain is prevalent in southern China, which can lead to acidification of surface waters and soils and cause ecosystem dysfunction, including loss of fish populations and forest dieback. In addition, about 7.3% of arable land is irrigated with sewage water, of which 20% has been polluted [2].

The impacts of the aforementioned environmental problems are significant and multifaceted, especially with respect to human health. Symptoms of arsenic poisoning from upstream mining activities have emerged among the about 180,000 local inhabitants of seven counties within 6100 km<sup>2</sup> in Hetao Area [3]. Furthermore, indoor air pollution from use of solid fuel in China is responsible for about 420,000 premature deaths annually.

The Chinese government has initiated numerous efforts in environmental and health protection in order to mitigate these problems. Recently, a concept of "scientific development" was proposed to achieve a harmonious society and a balanced relationship between human and nature. The country is

changing its mode of economic development and promoting a sustainable development. In the future, more investment will be allocated for better protection of environment and human health.

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## Ecotoxicology & Environmental Health

V10

### Ecotoxicity of surfactants in the terrestrial environment

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**Aim:** Synthetic surfactants belong to one of the most widely manufactured and used chemicals nowadays. They are usually classified on the basis of chemical structure of the hydrophilic group. According to this classification four groups of surfactants are distinguished: anionic, cationic, nonionic and amphoteric. Surfactants enter the terrestrial environment mainly through the application of pesticides and sludge disposal. Having entered into soils, they may adsorb on soil and subsequently affect the physico-chemical and biological properties of soils. Despite the fact that synthetic surfactants belong to one of most common pollutants found in soil, the data concerning their toxicity in the terrestrial environment are still scarce. Also the adsorptive properties of some groups of surfactants have not been deeply investigated so far. The aim of this work is to review and compare the ecotoxicological effect and environmental risk of the presence of the synthetic surfactants in the terrestrial compartment.

**Method:** In order to evaluate the environmental risk, the risk characterisation ratio (RCR) recommended by the European Union Technical Guidance Documents (TGD, 2003) was applied. RCR is defined as a quotient of the Predicted Environmental Concentration (PEC) to the Predicted No Effect Concentration (PNEC).

**Results:** The values of the RCR reported in Human & Environmental Risk Assessment on ingredients of European household cleaning products (HERA) documents for anionic, cationic and nonionic surfactants are less than 1 ([www.heraproject.com](http://www.heraproject.com)). It indicates that none of the investigated group of surfactants poses a risk to the terrestrial environment. The highest values of RCR were found for cationic surfactants (RCR=0.6) and secondary alkane sulphonates (RCR=0.29), which belong to anionics. For the other groups of surfactants: alkyl sulphates, linear alkylbenzene sulphonates, alcohol ethoxysulphates and alcohol ethoxylates, the RCR was not higher than 0.15. The performed literature review revealed that amphoteric surfactants and one of the most important group of nonionic surfactants, i.e. alkyl phenol ethoxylates (APE), have been hardly ever investigated with regard to their ecotoxicity as well as the risk assessment in the terrestrial environment (Ying, 2006; Garcia et al., 2008). Amphoteric surfactants are readily biodegradable under aerobic as well as anaerobic conditions. The lowest value of EC50 estimated for amphoterics within toxicity tests towards *Photobacterium phosphoreum* and *Daphnia magna* was equal to 5 mg l<sup>-1</sup> (Garcia et al., 2008). The aquatic toxicity data indicate that APE are less toxic than their degradation products octyl- and nonylphenols (Naylor, 1995, Singh et al., 2002). The latter are classified as endocrine disruptors. However, taking into account that APEs are persistent to biodegradation under anaerobic conditions and have good adsorptive properties (Ying, 2006; John et al., 2000), the risk assessment needs to be evaluated for them.

**Conclusions:** The ecotoxicological data obtained so far have indicated that the ecological risk of the contemporarily used synthetic surfactants is judged as relatively low. At the same time the risk assessment for some groups of surfactants should be re-evaluated or even evaluated with the use of ecotoxicological chronic data, which would be actual for the terrestrial compartment. In order to do this, more ecotoxicity tests should be performed.

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www.heraproject.com

## V11

### Toxicity of sediments and their leachates in samples from Portman Bay (SE, Spain)

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**Introduction:** The environmental persistence of metals in concert with their intensive use by modern society has created a concentration of metals in the biosphere (Kakkar and Jaffery, 2005). Determination of the contaminant content is not enough to evaluate the toxic effects or to characterise contaminated sites, because such a measure does not reflect the ecotoxicological danger in the environment and does not provide information on the effects of the chemical compounds. To estimate the risk of contaminants, chemical methods need to be complemented with biological methods (Leitgib et al., 2007). Ecotoxicity tests measure the bioavailability of the contaminants and the effects of the chemically not measured toxic compounds on the soil components (Gruiz, 2005). The aim of this study was to evaluate the sensitivity and applicability of two bioassays for the preliminary ecotoxicological screening of sediments from sites contaminated by mining activities: a test based on the inhibition of luminescence of *Vibrio fischeri* and a phytotoxicity test using *Lepidium sativum*, *Sorghum saccharatum* and *Sinapis alba* seeds. Since sediment is a complex and heterogeneous geological matrix, the toxicity associated with different exposure routes (solid and pore-water samples) was assessed.

**Material and methods:** For this study, 6 sediment samples were collected from Portman Bay (Murcia, SE Spain). Sediment samples were collected, air-dried, mixed and sieved through a 2 mm screen for general analytical determinations. The soil extract was prepared by saturating the soil with distilled water and allowing it to stand for four hours. Then, the soil was subjected to a vacuum pressure to extract the soil solution through filter paper.

To determine total heavy metal content, sediments were first ground to a fine powder using an agate ball mill. 0.1 g of soil samples was placed in Teflon vessels and 5 ml of concentrated HF acid solution, 200 µl of concentrated HNO<sub>3</sub> acid solution and 5 ml of water were added. When digestion was complete (15 minutes at 1000W in a Milestone ETHOS PLUS microwave), the samples were transferred to a volumetric flask and brought to 50 ml. The Zn and Fe content was determined by flame atomic absorption spectrometry (FAAS) using a Perkin-Elmer 1100B Atomic Absorption Spectrophotometer. The Pb, Cd and Cu content was determined by electrothermal atomization atomic absorption spectrometry (ETAAS) using an Unicam 929 AAS spectrometer. The As content was analysed by atomic fluorescence spectrometry using an automated continuous flow hydride generation (As-AFS) spectrometer (PSA Millennium Merlin 10055). The reliability of the results was verified by analysing a standard reference material (SRM 2711 Montana Soil).

The Microtox® bioassay is based on the inhibition of the bioluminescent marine bacteria *Vibrio fischeri* and was applied to the pore-water samples. Toxicity is expressed as the agent concentration which produces a 50% reduction of the initial luminescence (EC<sub>50</sub>) after 15 minutes of contact time (Azur Environmental Ltd., 1998). Bioluminescent responses were measured using a Microtox Model 500 analyser.

The Phytotoxkit® test measures the decrease in (or the absence of) seed germination and of the growth of the young roots after 3 days of exposure of seeds of selected higher plants to a contaminated matrix compared with the controls germinated in a reference soil. The plants selected for the Phytotoxkit® microbiotest were: the monocotyl *Sorghum saccharatum* (Sorgho) and the dicotyls *Lepidium sativum* (Garden cress) and *Sinapis alba* (mustard). The percent inhibition of seed

germination and root growth inhibition for each plant were calculated.

**Results and discussion:** Table 1 summarises the heavy metal content of sediments and pore-water samples. Total Pb concentration varied from 602 to 2517 ppm, with a mean value of 1206 ppm. The average content of Zn was 5357 ppm. The mean concentration of Cd and Cu was 23 and 59 ppm, respectively. Total As concentrations varied from 177 to 470 ppm, with an average value 284 ppm. Finally, the total Fe content ranged from 37% to 47%, with an average value of 40%. Pore-water samples showed neutral pH values and average electrical conductivity was 8.4 ds m<sup>-1</sup>. Mean heavy metal content in leachates from Portman Bay was 6.8 ppm for Pb, 0.1 ppm for Zn, 17 ppb for Cd, 5.6 ppb for Cu, 3.7 ppb for As and 0.6 ppm for Fe.

Sediment samples						
	S1	S2	S3	S4	S5	S6
Pb (ppm)	2517	975	602	889	1043	1211
Zn (ppm)	7929	4585	5970	3458	4762	5440
Cd (ppm)	21.1	22.2	15.2	15.1	20.3	42.1
Cu (ppm)	68.5	48.1	57.2	46.1	68.2	67.3
As (ppm)	307	220	224	177	308	470
Fe (%)	41.5	37.8	37.8	37.2	40.8	47.3

Leachates samples						
Pb (ppm)	6.3	<dl	<dl	<dl	<dl	7.2
Zn (ppm)	0.1	0.2	0.1	0.1	0.1	0.1
Cd (ppb)	6.4	10.4	22.1	35.6	21.8	5.5
Cu (ppb)	2.5	2.8	5.1	5.3	15.6	2.3
As (ppb)	3.8	4.3	3.6	3.6	3.4	3.7
Fe (ppm)	0.5	0.5	0.5	0.6	0.7	0.6

Table 1: Heavy metal content of soil samples and their leachates

The test with *V. fischeri* pointed to a significant toxic response following exposure of bacteria to water and pore-waters from Portman Bay. The results obtained suggested that the leached solutions showed a non-toxic effect when they were submitted to the Microtox® bioassay. As regards the phytotoxicity test, an influence on seed germination (SG) was observed in soil samples. In S4, S5 and S6 no seeds germinated for any plant species. In samples S1 and S2 ranged from 0% to 50% and in S3 ranged from 70% to 100%. When root length was evaluated, a significant inhibition of root growth (RI) was noticed. In the case of S4, S5 and S6 inhibition was 100%. In the case of S1 ranged from 4% to 39%, and for S2 it was in the 25% to 80% range. Finally, in S3 inhibition percentage ranged from 75% to 100% (Table 2).

	Microtox	L. sativum		S. saccharatum		S. alba	
		%	%	%	%	%	%
		germination	inhibition	germination	inhibition	germination	inhibition
S1	No tox	0	4	0	39	20	34
S2	No tox	50	25	10	40	50	80
S3	No tox	100	100	70	75	100	100
S4	No tox	100	100	100	100	100	100
S5	No tox	100	100	100	100	100	100
S6	No tox	100	100	100	100	100	100

Table 2: Bioassays results

**Conclusion:** In this study two environmental toxicity methods were compared for different contaminated sediments originated from polluted sites. The test organisms of the bioassays were: one bacteria, and three plants species. Both the whole soil and the soil extract were tested. The various

bioassays showed different sensitivities to the target metals. Of the bioassays employed, the *Vibrio fischeri* luminescence inhibition assay showed less sensitivity to the toxicants in the sediments than phytotoxicity assay. According to our results it is highly advisable to complement chemical analyses with environmental toxicity testing to characterise the risks presented by contaminated soils. Finally, these methods satisfy the requirements of environmental toxicology in their reliability, sensitivity, reproducibility, rapidity and low cost.

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## V12

### **Critical assessment of quantitative structure-toxicity models against tetrahymena pyriformis by focusing on applicability domain and prediction accuracy**

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In our previous study [1] we have developed several models to predict aquatic toxicity of molecules tested against *Tetrahymena pyriformis* [2-6] and demonstrated that consensus models yielded the highest chemical space coverage as well as prediction accuracy. The goal of this study was to expand upon the previous study in terms of most suitable quantitative estimates of model prediction accuracy and to provide a quantitative analysis of different types of Distance to Models (DM)s. In particular, we focused on the following questions. Are DM defined for one method/set of descriptors could be successfully used with other approaches? How can we benchmark different DM approaches? Is there a best definition for the DM? Can we estimate a priori errors of property prediction for molecules in the external sets?

Our results have indicated that the standard deviation of models in the ensemble provided the best estimation of the accuracy of predictions of models for the calculation of compound toxicity against *T. pyriformis*. The standard deviation measures the degree of disagreement or divergence of models for a new molecule. The larger is the disagreement, the lower accuracy of predictions is expected for this molecule. The disagreement appears due to structural features that are underrepresented in the training set or do not cover the same range of values in the training and validation sets. The more different is the analyzed molecule from the training set molecules, the higher variation of predictions of models is expected for it.

We have also shown that DM developed with one method and one set of descriptors could be also used to estimate the accuracy of models developed with different set of descriptors or/and machine learning methods. For example DM developed with neural networks, or k-Nearest Neighbors or consensus model, in most cases provided best discrimination of molecules with low and large errors for all analyzed models, even if these models were developed with different sets of descriptors and different machine learning methods.

Thus, the diversity and distribution of data in the training set but not the computational approaches and descriptors of molecules are the limiting factors determining the accuracy of predictions and applicability domain of the models. This conclusion is in tune with similar results for prediction of physico-chemical parameters, namely lipophilicity [7] and aqueous solubility [8] of molecules as well as it further confirm similar conclusions of Sheridan and co-workers [9].

The diversity of molecules in the training set naturally could limit the applicability of models developed in our study. Indeed, our estimations suggest that the developed models are able to predict only about 12% of 3182 molecules from the EPA High Production Volume (HPV) Challenge Program with accuracy comparable to the experimental one. The efforts of EU REACH program to register about 30,000 compounds during the next ten years will challenge dataset of similar or even greater chemical diversity. An application of our or other models to this set is unlikely to cover greater fractions of molecules with similar accuracy of prediction. New experimental measurements for most of compounds will be required. The toxicity of molecules against of *T. pyriformis* has been studied over twenty years [2-6]. Despite this fact the amount of data, but what is even more important, the chemical diversity of the dataset remains critically low. Moreover, considering results of Sheridan et al[9] and our studies, there is absolutely no reason why any other models developed with this training set and other descriptors will have significantly better accuracy of prediction. Considering that this property is one of the most extensively studied, the situation with availability of data for other end-points can be even much worse and even less predictable models can be expected. The similar conclusions and methodology also apply to ADME/T prediction [10].

Following our analysis we have also established best practices for model development/validation and implemented an on-line server, <http://www.qspr.org>, which predicts aquatic toxicity of chemical compounds from their structure using both individual and consensus models as well as provides robust estimates of the accuracy of predictions.

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## Environmental Health

### V14

#### **A bidirectional case-crossover study: Fine and coarse particulate matter and children's hospital admissions for asthma and respiratory diseases**

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Atmospheric pollutants result in a significant impact on the environment and human health. Increasing evidence of the rapid deterioration of air quality and the associated potential health impacts on populations in cities has initiated the action plans for urban air pollution control. Many epidemiological studies have focused adverse effects of air pollution on the prevalence of respiratory diseases in

children. The purpose of this study was to examine the association between air pollution and admissions for asthma and other respiratory infections among children who were younger than 15 years old. The study used data on respiratory hospital admissions and air pollutants, including thoracic particulate matter fine (PM<sub>2.5</sub>) and coarse (PM<sub>10-2.5</sub>) particulate matter in Zonguldak, Turkey. A bidirectional case-crossover design was used to calculate odds ratios for the admissions adjusted for daily meteorological parameters. Significant increases were observed for hospital admissions in children for asthma, allergic rhinitis, upper and lower respiratory diseases. All fraction of particulate matter in children showed significant positive associations with asthma admissions. The largest association found was 18% increase in asthma admissions in relation to a 10 µg/m<sup>3</sup> increase in PM<sub>10-2.5</sub> on the same day of admissions. The adjusted odds ratios for exposure to PM<sub>2.5</sub> with an increment of 10 µg/m<sup>3</sup> were 1.15 and 1.21 for asthma and allergic rhinitis with asthma, respectively. Our study suggested a stronger effect of fine and coarse PM on asthma hospital admissions.

## V15

### Ultrafine particles in the urban area of Rome

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**Aims:** Epidemiological studies have correlated atmospheric particulate matter (PM) to increase of mortality and to adverse human health effects, such as lung cancer, respiratory and cardiovascular diseases. PM pollution is presently regulated on mass basis through PM<sub>10</sub> convention that measures the mass of particles collected with a 50% efficiency for particles with an aerodynamic diameter of 10 µm, in that way including, coarse particles down to ultrafine particles (UFPs), <0.1 µm. UFPs deposit very efficiently in the lungs. Their small size, in relation to cellular structures, high number concentration and surface area allow them increased ability of absorption of organic molecules and penetration into cellular targets in the lung and systemic circulation (Li et al., 2003). Such characteristics account for their importance in explaining the health effects of PM.

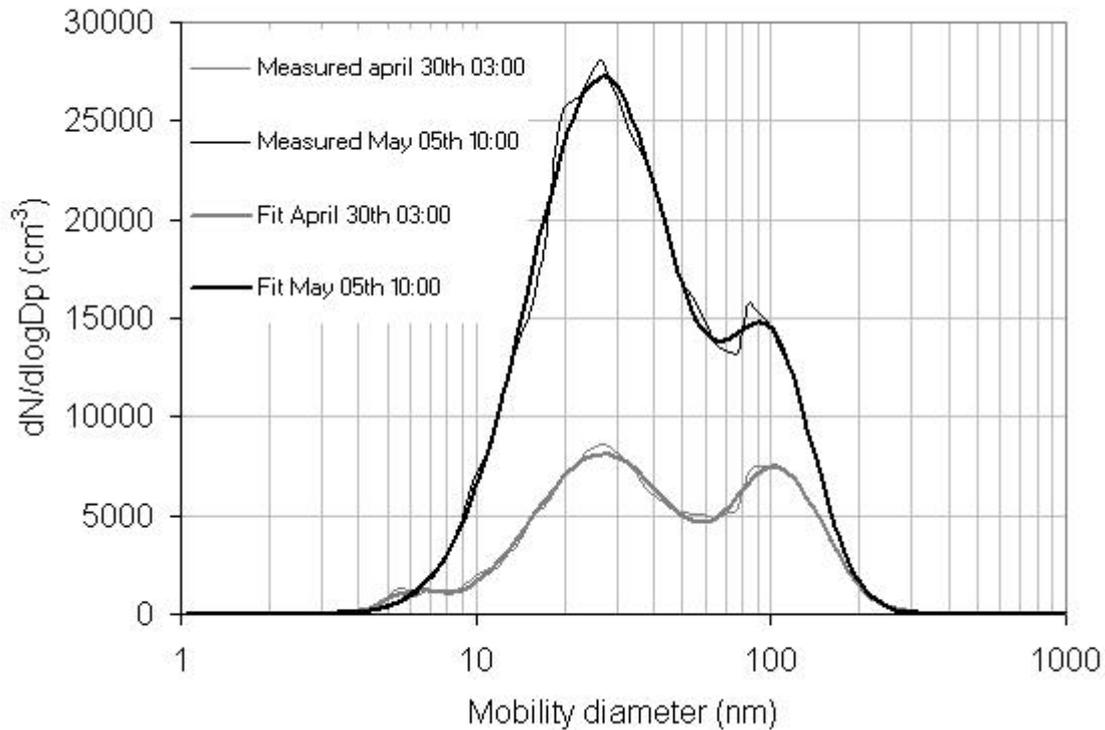
In this context it is important to gain more knowledge on UFP levels and on their dynamic of formation in urban areas where great part of the population is concentrated. With this purpose we report the results of a study started on May 2008 in the urban area of Rome.

**Methods:** The aerosol measurements were carried out at the ISPEL's Pilot Stations, located in a street canyon in downtown Rome (near S. Maggiore Cathedral), characterized by high density of automotive traffic.

UFP number concentration and size distribution were measured over a 5 minute measuring period, in the range from 3.5 up to 117 nm, by a water-based ultrafine condensation particle counter (CPC 3786, TSI Inc., MN USA), and a Scanning Mobility Particle Sizer (SMPS 3936, TSI Inc., MN USA), equipped with a TSI 3085 Differential Mobility Analyzer. Particle size distribution fitting was carried out by the TSI 390069 Data Merge Software.

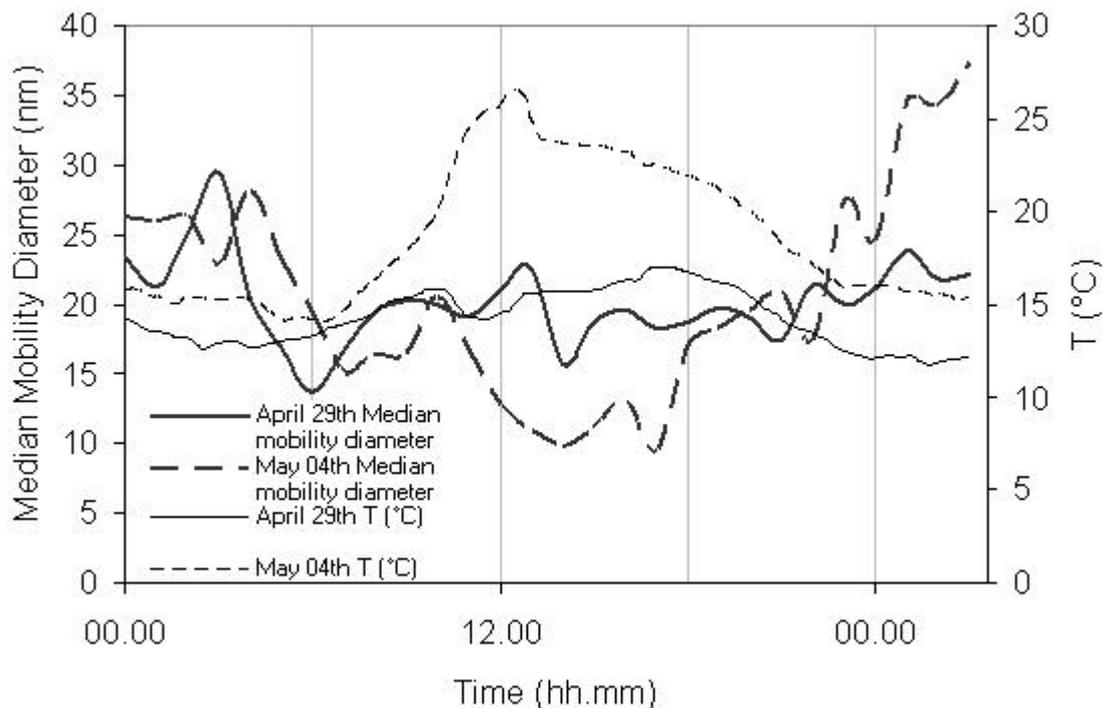
Nitrous acid concentration was measured by means of Differential Optical Absorption Spectroscopy (Opsis Sweden), averaging the data over a distance of about 250 m. Carbon monoxide concentrations were measured by means of an Airpointer analyzer (Recordum Mödling, Austria).

**Results:** The different size distributions measured very likely reflected the exhausts emitted by the different types of vehicle, passing within few metres from the measuring point. Dilution from the tailpipe to road, due to traffic generated turbulence (up to about 1000:1) and from the road to ambient (within 10:1), due to atmospheric turbulence, is another important factor that affects aerosol number distribution (Zhang and Wexler, 2004). Carbon monoxide, a typical primary pollutant associated to the automotive traffic, and total UFP number concentrations displayed similar patterns of variation, evidencing the common origin of the two pollutants. Total particle number concentrations showed a typical daily modulation, with minimum values measured during nocturnal hours, when the effect due to the reduction of the automotive traffic emission overcomes the decrease of the atmospheric mixing height. Hourly-average daily peak values ranged from 54.000 to 105.000 cm<sup>-3</sup> and minimum nocturnal values from about 6.000 to 16.000 cm<sup>-3</sup>. In the period studied, hourly average size distribution could be fitted with two log-normal functions, with maxima at about 20-30 nm and 70-100 nm, or three log-normal functions with a further maximum at about 5-15 nm (figure 1).



[Figure 1 Hourly average size distributions.]

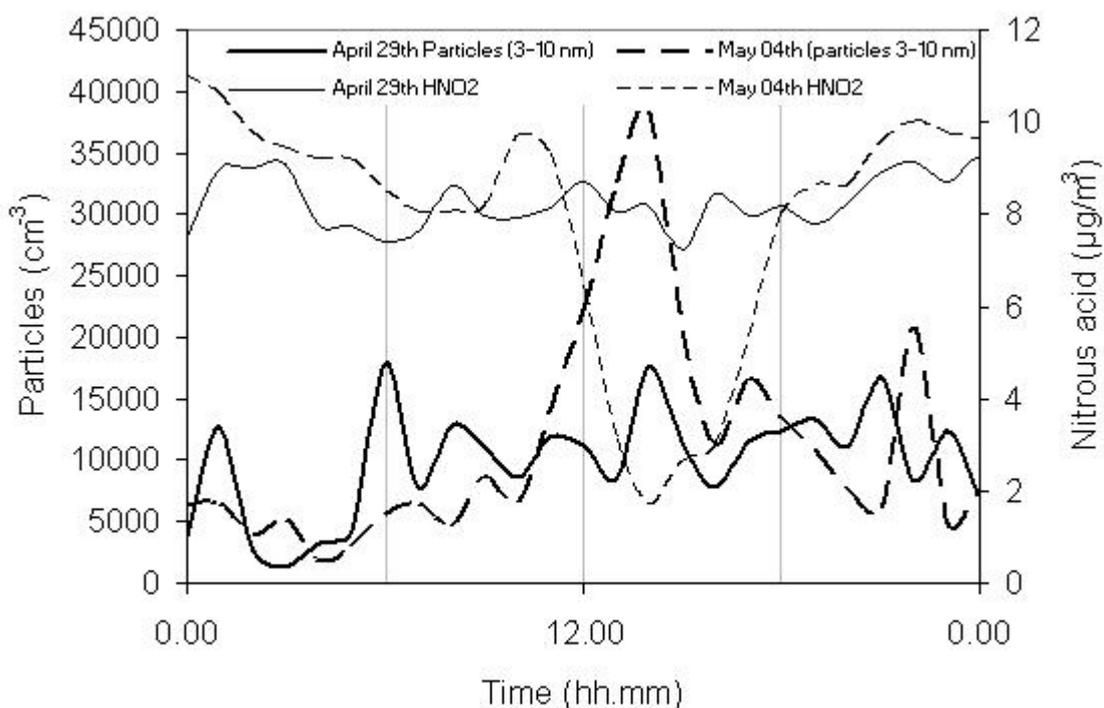
Median mobility diameter varied throughout the day, with maximum values, as high as about 37 nm measured in the early morning and in the nocturnal hours and minimum values, as low as about 9 nm measured at about midday (figure 2).



[Figure 2 Median mobility diameters and temperature]

Such trend was due to the higher radical oxidative activity characterizing the periods of high solar radiation and favouring the formations of particles from the gas phase. In fact UFP concentration in the

range from 3 to 10 nm, very close to the sizes of clusters formed from the gas-phase (nucleation mode), displayed a pattern of variation with maximum rate of particle formation in the same period when also the rate of photolysis of nitrous acid was maximum (May 04<sup>th</sup>, figure 3).



[Figure 3 UFPs (3-10 nm) and nitrous acid.]

Nitrous acid, that accumulates in the planetary boundary-layer at night, is photolysed during the day to form NO and the hydroxyl radical OH, that is the most important oxidizing species in the daytime atmosphere (Crutzen and Zimmerman, 1991), playing an important role in the formation of the nucleating species involved in new particle formation (Harrison et. al., 2000). Coherently, on May 04<sup>th</sup>, when the temperature varied from 14 °C to 26.6°C (higher solar radiation) nitrous acid concentration dropped at around midday (figure 3) as did the median mobility diameter (figure 2), while on April 29<sup>th</sup>, when the temperature varied from 12 °C to 17°C (lower solar radiation) both nitrous acid concentration (figure 3) and the median mobility diameter (figure 2) varied less markedly throughout the day.

**Conclusions:** Autovehicular traffic was the main source of UFPs in the urban area of Rome. The process of dilution of the vehicle exhausts played an important role in affecting the particle number distribution. Total UFP concentration followed a daily trend governed by the evolution of the atmospheric mixing height and by the variation of the autovehicular traffic intensity. In the period studied, in most cases, the hourly-average size distribution were bimodal or trimodal with maxima at about 5-15 nm, 20-30 nm and 70-100 nm. Particle formation in the nucleation mode was favoured in periods with high radical oxidative activity.

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V16

### **A comparative study of the impacts of NO<sub>x</sub> concentrations on public health in Athens, Greece and Nis, Serbia**

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The objective of this study is to present and interpret the health impacts with respect to the NO<sub>x</sub> concentrations in Athens, Greece and Nis, Serbia, during the period 2006-2007. Mean daily NO<sub>x</sub> concentrations recorded in the air pollution stations, in both cities, and medical data concerning dacryrrea, intensive headache and dyspnea, were used for the analysis.

The first step was to assess the spatial distribution of the NO<sub>x</sub> concentrations, using Kriging interpolation method, in the two cities and make a comparative analysis. In the process, the NO<sub>x</sub> impacts on public health were investigated. The most appropriate method analysing medical data is the application of the Generalized Linear Models, with Poisson distribution, because the examined symptoms present a great divergence from the normal distribution.

The findings of the performed analysis showed that there is a strong relationship between the examined symptoms and the NO<sub>x</sub> concentrations, in both cities, indicating that the air pollution originated mainly from automobiles traffic is responsible for the worsening of public health.

V17

### **Shipyards production chemicals, Hazardous wastes and their effects on human health**

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Production processes of shipyards are divided into two main divisions as new shipbuilding and ship repair industry. Both production methods of these two divisions are similar. New ship construction and ship repairing have many industrial processes in common. The shipbuilding and repair industry consists of several processes. Some of these processes include surface preparation, painting and coating, solvent cleaning, degreasing, welding, machining and metalworking, fiberglass manufacturing. Ship repairing generally includes all ship conversions, overhauls, maintenance programs, major damage repairs, and minor equipment repairs.

Raw material inputs to the shipbuilding and repair industry are primarily steel and other metals, paints and solvents, blasting abrasives, and machine and cutting oils. In addition a variety of chemicals are used for surface preparation and finishing such as solvent degreasers, acid and alkaline cleaners, and plating solutions containing heavy metal and cyanide ions. Pollutants and wastes generated include volatile organic compounds (VOCs), hazardous air Pollutants (HAPs) particulate matters (PM), waste solvents, oils and resins, metal bearing sludge and wastewater, waste paint, waste paint chips, and sent abrasives.

Painting wastes are believed to be the largest category of hazardous wastes produced in a shipyard. Paints are made up of three main ingredients: pigment, binder, and a solvent vehicle. Examples of pigments include: zinc oxide, talc, carbon, coal tar, lead, mica, aluminum, and zinc dust some typical solvents include acetone, mineral spirits, xylene, methyl ethyl ketone, and water. Organic solvents are useful to dissolve and disperse lubricants, oils, waxes, paints, varnishes, rubber and so on, and are widely used in many industrial processes. Most of them are also recognized as extremely hazardous chemicals and some of them might cause Alzheimer's disease, leukoencephalopathy, multiple sclerosis, neurobehavioral disorders and so on.

The fume from stainless steel welding process contains 20% of chrome and 10% of Nickel components. The effect of Chrome and Nickel fume can cause cancer on human health and classified as carcinogen. High levels of manganese exposure cause neurological disorder and inconvenience. Irritant gases such as carbon monoxide, ozone, nitrogen oxide are the outcome of welding processes. The epidemiologic studies show these gases as the subject of lung cancer. Latest researches show that respiratory of stainless steel welding fumes may cause to cancer due to high levels of chrome and nickel. On the other side, the study of genotoxicity reports the effect of stainless steel welding fume mutation o mammal cells. In Fiberglass manufacturing, air emissions include VOCs and HAPs that are generated from open containers and also due to evaporation from gelcoating operations. The major emission sources are exhausts from gel coat spray booths, room exhausts from the lamination area, and evaporation of acetone or other solvents during clean-up. Styrene emissions occur during the lamination of the deck, hull, and small parts, due to evaporation from the resin or gel coat over-spray and from vaporization from the applied resin or gel coat before polymerization occurs. In this study, the most chemical related processes are examined, the solid, liquid and gas wastes of painting, welding, blasting and fiberglass production are analyzed and their worker exposures are investigated.

## V18

### **Sea disaster in Kerch strait - 2007: ecology, hygiene, toxicology**

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Navigating conditions in Kerch strait connecting Black and Azov seas, is characterized by often storm during the autumn and winter period. The biggest accident has occurred on November, 11 2007, when during hurricane 4 vessels with dangerous goods on board have sunk. From 43 members of crews it is rescued 35, and 8 were lost. Tanker "Wolgoneft-139" with 4000 t of black oil on board has broken and from its tanks near 2000 t cargo has flowed out in the sea. The ships "Éível", "Nakhichevan" and "Volnogorsk" with a cargo of sulfur on board (all together 7220 t) have also sunk. Besides on board of the mention ships there were near 70 ò diesel fuel, 2 ò diesel and motor oil, 0,2 ò paints and other dangerous substances. The spread mineral oil has led to intensive pollution of the sea and a coastal strip of beaches, and also death of natatorial birds. There was a threat to all flora and fauna of this important fishing region, and also to zones of the mass recreation of the population. The rescue works have immediately been started. It has allowed to collect a significant part of black oil and the polluted sand and to minimize adverse ecological consequences.

## V19

### **Effect of heavy metals on the state of cardiovascular system in rats by E.C.G. indices, lipid metabolism and nonspecific resistance**

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At present cardiovascular diseases take the leading place. The occurrence of this pathology depends on many reasons, but predominantly on nutrition conditions, hypodynamia, bad habits (smoking, alcohol). Also, unfavorable occupational and environmental factors contribute to the incidences of cardiovascular diseases. In particular, exposure to heavy metals (mercury, lead) can cause developing hypo- and hypertension in workers. In this, cardiotoxic effect of metals is recorded directly in the heart or is indirectly caused by biochemical and immunological regulation mechanisms through impairment of vessel elasticity, changes of their tonus and arterial tension.

Any chronic occupational exposure to chemicals, including heavy metals, leads to changes in

cardiovascular system. It was reported that changes in cardiovascular system under lead exposure are characterized by unstable arterial pressure with the increase of tone of peripheral vessels, which in turn brings clear tendency to hypertension.

Among workers under long-term occupational exposure to relatively low concentrations of mercury and its compounds there is a tendency in increase of cardiovascular diseases. At the background of changes in myocardium functional status the significant number of arterial hypotonia cases was observed.

The purpose of this work was to study the effect of lead, mercury, manganese on cardiac rhythm, lipid metabolism, and indices of nonspecific resistance in rats.

**Material and methods:** Studies were conducted on male Wistar rats, aged 3 months (young rats with the body mass of 100-130 g) and 23 month (old rats, body mass of 270-300 g). The tested animals were administered intraperitoneally 5 days a week within 50 days by solutions of lead acetate (1.53 mg/kg body weight), mercury chloride (0.19 mg/kg) and manganese chloride (8.5 mg/kg). The controlled animals of the similar aged groups received injections of 0, 9% NaCl solution.

The effect of heavy metals on heart function of the subjected animals was estimated using a cardiographic unit "Cardio". For these purposes the frequency of cardiac contraction (FCC), RR interval - the length of cardiac cycle, PQ interval - the time of atrioventricular conduction, QT interval - electric systole, TP interval - electric diastole were measured.

The content of general cholesterol, general lipids,  $\beta$ -lipoproteins, triglycerides and phospholipids was detected, using standard test sets LACHEMA- and PHYLICIT-Diagnostics. The phagocyte activity of neutrophils (FAN) was estimated by test with latex, the level of circulating immune complexes (CIC) by precipitation reaction with polyethyleneglycol M=6000.

The comparative analysis of chronic exposure to mercury, lead and manganese on young rats allows us to come to conclusion that lead exposure did not influence much the ECG indices. Under chronic administration of mercury and manganese to young rats the rates of cardiac output decreased in the same way but the length of cardiac cycle increments changed in different way. Mercury exposure caused bradycardia, followed by increase of PQ and QT intervals and relative decrease of TP, while manganese exposure caused decrease of FCC, followed by increase of PQ and TP intervals and relative decrease of QT. Therefore, mercury exposure to young rats mostly changed the length of diastole, while manganese exposure caused changes in the length of systole. These changes were mostly caused by direct action of manganese to myocardium, which is also confirmed by other authors on the influence of manganese on FCC of isolated heart as well as on the status of slow calcium channels of myocardiocytes.

On the contrary to young rats old rats after mercury exposure showed tachycardia and appearance of several electrocardiographic indices of myocardium dystrophy. Manganese exposure influenced less the electric activity of heart of old rats comparing to young rats. Therefore, it can be concluded that myocardium of old rats is more sensitive to mercury and less sensitive to manganese comparing to young rats. It is well known that in most cases the progress of cardiovascular diseases is linked with lipid metabolism impairment. While studying lipid spectrum of patients with ischemic heart disease in most cases impairments of lipid or apolipoprotein metabolism are detected, which explains the appearance of atherosclerotic changes in vessel tone. The presence of significant quantities of free fatty acids in serum causes the decrease of myocardium contractility and increase of arrhythmia.

Intraperitoneal injection of mercury chloride caused only the tendency to decrease of cholesterol level by 7.7%, total lipids by 0.5% and phospholipids by 20.0% in young rats and the increase of  $\beta$ -lipoproteins by 26.9% and statistically significant increase of triglycerides by 44.7%. At the same exposure conditions both in old and young rats significant decrease of cholesterol level by 29.0% and total lipids by 14.3% took place comparing to control, followed by significant increase of  $\beta$ -lipoproteins by 88.2% and tendency to increased level of phospholipids and triglycerides by 12.1%.

Lead exposure after 50 injections caused significant increase of phospholipids by 98.2% and total lipids by 42.2% in young rats. Slight increase of  $\beta$ -lipoproteins content was also observed but that increase was not significant. Among old animals the significant increase of phospholipids by 85.5%, cholesterol by 62.6% and total lipids by 52.9% was observed as comparing to control.  $\beta$ -lipoproteins showed the tendency to increase by 41.7%, and also in young animals. At the same time the difference among young and old rats by triglycerides indices was statistically significant.

Manganese exposure after 50 injections did not cause significant changes of lipid metabolism indices of young rats, while significant increase of cholesterol, total lipids and triglycerides was observed by 25.7, 15.1 and 21.8% correspondingly comparing to control together with some tendency to decrease in phospholipids and  $\beta$ -lipoproteins. As for cardiovascular diseases several researchers indicated that immunological processes play significant role in atherosclerosis development, especially at the stages of appearance of fat fascia in vessels and their transformation into atherosclerotic plaques [11]. The content and distribution of CIC plays an important role in pathogenesis of cardiovascular diseases.

Among those with acute myocardial infarction the increased content of CIC was detected and it was supposed that they are responsible for vessels impairment. Mercury chloride stimulated red-ox processes in blood neutrophiles both in young and old rats. High-molecular and low-molecular CIC concentration decreased in serum of young rats and increased in serum of old rats. Changes of indices of unspecific resistance revealed under mercury exposure testify the activation of phagocyte activity of neutrophiles and elimination of already formed CIC from peripheral blood, while among old animals irrespective to red-ox processes stimulation in phagocytes, CIC levels increased. Exposure to lead acetate caused the depression of phagocyte activity of blood neutrophiles and stimulated increased formation of CIC in young animals. At the same time the stimulation of absorbing and bactericide activity of phagocytes at the background of increased CIC formation was detected in old animals. Exposure to manganese chloride stimulated phagocyte and bactericide activity of blood neutrophiles in young rats. As for old rats the decrease of absorbing and metabolic activity of phagocytes and decrease of low-molecular CIC was observed. Despite the synthesis of antibodies and formation of CIC under exposure to xenobiotics is kind of defense reaction, in some cases it can have pathological character, causing in turn complicated inflammatory reactions, localized in vessels, kidney and joints. Deposit of such complexes is evaluated as the main pathogenic factor for organ specific autoimmune diseases. Thus, it can be concluded that cardiotoxic effect of heavy metals is likely to be caused both by their direct toxic action on the heart myocardium and vessel endothelium, and by indirect action, involving biochemical mechanisms (lipid metabolism), immune mechanisms (phagocytosis, immune complexes) followed by disorders in processes of haemodynamics, blood filling and vessel tonus, changes of electrocardiographic indices of cardiac action.

## V20

### Pharmaceuticals and health - greening pharmacy

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The history of pharmaceutical sciences and industries is an impressive success story. Pharmaceuticals are present everywhere in every day life. Pharmaceuticals help to pursue the modern way of living. They contribute to our high living standard and health. In the present discussion of the environmental impact of pharmaceuticals improvement of synthesis is very prominent whereas the environmental properties and fate of the molecules themselves are somewhat underestimated. Pharmaceuticals are excreted more or less unchanged by patients and treated animals after administration. Very often they are not fully eliminated by sewage treatment. This makes it difficult to hold pharmaceuticals back efficiently. Accordingly, pharmaceuticals are present in the environment. Often, unknown transformation products are formed in the environment. Therefore, according to the principles of green chemistry and green pharmacy, the functionality of a pharmaceutical should not only include the properties of a pharmaceutical necessary for its application, but also easy, i.e. fast and complete degradability after its excretion. Taking into account the full life cycle of pharmaceuticals will lead to a different understanding of the functionality necessary for an green active pharmaceutical ingredient. To stimulate the discussion about the future role of degradable and greener pharmaceuticals several examples are presented to underline the feasibility and the economic potential of this approach called "benign by design".

## Resources & Waste

### V21

#### Sustainable development and renewable raw materials

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The encouragement of the environmentally sound and the sustainable use of renewable natural resources is an important aim of Agenda 21 on the way to a sustainable development. Fats and oils are at present the most important renewable raw materials for the chemical industry, and it can be expected that their importance will steadily increase in the future. The question will be discussed which chemical reactions and processes have to be developed to enhance the application of fats and oils in the chemical industry, especially for the synthesis of base chemicals. An important example is glycerol as a by-product of the biodiesel production. It is intriguing to follow the on-going substitution of production processes of base chemicals such as 1,2-propanediol, and epichlorohydrin based on petrochemical feedstock by new processes based on glycerol. A large number of novel fatty compounds have been synthesized by C,C-bond forming addition reactions to the C,C-double bond of unsaturated fatty compounds. Homogeneously transition metal catalyzed reactions, radical additions, Lewis acid induced electrophilic as well as pericyclic addition reactions will be discussed. Moreover, fatty acids derived from special plant oils such as calendula, tung and vernonia oil offer fascinating opportunities for organic synthesis. An important problem most narrowly connected with the industrial use of renewables for the production of chemicals, fuels as well as energy is the competition of the cultivation of food on the limited available agricultural area. Food demand and consumption will increase dramatically. The world population will rise from the present more than 6 billion to about 9 billion in 2050. It was suggested that the competition of the cultivation of food and of feedstock for industrial use may be met by a global program of reforestation of areas wasted in historical time by human activities and to use the biomass grown on these areas continuously for the production of the necessary energy, fuel, materials and chemicals.

## V22

### Green Chemistry and Biorefineries

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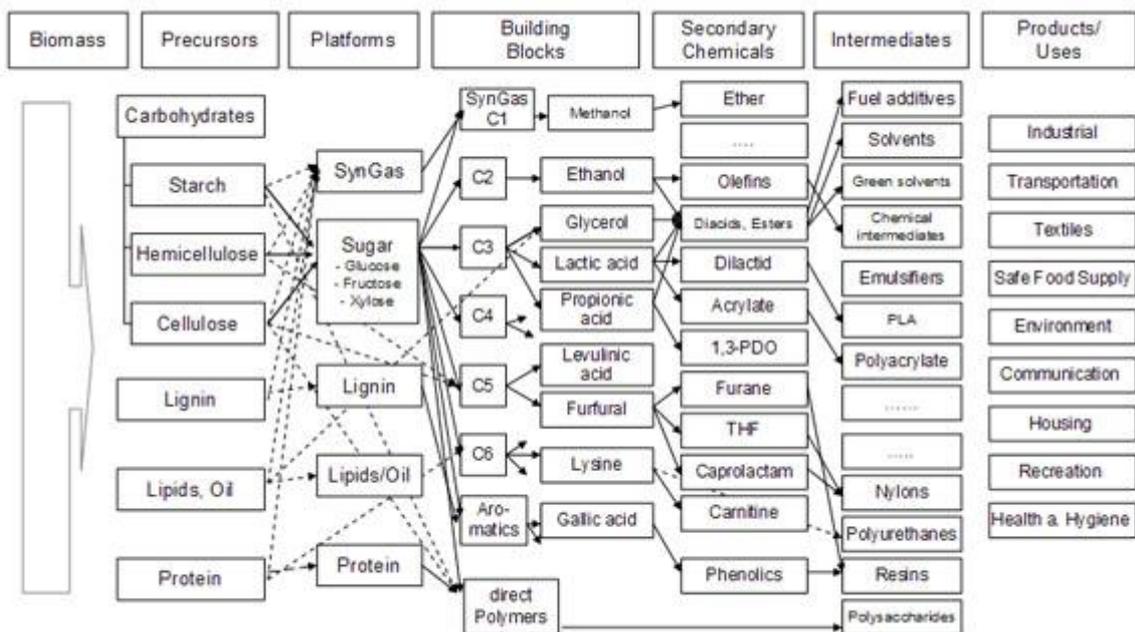
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One-hundred-and-fifty years after the beginning of coal-based chemistry and 50 years after the beginning of the petroleum-based chemistry industrial chemistry is now entering a new era. An essential part of a sustainable future will be based on appropriate and innovative uses of our biologically-based feedstocks [ 1].

One approach is the development of biorefinery technologies and systems. Biorefining is the transfer of the efficiency and logic of the fossil-based chemistry and substantial converting industry as well as the energy production onto the biomass industry [ 2].

Plant biomass always consists of the basic precursors carbohydrates, lignin, proteins and fats, beside various substances such as vitamins, dyes, flavours, aromatic essences of most different chemical structure. Biorefineries combine the essential technologies between biological raw materials and the industrial intermediates and final products.

In the presentation, the focus is directed to the combination the systems, technologies and products, in particular of the platform chemicals (building blocks) [ 3] (Fig.).



**Fig.: Model of a Biobased Product Flow-chart for Biomass Feedstock, cut out (acc. to [ 3])**

[Model]

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## V23

### New approaches to the development of plastic materials from renewables

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Considering the use of chemicals from plant sources on a broad scale for production of polymers in the future, one is concerned with the total different chemistry of platform chemicals from petroindustry and what one can obtain from downstream treatment of agricultural crops on large scale. Besides cellulose-esters and ethers, modern plastic materials often are copolymers or blockcopolymers of different kinds of polyesters or polyolefins, according to the physical needs of material quality. Direct substitution thus seems hardly to be feasible in many cases, because of lack of suitable monomers. Thermoplastic elastomers for example consist of a comonomer with increased tendency to crystallize ("hard-comonomer/ cooligomer", e.g. terephthalic acid esters) and a "soft" comonomer/oligomer, based on C2, C4, C6-dioles or even phenoles.

Using plant based monomers, the task is to find regimes of identical or nearly identical physical and material constants for the derived polymers. As sources of a large variety of bifunctional molecules, chemicals from sugar/polysaccharide bases have to be concerned. Fats and oils also are a useful source of aliphatic carbon chains. Traditional oleochemistry mainly suits the needs of tensile manufactures, so research demands are in the field of new reactions to derive bifunctionals from plant

oils. That means direct or indirect omega-functionalisation. In an attempt to provide a wholly plant based thermoplastic elastomer, we have produced a variety of such esters with high/low crystallinity and have tested its properties.

Of particular importance was the use of long chained bifunctionals (C14 to C22) from plant oils. We were interested in development of a suitable C=C double bond chemistry with unsaturated fatty acids by the now well established olefin metathesis of highly functionalized olefins. Olefin metathesis is a transition metal catalyzed reaction of C=C double bonds, whereby a formal exchange of substituents occurs. According to a suggestion originally made by Chauvin the reaction mechanism is not an exchange of substituents but a complete break and reformation of the olefinic bond with metal-carbene complexes as catalytically active intermediates. Quite different transition metal carbene complexes are able to catalyse this reaction and some technical processes based on tungsten, molybdenum or rhenium have been designed. In the last decade a huge progress has been made in the metathesis chemistry by ruthenium. The first consideration of unsaturated fatty acids as source of double bonds and useful chemicals with carbon chains of intermediate carbon atom number has been made by Boelhouwer. Using tungsten halides, he established the basic chemistry of the fatty acid metathesis but with low performance. Olefinic chemistry of the double bond in unsaturated fatty acids has been confined since mainly to epoxidation chemistry up to now, because the usual metal carbene catalyst precursors are highly reactive towards the carboxy function, with the notable exception of rhenium. The design of a cheap technical process of fatty acids metathesis is thus connected with establishing a catalyst of high tolerance towards oxygen, water and other common impurities of technical grade oils as well as a suitable downstream process of purification and catalyst recycling. Ruthenium carbene complexes with increased tolerance towards impurities are based on the exchange of the usually applied organophosphines with N-heterocyclic imidazolylidenes as ligands originally invented by Herrmann and Nolan. High reactivity and turnover numbers are neglected in favour of stability and insensitivity. The potential is exemplified on a kg-scale process of oleic acid metathesis for synthesis of intermediates to be used in the synthesis of thermoplastic elastomers. By application of selfmetathesis, a C18 dicarboxylic acid is produced. High selectivities are demonstrated also in the case of cross metathesis using functionalised olefins. Substituted olefins can yield much more stable secondary carbenes which drastically improves catalyst sensitivity. In addition, the often uttered possibility of complex product mixture is not always a matter of fact. Some processes selectively yield omega-undecenoic carboxylic acid and are an interesting example to study.

## V24

### **Production of activated carbon from waste olive cake and its adsorption characteristics for Zn<sup>2+</sup> ion**

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Activated carbon is one of the most widely employed adsorbents. It is mainly composed of carbonaceous material with various microporous structures. In the treatment of wastewater, it is used for purification, decolorization and the removal of toxic organics and heavy metal ions. As a result, the demand for activated carbon is increasing.

Physicochemical characteristics of activated carbon depend on the kind of raw material used and activation conditions. Presently, the materials being used to produce carbon are usually coal, wood, petroleum residue, sawdust, coconut shell, pulp sludge, and pitches resulting from the pyrolysis of fossil fuel.

In this study, waste olive cake was utilized as the raw material for the production of activated carbon by chemical activation and its adsorption capacity for heavy metal ions was evaluated. The olive cake used for the experiments was obtained from "ProBeira", a producer of pitted table olives and also an olive oil factory, located in Envendos (Portugal). The waste, after an initial drying stage at ambient temperature, was roughly grinded with a porcelain mortar and pestle. Part of the material was sieved in order to collect the fraction with > 2.00mm, which corresponds mainly to the olive stones by-product, present in the olive cake. Both materials were then additionally dried in a vacuum oven at 60 °C for further 24 h. Tests were conducted with the total biomass and with the fraction > 2.00 mm, in order to

determine the influence that this fractionation has on subsequent treatments.

Two different activated agents were used:  $\text{H}_2\text{SO}_4$  and NaOH. Activation with  $\text{H}_2\text{SO}_4$ : the materials were mixed in a 1:1 wt ratio with concentrated  $\text{H}_2\text{SO}_4$ , placed in an oven and heated to  $200^\circ\text{C}$  for 24 h. After this, the samples were allowed to cool to room temperature, washed with distilled water and soaked in 1%  $\text{NaHCO}_3$  solution to remove any remaining acid. The samples were then washed with distilled water until pH of the activated carbon reached 6, dried at  $105^\circ\text{C}$  for 24 h and sieved to obtain the desired particle size (1.00-2.00 mm). Activation with NaOH: the substrate (0.5 g) was added to 0.25 M NaOH solution and left for 1 h, after which the samples were neutralized with HCl. They were then washed thoroughly with distilled water, dried at  $105^\circ\text{C}$  for 24 h and sieved to obtain the desired particle size (1.00-2.00 mm). Moisture content, ash content, elemental analysis and ash elemental analysis, pH, surface area (BET) and iodine number were determined in order to characterize the materials, before and after the activation processes.

To estimate the applicability of produced activated carbon as an adsorbent for wastewater treatment, the adsorption test was performed using zinc ion as the adsorbate. For the preparation of synthetic zinc wastewater,  $\text{ZnCl}_2$  salt was used to make 1000 mg/l. This solution was diluted to 10, 50, 100 and 200 mg/l for adsorption experiments with different initial zinc concentrations. Known amounts of materials (1, 2.5, 5, 7.5 and 10 g of activated and non activated material and also of commercial activated carbon for comparison) were placed in a 250 ml conical flask and 100 ml of wastewater was added. The mixture was agitated at a speed of 200 rpm in a thermostatic shaker bath at  $25^\circ\text{C}$  for 24 h. After shaking the material was separated from solution by filtration. The concentration of zinc ion remaining in solution was measured by Atomic Absorption Spectrophotometry after diluting the filtrate to an adequate concentration.

Results show that employment of the waste olive cake as a raw material for the production of activated carbon, a highly value added product, is a useful recycling process. Furthermore, the superior adsorption capacity of the produced activated carbon suggests that the process is potentially commercializable. Results also indicate that the previous fractionation step, in order to obtain the > 2.00 mm fraction, doesn't produce an activated material with a superior adsorption capacity. So, this previous step shouldn't be considered in a commercial project. Results also show that chemical activation by NaOH produces an activated material with a superior adsorption capacity for zinc ion than with  $\text{H}_2\text{SO}_4$ . But, chemical activation with  $\text{H}_2\text{SO}_4$  produces an activated carbon with better characteristics than with NaOH.

## Green Products

### V25

#### Green processes and products

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Conceptually, the 12 principles of Green Chemistry indicate what is meant by "green" processes and products: non-toxic and degradable products with high value in use and inherently safe processes with high yield and low energy consumption (Anastas and Warner 1998). However, putting these concepts into practice is not straightforward because of two problems. First, *indicators* are needed in order to quantify the "green" properties of processes and products and, on this basis, to compare different processes or products to each other. Second, the different attributes that make a process or product "green" (toxicity, energy consumption etc.) are often in competition, i.e. the development of green processes and products is a multicriteria optimization problem.

As for the first problem, the definition of an appropriate indicator often requires careful consideration. An indicator forms a link between scientific results, on the one hand, and the evaluation of the benefits and disadvantages of a process or product, on the other hand. This evaluation is not a purely scientific question but is also driven by value judgements and normative considerations; in some cases, it is also influenced by public concerns. Indicators reflecting chemical properties that are in the focus of the 12 principles of Green Chemistry are, e.g. persistence, toxicity and cumulative energy demand of a chemical. To make an indicator effective in Green Chemistry requires two elements: first, there must be methods to determine the value of the indicator for different chemical processes or products and, secondly, new processes or products with better performance - according to the indicator - need to be developed. An example is the persistence of chemicals, which expresses how long environmental and human exposure to a chemical lasts. The persistence of chemicals can be determined with the OECD

Screening Tool for Persistence and Long-Range Transport Potential (Wegmann et al. 2008), which is publicly available from the OECD website. To make the persistence a driver for innovation in Green Chemistry means to systematically develop chemical products that provide a defined technical performance but are less persistent than existing products (Rieger et al. 2002).

The second problem, different attributes in competition, is the reason why there is not *the* green process or product. Because different properties such as low persistence, low toxicity and good technical performance cannot easily be achieved at the same time, a balance between these properties needs to be found. In many cases, the comparison of the different advantages and disadvantages of different solutions is complicated. Examples are dry-cleaning with chlorinated hydrocarbons (non-flammable but persistent) and hydrocarbons (flammable but less persistent) as different options or cooling systems with fluorinated hydrocarbons (non-flammable but potent greenhouse gases) and hydrocarbons (flammable, no greenhouse gases) as competing options. To illustrate the evaluation of potentially "green" chemical products, three case studies are discussed. The first is different types of solvents used in the chemical industry (Capello et al. 2007): what is a "green" solvent? The second case study is perfluorinated surfactants that are currently replaced by similar substances with shorter perfluorinated chains. Are short-chain perfluorinated surfactants "green" chemical products? The third case study is silver that is used as an antimicrobial agent in various applications, for example in household laundry where it helps to reduce the temperatures in the washing-machine.

**Solvents:** A wide variety of solvents are used in large amounts in the chemical industry and represent a major environmental and health impact in terms of energy consumption (production and disposal of solvents), waste (from solvent incineration), and toxicity of a solvent itself. The search for green solvents is therefore a high priority in the chemical industry. The evaluation of the environmental and health impacts of solvents demonstrates the effect of competing objectives that are represented by different indicators. One dimension is the inherent hazardous properties of a solvent, and a second dimension is the life-cycle-related impacts that include the production and disposal of the solvent. The hazardous properties of a solvent can be expressed by an EHS (environment, health and safety) score that consists of sub-scores for acute and chronic toxicity, persistence, irritation, fire/explosion hazard etc. (Sugiyama et al. 2006). The life-cycle impact can be represented by the cumulative energy demand (CED, in MJ) that represents energy consumption during synthesis of new solvent and incineration and/or distillation of waste solvent (Capello et al. 2007). Available tools for quantifying EHS scores and CED values of chemicals and an evaluation of different solvents according to these two dimensions will be presented in the talk.

**Perfluorinated chemicals (PFCs):** PFCs such as fluorotelomer alcohols offer a wide range of applications. Products based on PFCs can be used to make various items water, dirt and grease repellent, e.g. carpets, clothes, food contact material. PFCs are powerful surfactants that are contained in water-based paints and many other applications. However, their extreme persistence leads to the accumulation of PFCs in environmental media and human tissue in all regions of the world (Giesy and Kannan 2001). PFCs based on C8 chains, e.g. perfluorooctanesulfonate, PFOS, have been found to be retained in the human body for several years. This "biopersistence" is considerably shorter for the C6 and C4 analogues, which is a reason for the chemical industry to replace C8 PFCs by C4 and C6 PFCs. In some cases, this is pointed out as an example of Green Chemistry. In the talk, the properties and environmental fate of PFCs with various chain lengths are compared and the question of how "green" the shorter-chain substitutes are is discussed.

**Silver:** The silver ion, Ag<sup>+</sup>, is a strong antimicrobial agent and silver nanoparticles are increasingly used as a continuous and effective source of silver ions. Silver as an antimicrobial agent may replace other biocides that have more unwanted side effects or are more difficult to apply. It also may offer new applications such as in laundry where it helps reduce the washing temperature and save energy. The challenge for these applications of silver is to develop effective sources of silver that are economically competitive and technically feasible (Kumar et al. 2008). One disadvantage of an increased and broad use of silver as a biocide is that it will lead to increasing emissions of silver to the environment. The silver levels to be expected need to be estimated and evaluated; in the talk, assumptions and uncertainties of such an environmental exposure and risk assessment of nanosilver applications is presented (Blaser et al. 2008).

In conclusion, the development of "green" products and processes requires improvements and innovations in many directions. In many cases, the assessment of how "green" a product or process is can only be made in reference to existing products or processes that serve the same purpose. To reduce the multitude of possible options of what a "green" product or process may be, it is desirable to develop a hierarchy of indicators representing different aspects of the notion "green". Such a hierarchy would be based on value judgements about the importance of different indicators. Because of the many different contexts in which the "green" properties of a process or product have to be evaluated, such a hierarchy would be a useful guideline but, because of the multi-dimensional nature of the

problem, there would always be exceptions from the recommendations derived from such a guideline. For the environmental assessment of chemical products, which is one important aspect of the problem of green products, such a hierarchy of indicators is presented in the talk (Scheringer 2002).

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## V26

### Choline carboxylate soaps - biocompatible and highly water soluble

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Surfactants are ubiquitous in everyday life. Among them, the anionic sub-class still represents the most frequently used type. However, common anionic soaps, such as sodium or potassium carboxylates, are often limited in their applicability due to their limited solubility in water. Replacing the alkali counterions by tetraalkylammonium (TAA) ions provides an effective way to enhance the solubility of the respective surfactants [1]. However, TAA soaps are toxicologically questionable, since simple TAA ions are known to be toxic [2]. Choline as a quaternary ammonium ion of biological origin ensures a biologically compatible alternative thereto. Choline - formerly known as Vitamin B4 - plays several key roles in the human body and occurs in relatively large amounts in plant, animal and human tissues.

The present contribution deals with the preparation and the physicochemical characterisation of choline carboxylate surfactants (ChCm with m=12-18). Binary phase diagrams were established and the structural details were elucidated by SAXS analysis. Furthermore, the biocompatibility and cytotoxicity of ChCm soaps were studied.

Choline carboxylate surfactants have been found to combine the characteristics of common alkali carboxylates with a substantially increased solubility. For instance, the solubility temperature of sodium palmitate (NaC16) can be reduced from 60°C to 12°C with choline as counterion [3].

Moreover, choline soaps, consisting exclusively of biogenic material occurring in the human body, are physiologically and environmentally harmless, and as such convenient for e.g. drug delivery systems.

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V27

### Ecological assessment of ionic liquids` synthesis and application

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Many efforts have been already made in chemical R&D to reduce human health impacts, process safety risks and multiple impacts to the environment, e.g. by replacing toxic and hazardous substances or by waste reduction. In order to create more environmentally benign chemical processes, alternative solvents such as supercritical fluids, water, ionic liquids or solventfree processes gain growing interest as well. Ionic liquids for instance have the potential to be green alternatives to conventional organic solvents, since they inter alia offer considerable synthetic chemical advantages and have no significant vapour pressure. Otherwise, their partial toxicity [e.g. 1-3], their high production effort and environmental impact resulting from this [4;5] have to be recognised. In conclusion, the greenness of ionic liquids heavily depends on their application, toxicological properties and on the environmental impact over the whole life cycle including up- and downstream processes. Against this background, it is beneficial to start such investigations already during the development stage of ionic liquids, so that prospective environmental impacts arising from industrial scale production can be reduced.

To evaluate the greenness of ionic liquids in a holistic approach, we use the ECO (ecological and economic optimisation) Method, which was developed to accompany and optimise early stage work in chemical R&D.[6;7] The ECO Method uses a Simplified Life Cycle Assessment (SLCA) approach [8], and integrates criteria of energy demand, toxicity and costs of e.g. chemicals, auxiliaries and energies used during the life cycle stages of a chemical product or process.

Selected results regarding the assessment of ionic liquids` synthesis and application will be presented in detail. A number of synthesis alternatives will be compared and discussed in the context of the influence of single synthesis parameters. In addition, the application of ionic liquids in the Diels-Alder reaction in comparison to other solvent systems will be discussed in order to highlight opportunities and challenges of future ionic liquids development work.

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## Ethics, Policy, Education

V28

### Ethics and natural science

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#### 1. Bird's-eye View - Purpose, Functions and Limits of Ethics

##### a. Why Ethics?

Human beings ask questions like "what is the right thing to do?" Ethics is the search for answers to

questions of that kind. Therefore, ethics reflects on reasons and consequences of human actions. Moral rules seek to sum up succinctly the result of both individual and collective experience in balancing ethically relevant goods as well as the thought on that matter.

Theoretical considerations and reflections are only one step towards developing moral guidelines, it is by no means the whole way. Moral knowledge is for a large part a "sedimentary deposit" of these experiences and deliberations, found in the form of (socially acceptable) habits and emotions, as well as in the form of culturally evolved structures of society, both in laws and in organizations or institutions.

In order to be relevant to today's moral questions, ethic reflection needs to consider both individual motivation and the stabilization of morals.

### **b. Functions of Ethics**

A basic analysis of the functions of ethics in our post-modern society lets us identify three core tasks, namely critique, motivation, and integration.

#### *(1) Critique*

Ethics has to scrutinize reality and criticize in light of the pertinent moral guidelines what happens in society and what individuals do in fact. In a way, this function is that of a referee: ethics has to tell when factual behaviour does not conform to the universally agreed rules. Perhaps this is not comfortable, it is crucial nevertheless. Unlike a referee, ethics also pays close attention to the ruleset, which is not above its criticism.

The political debate on green issues in Germany may serve as an example for the critical function of ethics. The environmentalist movement has become a political factor mainly as a movement of social criticism. The German green movement condemned the use of nuclear energy and the NATO Double-Track Decision. This history may have led to a tendency to put forth scenarios of catastrophe, which in turn tend to contribute to paralyze rather than to motivate behavioural changes.

#### *(2) Motivation*

People need motivation in order to change their actual behaviour. For that reason ethics needs to consider carefully and systematically the problem of motivation.

In short, compliance with ethical norms needs to be worth its while. There should be incentives for socially and ecologically desirable behaviour. One needs to put in place structural conditions, which ensure that ethically compliant behaviour is at the same time an advantageous investment. For example, motivation for changes in the field of technology assessment and of environmental ethics could be an economic advantage. Indeed, economic analysis has shown that a culture of trust is a critical factor of success for management.

Desirable changes on an individual scale need stabilization on a social scale. Therefore, one needs to create structural conditions in both law and institution rewarding that behaviour. Socially and ecologically desirable behaviour has to be a rewarding investment in the future and people need to see it that way.

#### *(3) Integration*

Cooperative behaviour requires integration of different interest, convictions and perceptions. The environmental issue can again serve as an example. Particularly the set of problems in this field and developmental issues require the integration of diverse fields of sciences, social groups, and political issues as well as of international and intercontinental interests. The need for integration is a characteristic of the concept of sustainability.

However, without precise operationalization the integrative concept of sustainability becomes a door opener to arbitrariness. For this reason, today's ethical discussion tends to treat on the means rather than the goal itself. In that way, sustainability is a process of optimization and of carefully balancing competing claims and demands to achieve as well balanced a state as possible.

Integration proves itself by facilitating the dialogue of the different scientific disciplines and social communities. Ethics is an integrative theory; it is in that sense *Integrationswissenschaft* (Schöllgen). Ethics denies the claim to the absolute of any single perspective by examining the basic assumptions of any model put forward. By doing this, ethics serves to put part-truths into perspective. Its analysis is founded on the philosophy of science. This is the methodologically crucial starting point to build and ethics of science.

### **C. Limits of Ethics: The Pitfall of Being a Moralizer**

The need for ethical reflection arises mainly in times of radical change. The task of securing sustainable development poses substantial ecological and social challenges is big enough to constitute such an upheaval phase. This has far-reaching consequences for the social and regulatory framework for and feasible goals of scientific research.

At the same time, ethics has to avoid certain pitfalls. In today's differentiated societal structures, ethics all too often finds itself on the verge of social irrelevance. Whenever moral postulates ignore the material constraints of the actions they aim to govern, decision makers faced with such advice will discount it as "moralizing". What is more, the "moralizer" will probably be ignored in the future.

Consequently, the answers of ethical reflection must take into account the ever-increasing complexity of our situation.

## **2. The Four Elements of Responsibility**

The term responsibility has become firmly established as a key term in the field of ethical reflection on social, ecological, and technological problems of development of modern civilization. The “ethics of responsibility” approach (Max Weber) does not primarily judge an action by disposition, attitude, or intent of its author, but rather by its consequences. This approach takes into account even side effects of an action which are only partially intended or foreseeable.

*Responsibility* is a relational term. The relation called responsibility is comprised of four elements: (1) someone has to account (subject) (2) for something (object), (3) to somebody (authority answered to) (4) in accordance with certain standards (criteria).

### **(1) Subject**

The capability of being the subject of moral imputation of one’s acts is an integral part of being a person. Personality presupposes freedom, the existence of which cannot be objectively proven by methods of natural science. Freedom in turn arises through the exercising of responsibility.

The increase of choice is the main problem of responsibility in a (post-) modern society. The “crisis of responsibility” does not primarily stem from a decline of moral standards. The price for the openness and dynamics of modern society and for the increasing possibilities to act, which we have thanks to the progress in natural sciences, is an increased demand of morals (Höffe).

### **(2) Object**

Possible objects of responsibility can be organized into three categories: (1) responsibility for oneself, (2) responsibility for fellow humans, and (3) responsibility for the natural resources and basis for life on the whole. Article 20a of the German Constitution (the “Grundgesetz”) speaks of “responsibility toward future generations”, and leaves open the question whether responsibility for nature is an end of itself or just an end for the sake of mankind. Christianity maintains that nature has an intrinsic value, which has consequences in the making of laws regarding the protection of species or the patenting of living subject matter.

### **(3) Authority Answered To**

The authority man has to answer to is in the first place his own conscience. The central role of the conscience has led to the “turn to the subject” in modern ethics. Modern ethics is ethics of freedom. Governments in turn have to answer to public opinion. The media (newspapers, television, and the internet), the scientific community, and Nongovernmental Organisations (NGOs) and their communication constitute a forum that has to be answered to. Especially the NGOs often see themselves as the world’s conscience; some of them quite often voice their concern with chemical industries.

### **(4) Criteria**

The criteria by which conflicts at hand are to be decided are the “toolbox” of ethics. Three basic categories of criteria can be made out, namely compatibility or reconcilability with (1) the individual, (2) social welfare, and (3) environmental issues. The criterion of environmental compatibility demands, among other things, long-term provisions for avoidance of environmental damage and the acceptance of the “polluter pays principle”. Ecologic risks are to be measured by their expectation, the product of the expected extent of damage and the probability of its occurrence (actuarial principle). The ever-increasing complexity of technology assessment calls for a systemic view if one wants to be able to act in a responsible way.

## **3. Ethics of Responsibility and Green Genetic Engineering**

In recent years, green genetic engineering has become the focus of public perception of ethical problems of biochemical research and its application. The controversy surrounding the use of genetically modified plants in agriculture and food production is one of the key conflicts of technology assessment today.

### **a. Being of Age: Risk-Taking**

I propose as a lead criterion “Risikomündigkeit” - being of age with respect to taking risks and bear the consequences. The concept of “being of age for risk-taking” avoids the main faults of the two concepts of “zero risk” and of “segmented responsibility”: “Zero risk” is illusory and simply not attainable. On the other hand, there is the linear approach of segmenting responsibility in a way that results in ignorance of systemic risks in the field of ecology and masks interdependencies of agricultural policy.

### **b. Enhancing Risk Assessment**

The assessment of green genetic engineering requires an integrated approach that analyzes the different reference scales per se and then relates the findings systematically. To achieve this I propose an enhanced model of impact assessment combining natural-scientific and social-scientific aspects. A guiding concept for responsibility ethics today is the principle of sustainability. It meets the requirements of measurability (through indicators of sustainable development) and operationability, as is evidenced by the Sustainability Reporting Guidelines proposed by the Global Reporting Initiative

(GRI).

### **c. Fighting Hunger**

Green genetic engineering often is justified by the argument, that it is necessary for successfully fighting hunger. However, one needs to put that argument into perspective, because hunger is not primarily a problem of a lack of available food on the world market. Rather it is a problem of distribution of available food, as well as of the protection of water, and of soil, and of subsistence agricultural employment. The overcoming of hunger is primarily a question of justice, not of technological progress. On the other hand, technological innovations can contribute a great deal to the quest of fighting hunger, but without justice in agriculture and social structures technological progress will probably fail to succeed.

### **d. Research Challenge: Sustainable Genetic Engineering**

Only now — within the framework of sustainable development, just and equitable agricultural policy, and *Corporate Social Responsibility* (CSR) of both research facilities and business organizations — reasonable fields of application for green genetic engineering can be identified. The applications are presumably manifold, e. g., the improvement of drought resistance of crops or stem firmness of certain crop plant species, which may lead to faster adaptation of these plants to climate change which will otherwise (and perhaps even so) create enormous problems to secure worldwide supply of food.

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## **V29**

### **Handling complex systems**

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Technology and science are concerned mainly with systems near to thermodynamic equilibrium. Our every day life is dominated by simple and foreseeable actions. If one switches on the light the room gets bright, if one starts the car, the engine starts to work, if one presses the break the car stops, if one turns the gear to the right the car turns also to the right, and so on. The machines are accumulated systems which act independently and follow strong causal and linear relations (Dörner, 1996). Even in science the experiments are laid out in such a way to figure out the strong causal relations and to control the less important factors.

However, most abiotic and biotic systems including the human beings behave differently. They are open non-equilibrium systems which afford for their stability a continuous flow of energy or matter or of both. For their stability a net of weak causal relations with other cells of an organ or other members of an ecosystem is of mayor importance. It is this net of interactions which enable stable systems to cope with external disturbances. However, once the system is over-turned it disrupts completely (death) or it goes through chaotic transition states in a new stable state. It is almost not foreseeable when this point of transition is reached. Such sort of systems possesses their own history. In contrast to “the push button machines” these non-equilibrium systems react slowly on external impacts. If the limits of stability are reached the essential steps of deterioration may date back for a long time and the sequence of causal reaction chains cannot be figured out anymore.

All actions of human beings agriculture, harvesting trees from rain forests, mining, energy production, traffic, water management, waste disposal and many others can be considered as impacts in our environment. Haber (2007) calls the accompanied problems ecological traps. A particular case of such an impact is the release of chemicals in the environment. Any substance leaving the laboratory

containment gets sooner or later in contact with innumerable numbers of other chemicals or living systems. Very reactive substances can lead to violent reactions causing fire, explosions, illness or death. Stable less toxic compounds can have a long life time and can be moved around the earth in time and can cause adverse effects in different organisms or ecosystems. An example for such chemicals was the family of halogenated hydrocarbons which have highly advantageous properties for application and are not toxic, but they are so stable that they can escape in the stratosphere and contribute there to the depletion of ozone. Nobody could foresee this effect before application. Now the continuous increase of the CO<sub>2</sub> concentration in the atmosphere is the matter of concern. After concern on toxic substances the focus of interest should now be shifted towards the enormous quantities of material we are moving in the industrial processes (Schmidt-Bleek 1994, 2007). Schmidt-Bleek invented in the 90ties a measure of material consumption in our technological products. All the resources used, the energy and chemicals needed for harvesting them, the mine spoils and so on are added to a highly aggregated mass. The mass not appearing in the product is called by him the "ecological rucksack". It is Schmidt-Bleek's conviction that the enormous amounts of matter moved by the human beings spoils ecosystems dramatically, and cannot be compensated by nature in short terms. Since the use of resources will dramatically increase when people in developing countries would use the same amount of materials we are using in the industrial civilisations. In his opinion the consumption of resources has to be halved within the next 50 years not to overturn the restoration capacity of nature: that means we have to reduce our mass consumption by a factor 10 to give the other countries room for development. Our success in the development of the technical civilisation via the construction of independent systems with strong causation is now the greatest obstacle to recognize the special features of complex systems. The situation is not hopeless because tools to handle complex systems have been developed in the last forty years. A few of these tools shall be mentined:

- Monitoring the long term changes in our environment: efforts in this direction have started long ago and got a strong push through the large scale observation with satellites. However, the awareness that such sort of investigation is essential for our survival and that these monitoring systems need continuous effort and money is not well developed even in the scientific community.
- Complex systems cannot be treated as classical scientific problems in a laboratory. The whole earth is the laboratory. The possible way is to simulate interconnected systems in a model world or in a more restricted model ecosystem (a first trial of such simulations has been undertaken in the 70ties by Meadows et al, 1972). One can start with the most important elements controlling a model system and add additional elements to fine tune the results. The proof of the model is to calculate correctly measurable quantities determining the status of the whole system. That means it should simulate the development of these parameters from the past to the presence. The most elaborate models are now available for the development of the climate in times of global warming (see i.e. Schellnhuber and Wenzel, 1998).
- To extrapolate into the future it is necessary to continue these simulations under the assumption of possible future developments (szenarios). Several methods exist to construct such szenarios, and on the basis of these szenarios the development of essential quantities can be simulated. However, it is now quite clear that severe changes in our lifestyles are necessary to escape foreseeable ecological deadlocks. Important steps in this direction could be:
  - It must get common practice to distinguish complex nonlinear systems from the simple linear ones and to treat them with the adequate methods. Up to know we are not used to think in complex networks of weak interactions (Dörner, 1996).
  - The consumption of resources has to be reduced according to the recommendations of Weizsäcker et al. (1995) or Schmidt-Bleek (1994, 2007). In order to achieve this, the price of the resources has to be increased (by taxes, by higher income of the employed persons and to increase the ecological standards of mining), the materials longer should be kept longer in the technosphere, buying of machines should be replaced by buying functionalities ("Dienstleistungen"), a modular design which makes repair more reliable.
  - Time scales for technological developments should be adjusted to the time scale of recovery processes of the ecosystems. If this is not possible the impact of adverse substances or actions has to be reduced.
  - An interesting development with respect to chemicals is "green chemistry". That is not "new" or "alternative" chemistry. In the concept of "green chemistry" rules for integrating ecological considerations have been formulated which should be taken into account in the design of scientific and technological projects. The basis for deducing these rules is the experience from various activities towards the implementation of eco-friendly processes in industrial practice. It is a demand to extend these rules which are mostly focused on organic chemistry to the practice of mining and material science and other fields of industrial chemistry.

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### V30

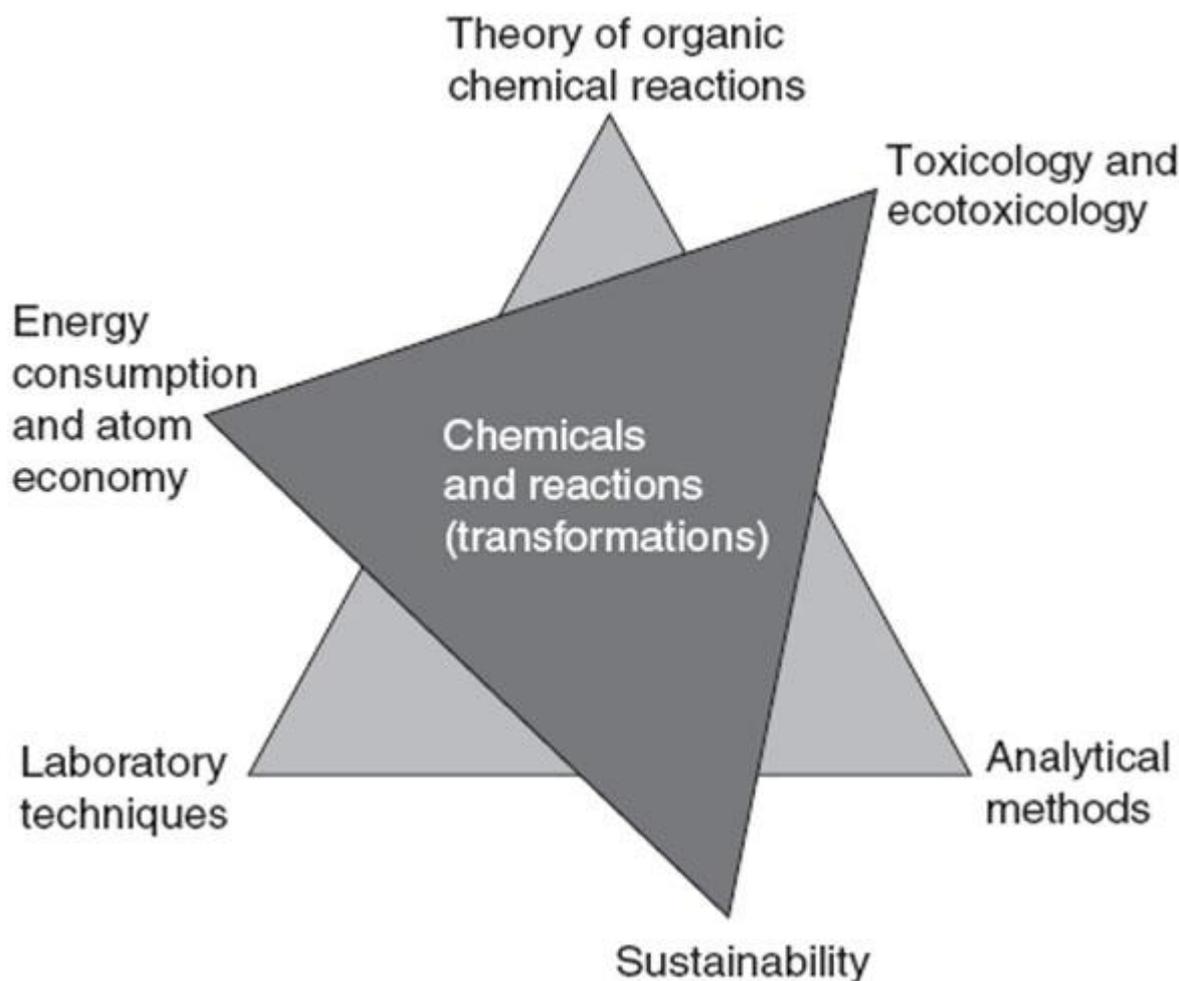
#### **NOP: An online, open-access, organic chemistry teaching resource to integrate sustainability concepts in the laboratory training**

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The key for a sustainable development is teaching its means and tasks to future professionals in an effective manner. Taking on this challenge for basic practical organic chemistry training in higher education, a collaborative project of six German universities has created a collection of lab experiments. The material is accompanied by background information on sustainable development and guidelines for the evaluation of chemical substances and reactions. This collection is freely accessible on the Internet in German, English and Italian, and currently translated into several other languages. The German title "Nachhaltigkeit im Organisch-chemischen Praktikum" (NOP) can be translated in English as "Sustainability in the Organic Chemistry Laboratory Course". Organic laboratory classes are a compulsory element in university education in chemistry, biochemistry, biology, pharmacy, physics, medicine, and even some areas of environmental or civil engineering. However, most curricula are still based on traditional laboratory classes in chemistry. They focus on teaching basic experimental techniques for synthesis and analysis and how to protect the experimentalist when dealing with hazardous chemicals. The efficiency of a chemical transformation is usually only measured by the chemical yield of the product obtained. Students do not learn how to get a more complete picture of a reaction by integrating indicators of its sustainability, and they are not provided with tools to increase the overall efficiency and sustainability of a chemical transformation.

The aspects of overall efficiency and sustainability of a reaction must be added to the content of lab classes in organic chemistry. Toxicological and ecotoxicological knowledge data must become part of the discussion of any experiment. Within this considerably wider scope (see Figure) students learn how to plan, set up, and analyze organic reactions, taking into account effects on the environment and human health. Sustainability starts with the conceptual planning of a chemical transformation. We discuss in the presentation the background, structure and use of the NOP database for sustainable chemistry education. Emphasis will be put on the strategy behind the project, which aims to create a self-developing and self-preserving electronic international open access tool for modern chemistry education.



[fig. 1]

## Risk & Reach

V32

### Hybrid regimes of knowledge: challenges for chemical policy in the context of REACH

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Over the last two decades there has been a remarkable shift of attention to scientific ignorance or non-knowledge, particularly to what J. Ravetz (1990: 26) has termed „science-based ignorance“, i.e. an absence of relevant knowledge generated by science itself. The concept of non-knowledge focuses on the inherent limitations of the dominant framings of „risk“ issues. The concept of non-knowledge emphasises the possibility of “unknown unknowns”, things we don’t know we don’t know. Why is this debate evolving? There are many cases of historical evidence about the power of non-knowledge (cp. EEA 2001). For example, risk analysis of CFCs in the 1930s had been completely unaware of the possibility of harm to the ozone layer caused by those substances - and the same would have applied even for a risk assessment conducted in the beginning 1960s. Therefore, the question arise: How to decide under such conditions of diverging and limited knowledge and incompatible social and cognitive framings of non-knowledge?

Against this background, the argumentation of the presentation is based on four lines. In the *first* step I will raise the question how the topos of non-knowledge emerged in different areas of risk politics. In the *second* step I will underline that in the regulation of chemicals under REACH the precautionary principle is brought into action and therefore non-knowledge played an important role in this process. But there are specific limitations due to different epistemic cultures involved (cp. Scheringer et al.

2006). In case of conflict between these cultures it is not clear what strategies of validation of knowledge are applicable. A kind of "epistemic no-man's land" arises. Against this background, I argue in the *third* step that, under the conditions of non-knowledge, the entanglements of knowledge and power are increasing and need to be analyzed more deeply. These entanglements will be referred to as hybrid regimes of knowledge. These regimes are hybrid with respect of the diverse and confused interactions between knowledge and power in the chemical policy field. Nevertheless, specific structures crystallize to what Sheila Jasanoff named "civic epistemologies". "Civic epistemology refers to the institutionalized practices by which members of a given society test and deploy knowledge claims used as a basis for making collective choices." (Jasanoff 2005: 255) But, the tension between knowledge and power remains - and therefore the conflicts of non-knowledge. Within the *fourth* step I cast a critical eye over different institutional and scientific strategies, which just have been implemented to pacify the conflicts of non-knowledge.

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### V33

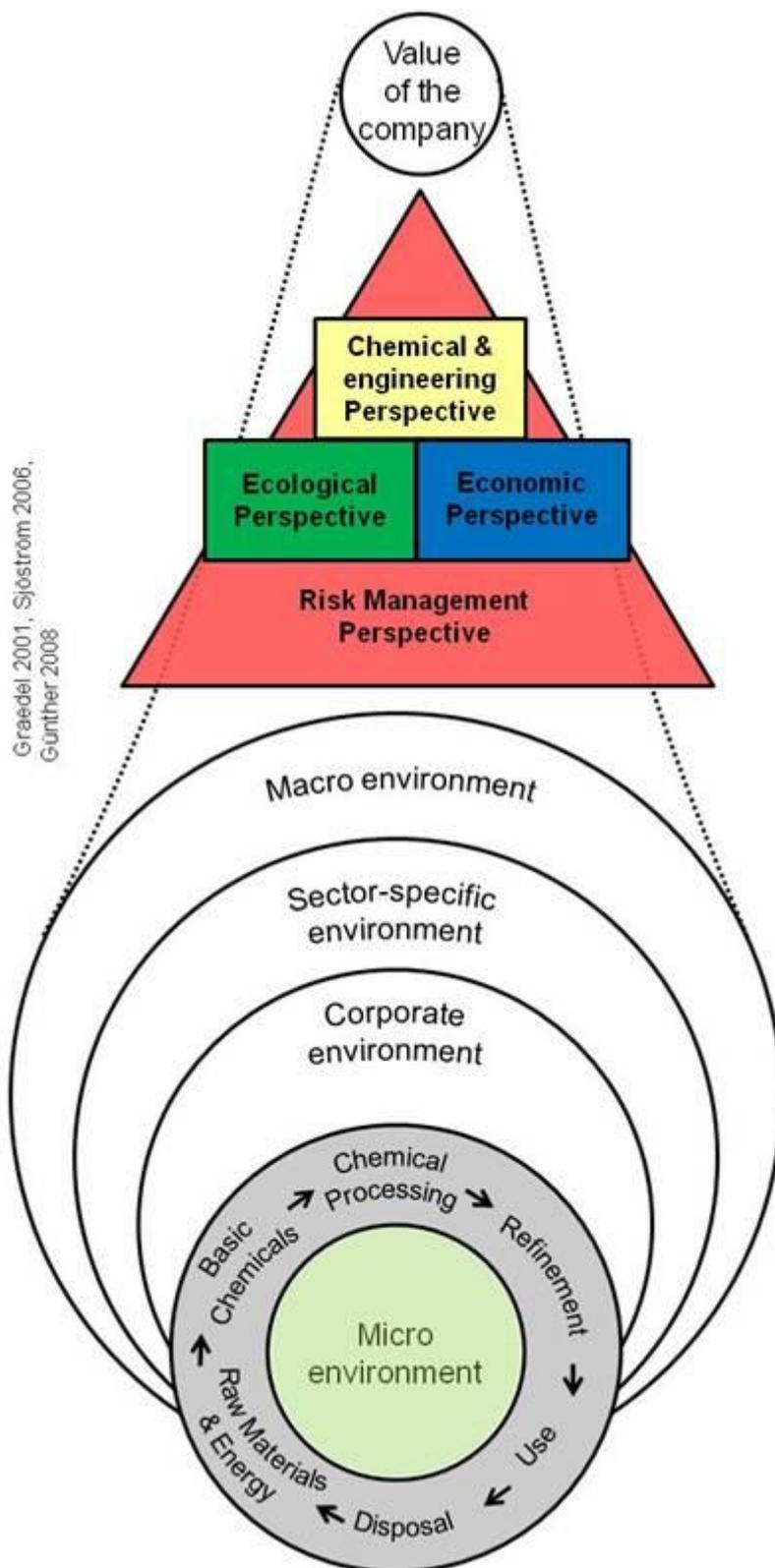
#### **Challenges to the implementation of Green Chemistry**

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Green Chemistry, as fundamental and promising approach to sustainable chemistry, has not yet established as common aspect in chemical industry. Chemical companies cannot resist the paradigm shift to a sustainable chemical industry at all, but it will be a competitive advantage to go beyond operational effectiveness and legal compliance proactively. The implementation of Green Chemistry can increase corporate value, mitigate a company's risk and strengthen the long-term competitiveness. So why does the implementation of Green Chemistry lag behind expectations? Because the primary issue from the company's perspective is that of economics we argue that a missing or incomplete linkage between the benefits of Green Chemistry and corporate value is one of the reasons. Even though companies are persuaded by the concept of Green Chemistry and take an active role in the transition to sustainable chemical industry, they will first ask for its contribution to the company value. In other words, unless there can be shown a value, they will not choose the green path. While in ideal case the maximization of the corporate value should satisfy all stakeholders, in real case trade-offs and conflicts between for example technological, economic or environmental aspects occur that are not measured by traditional concepts of company value.

At the large scale our research is about the enhancement of traditional concepts of corporate value with non-monetary data in order to capture the significant effects of Green Chemistry, which are not recognized by the traditional accounting system and therefore by the traditional concepts of company value. Therefore we derive indicators from a chemical/engineering, an ecological, an economic and a risk perspective. Green Chemistry needs to be considered as part of a company's specific environment - it takes place at the level of molecules and syntheses - from there it can unfold its effects to the whole lifecycle of chemical products. Furthermore it is determined by the company specific environment, but vice versa it may change some of these settings. To get an optimum it is necessary to look across the whole system - not in a single level. That approach is illustrated in figure 1.



Graedel 2001, Sjöström 2006,  
Günther 2008

[Figure 1: Concept Value Added of Green Chemistry]

The particular question for this presentation focuses on the impediments regarding Green Chemistry as part of the above mentioned risk perspective. As every adoption process, especially associated with innovations, is obstructed by impediments we analyze major barriers to the implementation of Green Chemistry. If hurdles are not relieved, the implementation of Green Chemistry might fail and it might become a threat for the company. The focus of the results presented here are the identification and assessment of the barriers.

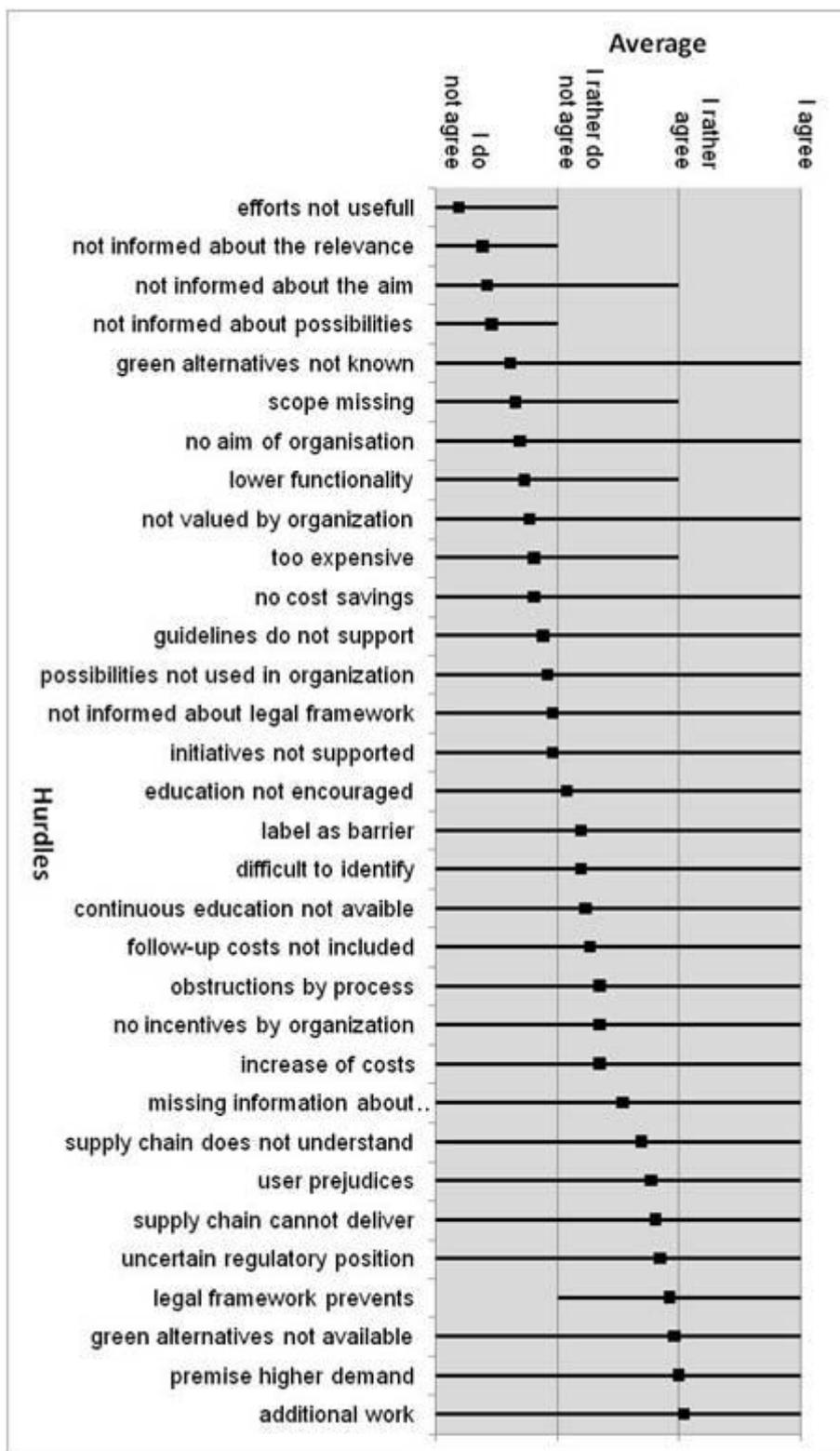
In order to analyse them, the instrument of the Hurdles Analysis was applied. It is the objective of the Hurdles Analysis to identify and assess those factors that may hamper, decelerate or even block

Green Chemistry. The observation items are the perceived, i.e. subjective hurdles, independent of their real existence. It is perception that influences human behavior and not objective measures. For example if actors perceive the legal framework conditions not to support Green Chemistry, they will decide with this knowledge background whether and how to foster Green Chemistry in their company. In this case the hurdle might not be a regulation hurdle, but a knowledge hurdle, but it impacts adoption. Perceived hurdles can be assessed by asking the actors in the process of Green Chemistry implementation.

Based on a comprehensive experience with the Hurdles Analysis in Green Procurement, the authors developed a questionnaire for Green Chemistry. Although not intended to be statistically valid, the survey was intended to assess hurdles for the not satisfactory implementation of Green Chemistry. The study was developed based on a pretest at the Green Chemistry Workshop at Harvard University in February 2007. The study was designed as a written, web-based survey.

Results from the explorative study indicate which impediments are perceived highest. For visualizing the results of the questionnaire the hurdles profile was chosen. This assessing method uses the averages and spreads to point out tendencies for probably existing hurdles and to evaluate their relevance. By using this assessing method it can be assessed, whether potential hurdles are perceived as hurdles (the higher the average the bigger is the perceived hurdle) as well as whether different views do exist about hurdles (the bigger the spread the more different is the perception of a hurdle). Results aimed at with this analysis are to point out first trends (e.g. all interviewees perceive one hurdle almost identically) and to identify starting points for the assessment of causes for hurdles (e.g. strongly differing views on hurdles implicate to have to look for the reasons).

The results from a first group of experts are analyzed. The following figure contains the hurdles profile. The hurdles are sorted according to the average of the answers. Hurdles perceived as high due to high average are located at the right side. The spread of the answers illustrates, if different views do exist about hurdles - the bigger the spread the more different is the perception of a hurdle.



[Figure 2: Hurdles Profile]

As further step of our analysis we matched these results with the six major barrier groups reported from the Harvard Workshop on Impediments of Green Chemistry (Matus, K. J. M., Anastas, P. T., Clark, W. C., Itameri-Kinter, K. (2007). Overcoming the challenges to the implementation of green chemistry. CID Working Paper No. 155). We sorted our hurdle statements using investigator triangulation according to those groups. The preliminary results show that within the majority of the groups some hurdles seem to be overcome whereas others still have to strive for. Within the next analysis step we classified our hurdles according to the steps of the generic innovation process. Those results show a more differentiated picture than the Harvard Groups. Hurdles seem to be perceived higher the later the stage of the innovation process.

The results of our study suggest that Green Chemistry as the most fundamental concept in sustainable chemistry has achieved a good awareness level. Activities to overcome hurdles regarding the implementation of Green Chemistry should focus on the adoption and diffusion stage. While different strategies like the stronger involvement of policies or the expansion of networks are advantageous we plead for the necessity of involving Green Chemistry aspects into corporate decision calculus.

## Green Processes

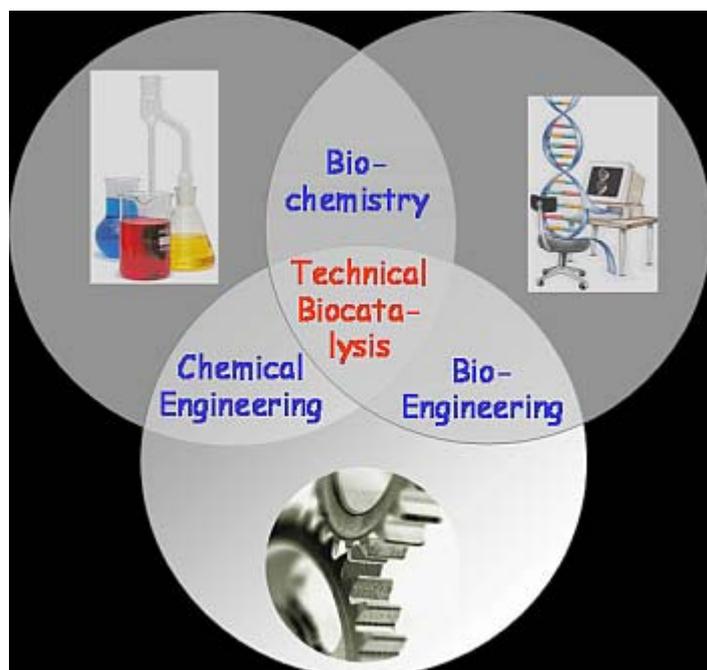
V35

### Sustainable chemical synthesis by means of biocatalysis

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The production of enantiopure compounds is of increasing importance to the chemical and biotechnological industries. Bioorganic transformations are predestined to meet this demand due to their inherent regio- and stereoselective nature. Indeed, a growing amount of enantiopure chemicals for pharmaceutical purposes are being produced biocatalytically today, in contrast to the production of racemic bulk commodities in the past. In this sense, biosynthesis needs to be understood as “chemistry by nature”. The biological principles optimized over thousands of years experience a new renaissance when applied to technical asymmetric catalysis. Nevertheless, one key tool or prerequisite for their application is the appropriate technology, namely reaction engineering. In this lecture selected biological principles as well as processes are described in chemical terms, to transfer, apply them to and combine them with the traditional concepts of chemical, i.e., homogeneous catalysis. Simultaneously, the aim is to design and to develop novel reactors, i.e., engineered systems based on these biological principles. Currently, in technical asymmetric synthesis different biological principles are already being applied without the scientific community at large being aware of it. In those examples namely, where additionally reaction engineering has been integrated, very efficient production processes were designed. This gives rise to high expectations for the future of a sustainable, technical asymmetric catalysis.



*[Interdisciplinarity as requirement]*

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## V36

### Photochemical reactions - green perspectives and the reality

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#### Photochemical processes: The environment

Preparative photooxygenation reactions using singlet excited molecular oxygen ( $^1\Delta_g$ - $^1O_2$ , Type II reaction) is the prime example of green chemistry (air & sunlight and some green leaves). What makes singlet oxygen capricious, however, is its constant refusal to fit into classical concepts of regio- and stereochemical control. Furthermore, the highest and thus synthetically most appealing lifetimes of singlet oxygen are reached in the gas phase (inexpedient) or in fluorinated/chlorinated solvents (not green).

→ In order to avoid these solvents (and solvents all) we have developed an effective, yet simple approach for the singlet oxygen ene- and [4+2]-cycloaddition with organic substrates performed in tetraarylporphyrin-loaded or protoporphyrin IX-copolymerized polystyrene (PS) beads.<sup>1,2</sup> Alternative solid supports investigated were cellulose acetate films, PLA (polylactic acid) films, PHB (polyhydroxy butyrate), PEG (polyethylene glycol) films, and PVAA (poly-N-vinylacetamid) polymer films. The photooxygenation of the allylic alcohol mesitylol in different supports was used to map the polarity and the hydrogen-bonding network in the microenvironment.

→ This photooxygenation approach was used for the synthesis of highly active antimalarial peroxides of the 1,2,4-trioxane type. Boron trifluoride catalyzed peroxyacetalization opens the route to a broad diversity of monocyclic, bicyclic and spirobicyclic peroxides with antimalarial and anti-tuberculosis activity.<sup>3</sup>

#### Photochemical processes: Excitation source (lamps)

The repertoire of excitation sources has been dramatically changed in the last decades. For the ultraviolet and vacuum-ultraviolet region, metal vapour lamps were in use for long time (and still are) and likewise sodium or halogen lamps for the visible region. These lamps produce thermoluminescence in the infrared and thus severe cooling costs had to be added to the electricity consumption. The noble gas excimer and exciplex lamps have reduced the infrared emission and produce nearly monochromatic light in the UV-A up to the vacuum VUV (152 nm).<sup>4,5</sup>

Electroluminescence as the direct way to convert electric power into photons has also reached the UV-A region with the newest LED and OLED technology. Of course, LED lamps are more efficient for excitation in the blue and red part of the visible spectrum. Finally, solar radiation is still an option for photochemistry and possible application are described.

#### Photochemical processes: The chemistry

Photochemistry in order to be compatible with thermal reactions has to offer special advantages from the reactivity (realizing the impossible), selectivity (realizing the improbable way) or from the energetically point of view (avoiding expensive reagents, catalysts or reaction conditions). Direct excitation and photoinduced electron transfer are two possibilities leading to highly excited states (with 3-4 eV energy input) or to radical ion species with high reactivities. Examples for both pathways are discussed.

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## V37

### Catalysis

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A catalyst is a substance, which alters the speed of a chemical reaction by its presence although not being consumed. A catalyst accelerates a chemical reaction in both directions equally. Therefore, a catalyst does not affect the position of the equilibrium of a chemical reaction, it affects only the rate at which it is attained, usually by opening a different, faster reaction pathway. Because a catalyst is not consumed in the process, each catalyst molecule can participate in many consecutive cycles, so that a very tiny amount of catalyst is needed relative to the substrate. Catalysis is accordingly an important tool for waste minimization and to reach sustainable processes, optimizing the use of resources.

The substrate/catalyst ratio reflects the catalyst's efficiency, which is measured as turnover number (TON) and turnover frequency (TOF). The Turnover frequency quantifies the specific activity of a catalytic center for a special reaction under defined reaction conditions by the number of molecular reactions (catalytic cycles) occurring at the center per unit time. The turnover number specifies the maximum use that can be made of a catalyst for a special reaction under defined reaction conditions by the number of molecular reactions (reaction cycles) occurring at the reactive center up to the decay of activity. It represents the maximum yield of products attainable from a catalytic center. In the case of an ideal catalyst as described by its definition, the TON would be infinite. In the case of a real catalyst, however, it is unfortunately lower. One of the goals of catalysis research therefore is to prolong the lifetime of real catalysts. A key issue of the use of catalysts is to utilize them in as many reaction cycles as possible. In the case of batch reactions the catalyst recyclization is often a serious challenge. There are two different ways of applying a catalyst: homogeneous and heterogeneous catalysis. Catalytic processes in which the catalyst(s) and the reaction partners are present in the same phase are named homogeneous catalysis. Catalytic processes in which the catalyst(s) and the reaction partners are not present in the same phase are known as heterogeneous catalysts. The key advantages of homogeneous catalysts are defined structures and stoichiometry, no or few diffusion problems, mild reaction conditions and high selectivity. These advantages are due to the defined character of homogeneous catalysts, with a quantitative presence of active centers. The main disadvantage of homogeneous catalysts is the usually difficult or energy consuming catalyst separation. Accordingly, industrial applications are still dominated by heterogeneous catalysts, which are in almost all cases easy to separate from the reaction partners and products. An important area of current research is therefore the immobilization of homogeneous catalysts in order to combine the main advantages of homogeneous and heterogeneous catalysis. This immobilization can be done for examples on surfaces (carrier materials, e. g. mesoporous materials, nanotubes, membranes, polymers), or in different phases (biphasic and multiphase catalysis, e. g. ionic liquids/organic solvents, aqueous phase/organic solvents etc.).

A key issue in catalysis is the selectivity of a specific catalyst. It provides a comparison between the amounts of desired and undesired products formed in a complex reaction. Selectivity on a quantitative level is obtained by dividing the amount of desired product formed (in Mol) through the amount of substrate converted (in Mol). In case of several starting materials, so called substrates, the compound to which the selectivity refers has to be designed in a reasonable manner.

Although catalysts are at work in living organisms (e. g. enzymes) and in nature since billions of years the concept of catalysis in science is comparatively young. The terms "catalyst" and "catalysis" were coined by Jöns Jacob Berzelius in 1836, derived from the old Greek word for activate and unleash. The exact function of a catalyst has been examined and defined much later, e. g. by Wilhelm Ostwald. Nevertheless, practical applications for catalysts have been found already in the 19th century, e. g. by Johann W. Döbereiner with this lighter, which was a best seller in the European high society in the first half of the 19th century. Technical applications of catalysis began to emerge in the last decades of the

19th and in the early 20th century, the catalytic synthesis of ammonia being one of the most important early catalyst applications in industry.

In the 20th industrial chemistry changed and influenced human lives more strongly and notably than ever before. Unfortunately, for several reasons the image of chemistry grew increasingly poor in the eyes of the public in the decades after the second world war. This may be in part due to misunderstandings, misconceptions and media scares, but there has been valid reason as well. The traditional chemical industry, certainly until the 1980ies was to a significant extent a hazardous and polluting one and the chemistry classes in school were often boring and unnecessarily complicated. Apart from the immediate health and environment hazards, there is also the problem of resource management. The chemical industry drew heavily on irreplaceable fossil resources, often built of millions of years and under unique conditions. Today, the increasing costs of petrochemicals and the growing energy and raw material demands, particularly in heavily populated Asian countries are forcing a change. A popular term associated with this change is sustainability, meaning that the needs of the current human population are met without sacrificing the ability to meet the needs of future generations.

Catalysis is one of the means of reaching higher sustainability in industry. Due to its application for waste reduction, achieved by high selectivity and for low energy consumption (due to mild reaction conditions) it is indeed a corner stone on the way of reaching a less wasteful society. Furthermore, catalysis assists in applying the concept of atom economy and reaching low E-factors. The first term was coined by Barry Trost in 1991 and considers how many and which atoms of the reactants are incorporated into the desired products. The second term was introduced by Roger Sheldon in 1994. It defines the amount of waste (in mass units) produced per mass unit of desired product. These two quantitative concepts help to evaluate chemical reactions with respect to their "eco-friendliness". It has to be considered, however, that by-products are not necessarily hazardous and additional factors, such as the environmental quotient have been suggested to distinguish between different types of waste. Nevertheless, catalysis will certainly play an increasing role in waste reduction, energy efficiency and in the utilization of non-fossil resources in the future. Many efforts have to be dedicated from different areas of science in general and chemistry in particular to create more efficient catalysts and to fully understand and improve their function and performance.

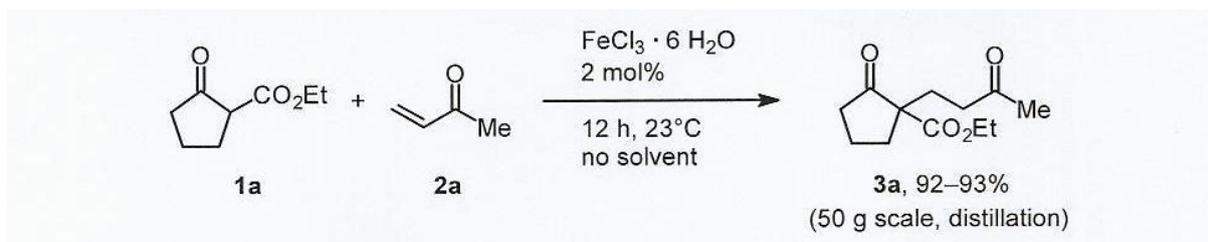
## V38

### Iron-catalyzed Michael reactions - from experiment to theory and back

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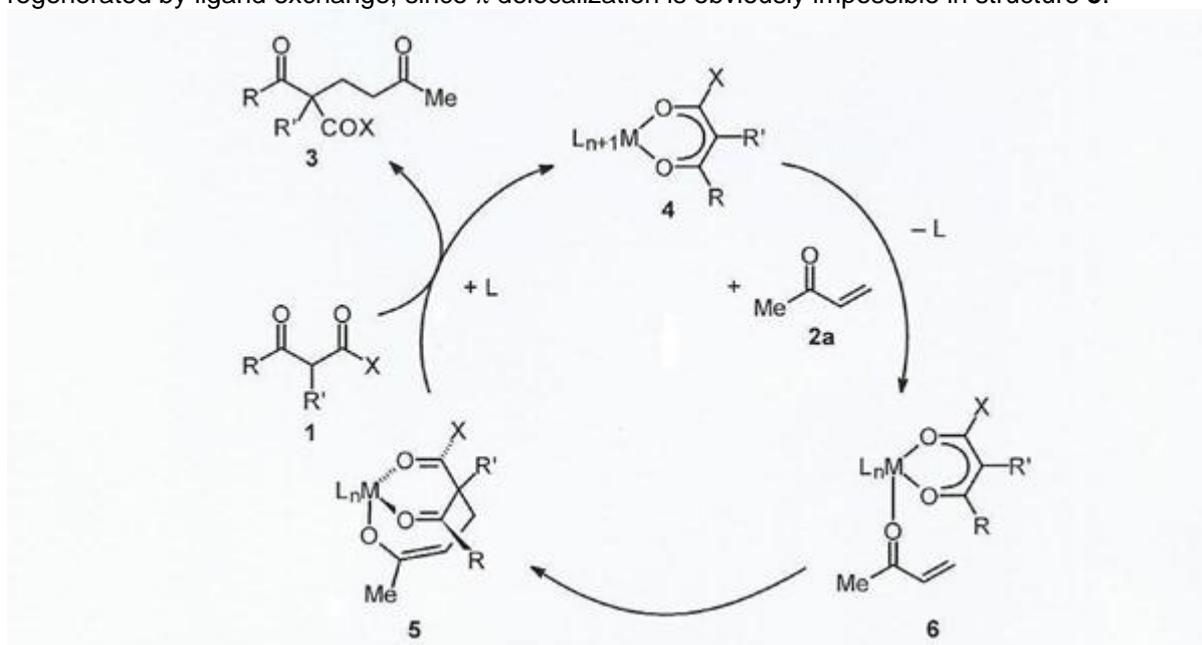
The Michael reaction is the conjugate addition of a  $\beta$  dicarbonyl compound **1** to an acceptor activated olefin like **2a** resulting in a 1,5 dioxo constituted product **3** (Scheme 1). Traditionally, these reactions are catalyzed by Brønstedt bases. However, the strongly basic conditions are often a limiting factor since they can cause undesirable side- and subsequent reactions, such as aldol cyclizations and retro-Claisen type decompositions. To address this issue, ferric chloride hexahydrate was introduced in 1997 by our group as the to date most efficient catalyst for Michael reactions of  $\beta$  dicarbonyl compounds with enones,<sup>[1,2]</sup> allowing quantitative conversions under extraordinary mild conditions and even without the need for any solvent. The conversion of **1a** with **2a** was optimized and scaled up to yield 50 g of the analytically pure product **3a** after distillation (Scheme 1).<sup>[3]</sup> The efficiency of the iron catalysis is remarkable: No inert conditions are required, since oxygen and moisture are tolerated. As long as the starting materials and the products are liquid at ambient temperature no solvents are necessary. A few milligrams of  $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$  are simply added to a stoichiometric mixture of the starting materials. With this method Brønstedt basic conditions are avoided resulting in excellent chemoselectivities. Because of quantitative conversions, workup and purification are extraordinarily simple: Separation of the product from the catalyst is achieved by either distillation or filtration through some silica. Moreover, the catalyst  $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$  is in terms of ecological and economical considerations the transition metal compound of choice.



[1]

Scheme 1 The efficiency of the iron catalysis

The catalytic activity of  $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$  is closely related to its ability to give dionato chelate complexes **4** with  $\beta$ -dicarbonyl compounds. The ligand in a dionato complex **4** is planar and particularly stabilized by  $\pi$ -delocalization. By ligand exchange, the enone **2a** is proposed to coordinate at a vacant site to form species **6** (Scheme 2). The function of the center metal is not only to hold the acceptor in proximity to the donor. Additionally, the enone is activated by the Lewis acidity of the metal. Subsequently, the nucleophilic carbon atom of the dionato ligand is alkylated by the coordinating enone to form intermediate **5**. From this species **5**, the product **3** is liberated readily and complex **4** regenerated by ligand exchange, since  $\pi$  delocalization is obviously impossible in structure **5**.



[2]

Scheme 2 Mechanism for the iron ( $M = \text{Fe}$ ) catalyzed Michael reaction

Density functional calculations have been performed as a further source of information. Several combinations of ligands and acceptors were taken into account and their energy barriers on the way from complex **6** to species **5** were calculated. As the result, the lowest energy barrier for the C-C bond forming step on the potential hypersurface was achieved with a bisdiketonato iron(III) complex with water molecules ( $L = \text{OH}_2$ ) as spectator ligands.<sup>[4]</sup>

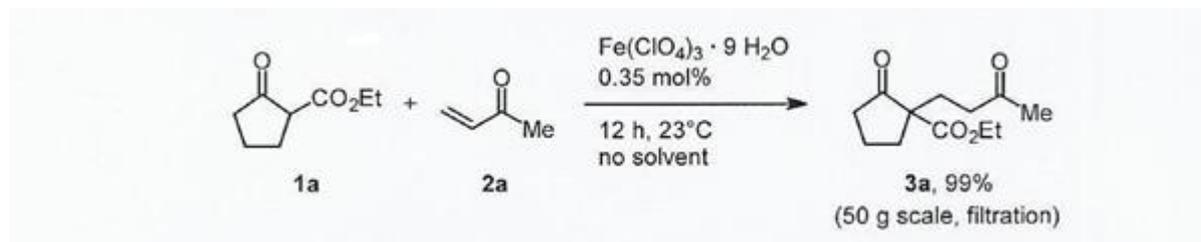
To identify the iron species present under reaction conditions, EXAFS and Raman were applied as *in operando* spectroscopic methods. The nature of the iron complexes present in a solution of  $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$  and  $\text{Fe}(\text{ClO}_4)_3 \cdot 9 \text{H}_2\text{O}$  in  $\beta$ -oxoester **1a**, respectively, were investigated. In both cases the EXAFS spectroscopy showed that the iron center in the forming complex is six-fold surrounded by oxygen atoms in an octahedral coordination sphere. For the mixture of  $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$  and **1a** XANES measurements gave an additional so-called pre-peak indicating a second tetrahedral iron species. This iron compound could clearly be identified as  $[\text{FeCl}_4]^-$  by Raman spectroscopy.<sup>[5]</sup> These results were confirmed by ESI-MS receiving a molecular peak for the bisdiketonato complex in the anion mode and the tetrachloroferrate in the cation mode, respectively.

To study the actual effect of chloride ions in the reaction mixture,  $\text{Fe}(\text{ClO}_3)_4 \cdot 9 \text{H}_2\text{O}$  was applied as the catalyst and the initial rate was determined depending on the concentration of an additional chloride source in the reaction mixture. These examinations clearly indicated a linear, inhibiting influence of the chloride counterions.

Summarizing the spectroscopic, theoretical and kinetic studies it can be concluded: Chloride ions in the reaction mixture are forming the catalytically inactive species  $[\text{FeCl}_4]^-$  as a thermodynamic iron

sink. More simply spoken: Chloride counterions behave like a catalyst poison by removing significant amounts of Fe(III) from the pool of catalytically active material.

As a consequence from these results, an optimized protocol for the iron catalysis of Michael reactions could be developed simply by the application of chloride-free iron salts as the catalysts. The perchlorate for example, is a commercially available material at a reasonable price. With only 0.35 mol% of  $\text{Fe}(\text{ClO}_4)_3 \cdot 9 \text{H}_2\text{O}$  of this catalyst, quantitative conversions of oxoester **1a** with methyl vinyl ketone (**2a**) were achieved within 12 h to give the product **3a** in 99% yield after removal of the catalyst by simple filtration. Compared to the conditions in Scheme 1 using iron chloride, this is an optimization of a factor of six.



[3]

Scheme 3 Optimized protocol for iron catalysis.

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## V39

### On the road to sustainable reactions - alternative sources and forms of energy

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The world-wide consumption of fossil and synthetic carbon-containing resources by the relevant industries is enhanced, as new chemical and biochemical products influence each year the market and new markets are developed in parts of the world for already existing products. It is evident, the rapid growth of the world-wide population based on the general growth in human wealth and the growth in consumer's needs are the significant reasons of the increased consumption of chemical and biochemical products.

This situation is - in other words - not sustainable.

Some sources predict that in the 21st century the human race will face a dramatic decrease of the oil production. Other non-renewable resources will follow the same path - sooner or later. The mean efficiency at which resources are converted into the final products is often very low.

## "Green" Chemistry



[graph1]

our institute is engaged to develop attractive ideal synthesis protocols. In the centre all our activities the question of energy efficiency is standing.

The very popular nonclassical heating technique based on microwaves, often named the "Bunsen burner of the 21st century". One aim of using of emerging MW-assisted chemical techniques in interaction with green reaction media (aqueous, ionic liquid, and solventfree) is to reduce the chemical waste and reaction times in organic syntheses and transformations.

Within the last decade green chemistry has obtained the symbol of a major scientific working field. The investigation and application of green chemistry principles were and are very important for development of cleaner and more benign chemical processes. Each year many new technologies are being developed. Synthetic preparators in both academia and industry are constantly challenged to reflect more environmentally benign and sustainable preparation methods for the production of desired target substances.

From our view of point and experiences in ecobalances among the 12 principles of green chemistry the acceptance of energy efficiency is one of the key principles of relevance to (bio)chemists.

In all chemical processes a main adverse effect to the environment is the consumption of energy of heating and, not to forget, cooling. To overshall these conflicts it is highly required to need efficient methods that use alternative sources and forms. In the context of this paper the question of efficiency and therefore of relative sustainability of microwave irradiation compared to convective heating processes and to processes which are performed under the influence of ultrasound or mechanochemical energy must be discussed.

Some foreign published (preliminary) results inform on that microave-assisted reactions can be significantly more energy-efficient than common heating. The comparison with mechanochemical experiments is still not enough be investigated. The best protocol would be chemical conversions start at room temperature, the quantitative conversion is reached within a few minutes and a quantitative isolated product yield is possible without ecological problems. The reality is mostly combined with risks, which are to omit or to reduce.

## A Series of Reductions



[graph2]

The paper informs on selected research and development projects on

- MW-assisted liquid-phase oxidation reactions
- MW-assisted liquid-phase hydrogenation reactions
- MW-assisted liquid-phase phosgenation reactions
- MW-assisted liquid-phase C-C-coupling reactions (Suzuki, Heck, Sonogashira).

Some remarks are dedicated to simultaneous influence of

- microwave and ultraviolet irradiation on the synthesis of fine chemicals
- microwave irradiation and microreactor on the Kolbe-Schmitt reaction in presence of selected ionic liquids
- microwaves and ultrasound.

At the end recent results are introduced and discussed, which are obtained under the reaction regime of solventfree conditions. Two examples (Konovenagel, Suzuki) demonstrate the possible importance of mechanochemical regime, partly in comparison of additional influence of microwave irradiation.

V40

### **New heterogeneously catalyzed processes for environmentally benign and sustainable chemical production**

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Environment concerns and regulations have been increased in the public, political and economical world over the last 20 years because quality of life is strongly connected to a clean environment. The impulse for developing new, more efficient and selective catalysts and for the realization of new and sustainable process technology is strongly related to environmental compatibility. In principal this target can be achieved in two ways:

- One is the so called "end-of pipe" technology in which processes are adapted to the more and more severe emission control regulations via consecutive costly separation procedures and catalytic transformations, such as in exhaust gas car converters and DeNO<sub>x</sub>-units.
- The second more elegant approach is the so called production or reactor integrated environmental protection. Thereby the formation of pollutants is diminished or even completely avoided by the

development of alternative technology in chemical transformations. The interest of the chemical industry is in sustainable and green developments in which catalysts act as modern tools to carry out reactions very selective and in which they help to synthesize the desired products of the petrochemical and chemical industry in a competitive way under extensive utilization of the resources as well as without formation of by-products and waste.

In the present contribution examples for such production integrated and sustainable developments will be given, chosen right at the borderline of fine and intermediate chemicals.

Thereby, two severe problems are selected :

- The replacement of homogeneous Brønsted and Lewis acids by solid acidic materials.

- Oxidation reactions in the presence of environmentally benign oxidants.

In addition the application of renewable feedstock contributes to sustainable chemical production as well. One or two examples out of our research such as the transformation of glycerol to acrolein will be presented.

## V41

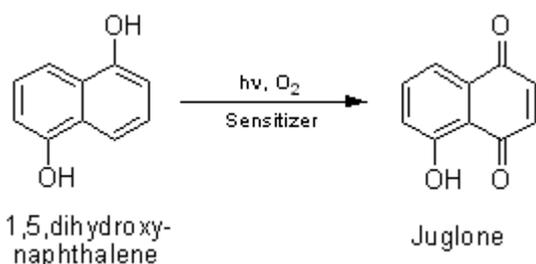
### “Green photochemistry” - solar photooxygenations and development of novel sensitizer immobilised biopolymer beads

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With the ongoing and inevitable decrease in the level of the Earth's fossil fuels and increasing levels of CO<sub>2</sub> the term “sustainable development” has been coined. This concept calls for the development of clean, renewable and environmentally friendly processes in both industry and everyday life. Although this idea is by no means new its importance has never been greater. This is also true within the fine chemical industry where every year hundreds of thousands of tonnes of waste are produced. In 2006 the Irish Environmental Protection Agency (EPA) carried out a survey and showed that 155,570 tonnes of fine chemical waste were produced in Ireland alone. This equated to € 14 million in safe disposal costs (typically incineration). In addition to this large amount of waste it is also important to note that such chemical wastes can often be highly toxic to the environment.

In this presentation we hope to show how the field of synthetic photochemistry in particular dye sensitized photooxygenations can be a viable “green” solution to many of the problems currently faced within the fine chemicals industry. We are using the synthesis of Juglone, (Scheme 1) an important synthon in the pharmaceutical industry to illustrate the importance of synthetic photochemistry in the future. We have also selected the synthesis of Ascaridole and Rose Oxide as further examples of sustainable “green” chemistry.



[Scheme 1: Synthesis of Juglone]

Early literature for the synthesis of Juglone involved the use of harsh and toxic oxidising agents. These thermal processes possess known toxic effects to the environment and commonly use halogenated solvents as their reaction media. These themselves are also toxic to the environment. Indeed even early photochemical methods for the synthesis of Juglone required the use of halogenated solvents. Our research builds on these initial photochemical successes in an effort to show that such methods can be made more environmentally friendly. The focus of the research was two-fold; 1) To optimise known photooxygenation reactions and show that fine chemical synthesis is viable on a large scale yet remaining environmentally friendly and 2) to develop a reusable environmentally friendly solid

supported sensitizer.

1) The synthesis of Juglone (our model reaction) was carried out in different alcohols with particular attention being drawn to 2-methyl-2-butanol. This environmentally safe alcohol has shown to produce Juglone in high yields in both natural and artificial light (500 W halogen lamp). Large scale synthesis (8 L) has also been carried out using a Flatbed reactor at DCU. In addition to this direct comparisons were made between the two methods for energy consumption using energy flow meters while artificially irradiating the reaction solutions. Recently a Compound Parabolic trough Collector (CPC) reactor similar to those at the DLR in Germany has been purchased and will be set up at DCU. This 66 L reactor will allow us to scale our experiments up to industrial levels. Once we had selected our solvent and optimised our procedure we moved forward to the synthesis of Ascaridole and Rose Oxide.

2) Rose Bengal was the sensitizer of choice during our photooxygenation reactions due to solubility issues with other sensitizers in our solvent 2-methyl-2-butanol. As a result of this we carried out an investigation into sensitizer encapsulated beads to overcome such solvation issues. We looked primarily at a completely natural polymer derived from seaweed called Sodium Alginate. Using this polymer in aqueous solutions we were able to encapsulate the sensitizers Rose Bengal, TPP and Co(SALEN), the latter two insoluble in 2-methyl-2-butanol. Using these beads we successfully synthesized Juglone, Ascaridol and Rose Oxide in good yields and could successfully reuse these beads for further dye sensitized photooxygenation reactions.



[Figure 1: Biopolymer Beads, Flatbed & CPC reactors]

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V42

### **Sustainable isolation of valuable or undesirable substances using adsorptive bubble separation**

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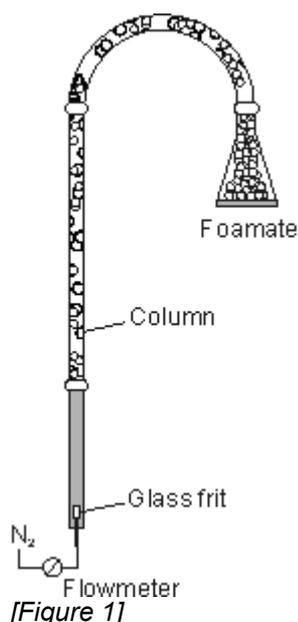
<sup>1</sup>TU Munich, Chemical-Technical Analysis, Freising-Weihenstephan, Germany, <sup>2</sup>Hacettepe University, Ankara, Turkey

**Introduction:** The food and pharmaceutical industry has always strived to use effective and sustainable methods for the isolation of valuable or undesirable substances. Products developed in such a manner can be marketed as being produced eco-friendly, or simply can help to effectively produce under reduced costs, since commonly applied methods such as the solvent extraction and/or supercritical fluid extraction are long known for being environmentally questionable, or have high demands on personnel and expenses.

The so-called foam fractionation may serve as an alternative in order to effectively and sustainably enrich substances from liquids. In principle surface active substances enrich on bubbles that are generated after gas is lead through the liquid at specific flow rates. The foam produced thereby degenerates back to liquid ("foamate"), and contains the desirable substances in highly concentrated form. The process needs careful attention as to the proper adjustment of certain parameters, which most importantly are the pH, foaming time, gas flow rate, surfactants to enhance foaming, column dimensions, initial volume, and others. Here we exclusively strived to figure out the potential of this

technique in order to enriching effectively and sustainably technologically and pharmaceutically important natural principles.

**Material and methods:** A typical foam fractionation apparatus in laboratory scale is shown in Fig. 1. The process efficiency was evaluated by calculating the enrichment factor (EF; concentration in the foam vs. concentration in the start solution) and the yield (Concentration in the foam \* volume of foam vs. concentration in the initial solution \* volume of the initial solution (in %)). Foam fractionation parameters were standardized as follows: start volume: 100 ml, saponin: 30 mg/100 ml, duration: 60 min; nitrogen flow rate: 15-30 ml/h (individually adjusted for each substance); initial concentration of substances between 0.40 and 7.50 mg, depending on the extract under investigation. Mainly HPLC methods were used for quantification. All chemicals were of p.a. quality. The log Pow value was determined experimentally according to OECD guideline. Experiments were performed 3-fold.



**Results and discussion:** At first, different pH values and two temperatures were chosen, and the corresponding log Pow values were determined to figure out dependencies with regard to obtaining best efficiency values. Preliminary trials with model substances revealed a distinct dependency between log Pow and the efficiency (Fig. 2 A). In general, the higher the log Pow of a substance, the more enhanced are both efficiency values. The following foaming experiments performed with aqueous plant extracts confirmed this tendency, especially with regard to the gingerols and carnosol (Table 1, Fig. 2B). Particularly at pH 6 best results as to high yields can be obtained. Rosemarinic acid, however, with log Pow around zero, could not be enriched. Flavokavin B presents an exception, as it can well be enriched with high yields at pH 6 and at both chosen temperatures, despite its low log Pow of ca. 0.3. Here it can be assumed that the Kava Kava extract already contains sufficient amounts of surface active compounds to cause foaming without the addition of surfactants. A satisfactory correlation tendency for these experiments can only be noted between the log Pow and yield but not for the enrichment respectively (Fig. 2B).

Rosemarinic acid	pH: 3, 6, 10	lg Pow: 0.27, 0.20, 0.0	T 25 °C	Yield: 0, 0, 0	EF: 0, 0, 0
	pH: 3, 6, 10	Log Pow: 0.25, 0.18, 0.0	T 5 °C	Yield: 0, 0, 0	EF: 0, 0, 0
Flavokavin B	pH: 3, 6, 10	Log Pow: 0.30, 0.25, 0.0	T 25 °C	Yield (%): 57.8, 99.6, 42.0	EF: 60.0, 220.0, 52.5
	pH: 3, 6, 10	Log Pow: 0.32, 0.30, 0.0	T 5 °C	Yield (%): 55.5, 100.0, 41.1	EF: 55.5, 220.7, 50.3
[6]-Gingerol	pH: 3, 6, 10	Log Pow:	T 25 °C	Yield (%):	EF: 29.7,

		3.20, 3.15, 0.0		79.0, 99.0, 0.0	39.6, 0.0
	pH: 3, 6, 10	Log Pow: 3.20, 3.20, 0.0	T 5 °C	Yield (%): 72.0, 98.0, 0.0	EF: 25.6, 38.5, 0.0
[8]-Gingerol	pH: 3, 6, 10	Log Pow: 3.20, 3.15, 0.0	T 25 °C	Yield (%): 63.0, 89.0, 0.0	EF: 55.8, 63.2, 0.0
	pH: 3, 6, 10	Log Pow: 3.20, 3.20, 0.0	T 5 °C	Yield (%): 60.0, 90.1, 0.0	EF: 52.7, 66.1, 0.0
Carnosol	pH: 3, 6, 10	Log Pow: 4.40, 4.35, 0.0	T 25 °C	Yield (%): 99.4, 86.05, 0.0	EF: 52.0, 41.8, 0.0
	pH: 3, 6, 10	Log Pow: 4.40, 4.35, 0.0	T 5 °C	Yield (%): 100.0, 92.0, 0.0	EF: 52.0, 44.0, 0.0

Further experiments for confirming and/or enhancing the results were performed using plant extracts from hop, green tea, curcuma, carrot, orange, and cannabis at again three different pH values but with a chosen temperature of 25°C. The humulones, having high log Pows between 2 and 3, were enriched with high yields and enrichment factors at low pHs, while the catechins did not deliver the same satisfactory results (Table 2).

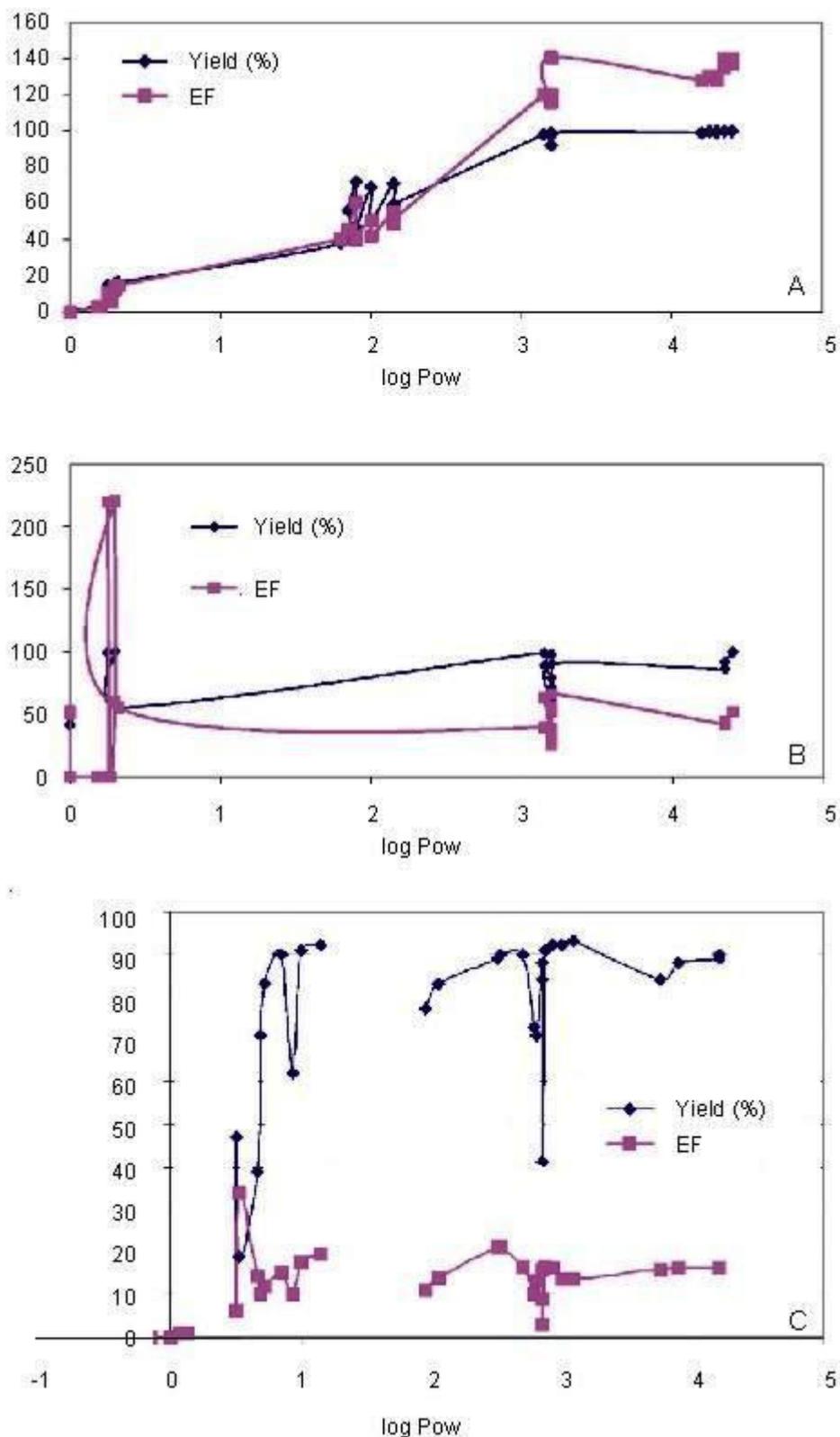
Humulus lupulus L. (Hop)	Co-Humulon	pH 3, 6, 10	log Pow: 2.92, 2.81, 0.0	Yield (%): 92, 71, 0	EF: 16.3, 13.4, 0.0
	n-Humulon	pH 3, 6, 10	log Pow: 3.09, 2.85, 0.0	Yield (%): 93, 88, 0	EF: 13.8, 9.3, 0.0
	Ad-Humulon	pH 3, 6, 10	log Pow: 3.00, 2.79, 0.0	Yield (%): 92, 73, 0	EF: 13.8, 10.0, 0.0
	Co-Iso-Humulon	pH 3, 6, 10	log Pow: 2.05, 1.96, 0.0	Yield (%): 83, 77, 0	EF: 14.0, 11.0, 0.0
	n-Iso-Humulon	pH 3, 6, 10	log Pow: 2.87, 2.70, 0.0	Yield (%): 91, 90, 0	EF: 16.8, 16.7, 0.0
	Ad-Iso-Humulon	pH 3, 6, 10	log Pow: 2.53, 2.50, 0.0	Yield (%): 90, 89, 0	EF: 21.4, 21.4, 0.0
Camellia sinensis L. (Green Tea)	(+)-Catechin	pH 3, 6.5, 10	log Pow: 0.30, 0.53, 0.0	Yield (%): n.d., 19, 0.0	EF: n.d., 34.0, 0.0
	(+)-Gallocatechin gallate	pH 3, 6.5, 10	log Pow: 0.10, 0.12, 0.0	Yield (%): n.d., n.d., 0.0	EF: 1.0, 1.0, 0.0
	(-)-Epigallocatechin gallate	pH 3, 6.5, 10	log Pow: n.d., 0.09, 0.0	Yield (%): n.d., 1.0, n.d.	EF: n.d., 1.0, n.d.
	(-)-Epicatechin	pH 3, 6.5, 10	log Pow: n.d., 0.67, 0.0	Yield (%): n.d., 39, 0.0	EF: n.d., 14.3, 0.0

Only (+)-catechin and (-)-epicatechin were enriched effectively at pH 6.5. For the other catechins matrix effects may have played a role by hampering the enrichment process (c.f. Table 3). It is, however, known from experience that when catechins have formed complexes with caffeine, it is

possible to transfer them into the foam phase.

Camellia sinensis L. (Green tea)	(-)-Epicatechin gallate	pH 3, 6.5, 10	log Pow: 0.07, 0.07, 0.0	Yield (%): n.d., n.d., 0.0	EF: 1.0, 1.0, 0.0
	(-)-Epigallocatechin	pH 3, 6.5, 10	log Pow: 0.13, 0.13, 0.0	Yield (%): n.d., n.d., 0.0	EF: 1.0, 1.0, 0.0
Curcuma longa L. (Curcuma)	Curcumin	pH 3, 6, 10	log Pow: 0.94, 1.15, 0.0	Yield (%): 62, 92, 0.0	EF: 10.0, 19.5, 0.0
	Demethoxycurcumin	pH 3, 6, 10	log Pow: 0.72, 1.0, 0.0	Yield (%): 83, 91, 0.0	EF: 12.0, 17.6, 0.0
	Bis-demethoxycurcumin	pH 3, 6, 10	log Pow: 0.69, 0.85, 0.0	Yield (%): 71, 90, 0.0	EF: 10.1, 15.4, 0.0
Daucus carota L. (carrot)	$\beta$ -carotin	pH 3, 6, 10	log Pow: 4.20, 4.20, 4.20	Yield (%): 89, 90, 90,	EF: 16.2, 16.3, 16.3
	Lutein	pH 3, 6, 10	log Pow: 3.75, 3.89, 2.85	Yield (%): 84, 88, 84	EF: 16.0, 16.3, 16.0
Citrus sinensis L. (Orange)	Naringin	pH 3, 6, 10	log Pow: n.d., -0.15, n.d.	Yield (%): n.d., 0.0, n.d.	EF: n.d., 0.0, n.d.
Cannabis sativa L. (Cannabis)	$\Delta^9$ -Tetrahydrocannabinol (THC)	pH 3, 6, 10	log Pow: 1.60, 2.85, 0.51	Yield (%): n.d., 41.2, 47.0	EF: n.d., 3.0, 6.2

Throughout the experiments, but not at pH 10, high efficiency rates could be obtained for all curcumines with the exception that  $\beta$ -carotene was also effectively enriched at pH 10. Worse results were obtained for naringin, for which the glycosidic side chain can be held responsible, which increases the polarity of the molecule. Interesting are the results for tetrahydrocannabiole (THF), which in the contrary to the low pHs for the other compounds, could be enriched effectively at pH 10. Generally this substance is of pharmaceutical interest due euphoric, relaxing and increased sensitivity (for taste, hearing and groping) characteristics. Only the correlation between log Pow and yield can be regarded satisfactory ( $r = 0.83$ ), while the correlation towards the enrichment can not (Fig. 2C).



[Figure 2]

**Conclusion:** Numerous of pharmaceutically and technologically interesting substances could be effectively enriched by using foam fractionation technique. The substances of interest should possess log Pow values best over 3, and the process in general should be performed at relatively low pHs and temperatures, proving thereby the mildness of the method. The method itself, belonging to the adsorptive bubble separation techniques, can be considered sustainable, as solvents can be omitted and, furthermore, the equipment used is simple and the expenses for acquisition and maintenance are low. Future investigation should involve feasibility tests at pilot plant scale in order to give the industry an interesting tool for separating compounds in pure form and with high yields, sufficient enough for

product formulation.

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