

# BULLETIN

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## WELCOME TO ISSUE N°2 OF THE NORMAN NETWORK BULLETIN

The aim of the NORMAN network is to enhance the exchange of information on emerging environmental substances, and to encourage the validation and harmonisation of common measurement methods and monitoring tools so that the requirements of risk assessors and risk managers can be better met. It specifically seeks both to promote and to benefit from the synergies between research teams from different countries in the field of emerging substances. The NORMAN Bulletin is for everyone interested in emerging substances in the environment. This Bulletin keeps you up to date on scientific advances in this area and highlights the activities and events of the EU NORMAN Network.

### Editorial

## **NORMAN members help to close the knowledge gaps on emerging substances**

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Welcome to the second issue of the NORMAN Bulletin, in which we continue to address environmental and health agencies and public authorities on the subject of emerging substances and the work being done to close the knowledge gaps in this field. As ever, we do this in order to improve the quality of decision-making.

We start with a quick look at two milestones that have been – or are about to be – reached.

First, in the field of water policy, the work to define the new list of Priority Substances under the Water Framework Directive (WFD) is reaching its final phase. The WFD attaches great importance to experimental data, and intensive work has been done over the past five years to collect monitoring data and to define environmental quality standards, all involving extensive consultations and discussions between experts from Member States, stakeholders and Commission services. The results of this work are welcomed as a major contribution to the assessment of the risks associated with environmental contaminants, but there are still significant information gaps for substances that are currently not – or seldom – monitored and which might pose a risk to aquatic ecosystems or to human health. As also pointed out by the NORMAN–JRC workshop in Stresa (June 2010), the resources for setting up research programmes for emerging substances are often limited. Additionally, the use of screening methods is in many instances still rather limited. Very few countries provided data on sub-

stances that can be considered as substances of emerging concern today. And the provided data were mainly on pharmaceuticals.

Second, as regards the environmental risk assessment of chemicals under REACH, December 2010 marked an important milestone in the implementation of the REACH Regulation. By this first registration deadline, more than 25 000 dossiers had been produced by industry for the most hazardous and commonly used substances. As a result, there is now a wealth of information available at ECHA about these chemicals. The challenge is now to evaluate these dossiers and ECHA has expressed its willingness to make substance-specific information available on its website.

We believe that the work being done by the NORMAN network – and highlighted in this Bulletin – will continue to help raise the level of scientific knowledge available to decision-makers in these environmental policy areas. This will be particularly important in defining and prioritising the research programmes to be launched in order to close the current knowledge gaps.

The first topic addressed below is siloxanes, on which we reported in the previous edition of the Bulletin. We provide here an update on developments in this research field, where the questions about the persistence and susceptibility to bioaccumulation of these compounds remain open mainly because of the analytical challenges

yet to be overcome and the paucity of field data on which to base independent scientific decisions.

We also revisit Environmental Specimen Banking (ESB), which was the subject of the NORMAN-UBA conference in June 2010. It is now recognised that ESBs could play an important role in the gathering of exposure information to check temporal trends of emerging substances. Their contribution will, however, only be maximised once they are organised as a network at the European or international level.

We then offer further insight into the concerns associated with wastewater reuse and the presence of xenobiotics. There are currently several gaps in our knowledge of degradation mechanisms, transformation products and, consequently, the potential effects that wastewater reuse practices might have on non-target organisms in the environment and on human health through biomagnification in the food chain.

We also present thematic summaries to point up the main outcomes of workshops and other activities organised in 2010.

Of particular interest is the workshop organised by BfG on "Engineered Nanomaterials in the Aquatic Environment", as a result of which a new expert group meeting is to be organised in 2011 to set the future research direction in this area.

Another topic on which NORMAN has worked in 2010 and will continue to do so in 2011 is the application of passive sampling for emerging substances. A Position Paper was published this year as a result of the Expert Group meeting in Prague in 2008, which provides an exhaustive review of the application of this tool in aquatic monitoring for the most frequently discussed groups of emerging compounds. An executive summary of the Position Paper is provided in this issue.

NORMAN's 2011 programme will also include activities in the field of flame retardants, in particular a close look at organophosphorus and the so-called "new" brominated flame retardants (BFR). This will also be the opportunity to present ENFIRO, an EU research project on options for a number of BFRs for better, safer alternatives.

We hope you find the content of this Bulletin both interesting and useful.

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## Siloxanes : Cyclic methyl volatile siloxanes (cVMS) in the environment

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### INTRODUCTION

Cyclic volatile methylsiloxanes, cVMS, are clear, volatile, low-viscosity fluids used as precursors in the production of silicone polymers and as solvents or carriers in personal care/ household products and cleaning agents. The major cVMS in production are octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5), and dodecamethylcyclohexasiloxane (D6). D5 is the major cVMS used in personal care products and has the highest estimated emissions to the environment; it has received the most research attention. Recently, D4, D5, and D6 were proposed as priority chemicals for environmental risk assessment due to their suspected persistence in the environment and susceptibility to bioaccumulation as well as their large volume of usage (Muir and Howard, 2006; Howard and Muir, 2010). D5 has been risk assessed by the Canadian government and is currently listed for classification (Environment Canada, 2008), whereby this decision is currently under review. A risk assessment of D4, D5, and D6 in the European Union has been conducted (Brooke et al., 2009a-c), with the current recommendations being that D4 be classified as vPvB and PBT and D5 as vPvB under REACH.

The central concerns about the potential environmental risks of D5 are its persistence, its bioaccumulation, and its long range transport. Much of the research in this area has been conducted by the producing industry and has not been made freely available to the research community. Consequently, the best sources of information are the comprehensive risk assessments prepared by the UK Environment Agency, which has had access to the results of industry research (Brooke et al., 2009a-c). However, a wealth of information has become available since the release of those reports in April 2009. This article summarises some of these new findings, focussing on the work presented at a session on cVMS held at the SETAC Europe meeting in May in Seville and at a EU member states siloxane workshop held on 10-11 June 2010 in Helsinki.

### ANALYTICAL METHODS

The paucity of analytical methods suitable for the environmental trace analysis of cVMS has been a major hindrance in the study of these compounds. Blank problems are the major concern due to cVMS use in personal care products and their presence in chemicals, solvents, and in silicon parts/lubricants in laboratory equipment and instrumentation. A major breakthrough was achieved in 2010, with the first report of a successful interlaboratory comparison for the analysis of cVMS at trace levels. Liver from Atlantic cod was analysed, and the three participating labs (Dow Corning, Evonik, NILU) obtained similar results. Furthermore, they reported method detection limits in the low ng/g wet weight range (Warner et al., 2010a). Another interlaboratory comparison was conducted by Environment Canada, but the results are not yet available.

Two new analytical methods have also been reported. A method for D5 in air was developed based on sampling with Isolute ENV+. It was shown to be robust, reproducible, and had a limit of quantification of 0.3 ng/m<sup>3</sup>, which was sufficient for measuring D5 in rural air in Sweden (Kierkegaard and McLachlan, 2010a). The same sorbent was used in a purge and trap method to analyse cVMS in biota. This method offered several advantages over the existing cold solvent extraction method, including cleaner extracts and somewhat lower limits of quantification (Kierkegaard et al., 2010a).

### LONG-RANGE TRANSPORT

The atmospheric fate of D5 was assessed in a combined measurement and modelling study. The concentrations in air were measured every 24 h over a 5 month period at a rural site in Sweden. The measured values were then compared with concentrations predicted by a hemispheric scale atmospheric circulation and fate model driven by emission estimates derived from consumer product use. Excellent agreement was obtained, indicating that there is a good understanding of emissions and fate of D5 in air. The work showed that D5 is clearly subject to long-range atmospheric transport, but that only a very small portion of it is deposited to surfaces in remote regions. It is eliminated from the atmosphere via reaction with OH radicals at a rate that varies strongly with latitude and season, but reflects an average atmospheric half life of ~10 days (McLachlan et al., 2010).

This relatively rapid degradation of D5 combined with the low rate of deposition to terrestrial and aquatic ecosystems means that emissions of D5 to air are considered to be relatively unproblematic. Some 90 % of D5 is estimated to be emitted to air, while 10 % is released to water. Of this 10 %, about 95 % is estimated to be removed in wastewater treatment plants (WWTPs). Nevertheless, it is the discharge via WWTP effluent (just ~0.5 % of emissions!) that is the major regulatory concern (Brooke et al., 2009b).

### BIOACCUMULATION

In line with this concern, the major focus of the bioaccumulation work to date has been on aquatic organisms, and in particular fish. During the last year the first data on D5 levels in fish sampled distant from point sources were reported. D4, D5, and D6 were shown to be present at mid ng/g lipid levels in herring sampled at 10 stations along the Swedish coast of the Baltic Sea and the Skagerrak, as well as in 7 further fish species from one of these stations (Kierkegaard et al., 2010b). These chemicals were also measured in livers from Atlantic cod and sculpin sampled in 3 fjords in Spitzbergen, whereby a relationship between the measured concentrations and the proximity to municipal wastewater discharges was observed (Warner et al., 2010b).

In an effort to quantitatively evaluate bioaccumulation of cVMS in the field, trophic magnification factors were determined in a food web in Lake Pepin, a lake in the Mississippi River downstream of the metropolis Minneapolis/Saint Paul. D4 and D5 were analysed to excellent quality standards in 2 benthic invertebrates and 15 species of fish. The trophic magnification factors were 0.31 and 0.18, for D4 and D5, indicating that the lipid normalised concentrations of these chemicals tended to decrease as they moved up the food chain (Woodburn et al., 2010).

Two other studies took a different approach to quantifying bioaccumulation. This was motivated by the very low concentrations of cVMS in water. The underlying premise was that bioaccumulation is the fraction of the chemical present in the aquatic environment that is transferred to fish. Since sediment is the major reservoir of D5 in the aquatic environment, this transfer was estimated using the ratio of the D5 concentrations in fish and sediment. To provide a basis of comparison, the same ratio was calculated for PCB180. Measurements were conducted for lugworms and flounder in the Humber estuary and perch in six Swedish lakes. The ratio for D5 was similar to or greater than the ratio for PCB180, indicating that the bioaccumulation of D5 was similar to or greater than PCB180 (Kierkegaard and McLachlan, 2010b; van Egmond et al., 2010a).

## PERSISTENCE

The concerns about environmental persistence of cVMS are focused on their fate in surface media following emissions to wastewater. cVMS have been shown to hydrolyse in water. However, when released to water, their extreme hydrophobicity results in a significant portion of the emissions partitioning to sediment. Once in sediment they appear to degrade very slowly if at all (Brooke et al., 2009a-c). This has led some to conclude that the cVMS are persistent in sediment. However, there was a growing recognition at the Helsinki meeting that persistence in sediment cannot be assessed based on degradation alone. The major loss mechanism for cVMS will be desorption from the sediment to water followed by hydrolysis, or, in many cases, transport to the water surface, volatilisation, and phototransformation in the atmosphere.

One important factor governing this loss mechanism is the partitioning of cVMS between sediment and water. There is growing evidence that the partition coefficients are considerably lower than one would expect

from the high octanol/water partition coefficients of these chemicals (van Egmond et al., 2010b). However, there are to date no field studies on the persistence of cVMS in soils or sediments.

## DISCUSSION

Although they have only recently been identified as “emerging” pollutants, the regulatory assessment of the cVMS is proceeding quickly. While this is to be welcomed on the one hand, on the other the assessment is being conducted on the basis of very few field data. Given the unusual properties of these chemicals, which means that we have no similar precedents on which to base decisions, this is a risky strategy. There is an urgent need for good independent science to inform the assessment process, in particular science based on field observations. The recent advances in analytical methodologies now make it possible to study these compounds in many environments. Hopefully this will help to stimulate research that will resolve the important open questions such as the environmental persistence of these substances.

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# Use of environmental specimen banks for investigations of emerging pollutants - recent case studies and outlook for future applications

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Environmental specimen banks (ESBs) could play an important role in gathering exposure information, especially on emerging substances (see NORMAN Bulletin 1, pp 2–4, December 2009). Past studies revealed that consumption patterns of chemicals and tissue concentrations in biota are correlated (e.g., for musk fragrances). It could also be proven that concentrations in exposed biota decreased after banning or phasing out compounds of concern (e.g., lead, tributyltin, alkylphenols). Moreover, the use of archived biological samples allows the fast analysis of samples from different years and regions under comparable conditions. Thus the results of retrospective monitoring could help to assess the relevance of compounds in question with respect to concentration levels and temporal trends (exposure monitoring).

The following case studies taken from recent publications should demonstrate the potential for the application of ESBs. Two studies are covering perfluorinated compounds (PFC) while the third example deals with a brominated flame retardant, hexabromocyclododecane (HBCD). One PFC, perfluorooctane sulphonic acid (PFOS) is already covered by the Stockholm Convention on Persistent Organic Pollutants (POPs; <http://chm.pops.int/>), while HBCD is currently under review.

## CASE STUDY 1: ANALYSIS OF PERFLUOROCTANE SULPHONIC ACID (PFOS) IN HISTORICAL EEL SAMPLES FROM THE RHINE

Although PFCs have been used for many applications since the 1950s, it is only in recent years that their environmental relevance has become apparent. Meanwhile the persistent, bioaccumulative and toxic potential of several PFCs has been proven.

Kwadijk et al. (2010) investigated the occurrence of PFCs including perfluorooctane sulphonic acid (PFOS) in eel (*Anguilla anguilla*) and other matrices collected from several locations in The Netherlands. Eels were caught using electric fishing. For each site, filets from 30 individuals with a length of 30–45 cm were randomly selected and homogenised using a stainless steel blender. Samples were then stored at -20 °C until analysis. For the locations Lobith on the river Rhine and two inland lakes (Hollands Diep and Haringvliet East) historical eel tissue samples were available which were collected from 1978 onward for monitoring purposes (only since 1990 for Haringvliet East). Thus time series spanning up to 30 years could now be measured for PFOS levels for these locations. PFOS levels were quite comparable for eel from the Rhine site (27–120 ng/g wet weight, ww) and from Haringvliet East (43–93 ng/g ww), but lower for eel from the third site (Hollands Diep: 5.9–42 ng/g ww).

The authors found a statistically significant upward trend in PFOS concentration at Lobith between 1978 and 1991 ( $p < 0.005$ ;  $n = 14$ ). The highest values were detected in the samples from 1988 and 1991. From 1999 on, a decreasing trend of PFOS levels in eel was detected ( $p < 0.0005$ ;  $n = 8$ ). The current levels of the Rhine eel are quite comparable to those from the beginning of the time series in 1978. In contrast to the first period for the Rhine site, no significant trend was detected in eel from Hollands Diep for the period 1979–1994. However, a downward trend comparable to that observed at the Rhine site was also observed for nearly the complete time series available for the Haringvliet East site (period 1991–2006;  $p < 0.03$ ;  $n = 14$ ). Summarising, the retrospective analysis revealed that PFOS concentrations increased by factors of 2–4 until the mid-1990s, followed by a decrease to the levels at the start of the time series. The authors comment that this concentration pattern now

detected for The Netherlands was also reported for PFC in biota from other industrialised countries. However, interestingly the declining trend started before the PFOS phase-out by 3M became fully effective (2002).

If a correlation to consumption patterns is assumed, possible explanations for the declining trend could be that emissions were reduced more efficiently or industry started to substitute PFOS and its precursor compounds even before the production stop became effective. Paul et al. (2009) reported that the global production was highest and quite constant in the period 1990–2002 (based on production of the precursor compound POSF), and that it dropped by about 80% after 3M's production stop became effective in 2002.

## CASE STUDY 2: LEVELS OF PERFLUORINATED COMPOUNDS (PFC) IN HERRING GULL EGGS FROM GERMAN COASTAL WATERS

Retrospective monitoring was performed to assess concentration trends of PFCs in marine biota from the German Environmental Specimen Bank (ESB). Archived annual pool samples of eggs of herring gull (*Larus argentatus*) covering the periods 1988–2008 (North Sea; Trischen and Mellum islands) and 1991–2008 (Baltic Sea; Heuwiese island) were analysed for a set of PFCs (Rüdel et al. 2010). The sampling sites are located in National Parks, but Mellum is influenced by the estuary of the river Weser and Trischen by the estuary of the river Elbe. The Baltic Sea island Heuwiese, on the other hand, is in a quite pristine region with negligible anthropogenic impacts. The water exchange with the open Baltic Sea is also reduced by surrounding islands. Correspondingly, North Sea eggs had higher PFC concentrations than Baltic Sea eggs in most years. Compounds detected with highest levels were perfluorooctane sulphonate (PFOS) and perfluorooctanoate (PFOA). The median values for PFOS in herring gull eggs were about 70 ng/g ww and 80 ng/g ww for the North Sea sites Mellum and Trischen, respectively, and 60 ng/g ww for the Baltic Sea site. However, while the PFOS time series for North Sea eggs showed varying concentrations with highest values between about 1993 and 2002, Baltic Sea eggs revealed a significant increasing trend from about 20 ng/g ww in 1991 to about 160 ng/g ww in 2008. Thus concentration differences for PFOS between North Sea and Baltic Sea eggs diminished in the later years. Eggs from Heuwiese had lower PFOA levels (mostly in the range of the limit of quantification of 0.5 ng/g wet weight, ww) than North Sea eggs which, in some years in particular, showed quite high concentrations (median PFOA values: about 10 ng/g ww; maximum concentrations up to 120 ng/g ww). As well as PFOS and PFOA, the C7-, C10- and C11-perfluorinated acids and the C6- and C7-sulphonic acids were found at low concentrations in the herring gull eggs. The authors conclude that the voluntary cease in production of PFOS and respective precursor substances declared by 3M by 2002 is not mirrored so far in continuously decreasing PFOS concentrations in wildlife. It seems that the situation may be different at specific sites, as the increasing PFOS levels in the herring gull eggs sampled from the Baltic Sea island Heuwiese reveal.

Generally, a delay of several years can be expected between concentration trends in freshwater and marine biota (compare PFC maximum for PFC in freshwater fish in the study by Kwadijk et al. 2010).

### CASE STUDY 3: ANALYSIS OF HEXABROMOCYCLODODECANE (HBCD) IN HERRING GULL EGG SAMPLES FROM GERMAN COASTAL WATERS

Hexabromocyclododecane (HBCD) is a brominated flame retardant applied mainly in extruded and expanded polystyrene foams which are used as thermal insulation in the building industry. In 2001, the estimated annual HBCD demand in Europe was 9500 tons (no current usage data available). During recent years, emissions control programmes have been implemented by the HBCD industry in order to reduce potential environmental burdens from production and processing.

The German Federal Environment Agency initiated a retrospective monitoring study for HBCD with archived samples from the German ESB (Esslinger et al. 2010). The aim was to determine the trend of HBCD burden in the marine environment over a 20-year period. For this purpose pooled annual samples of whole eggs of herring gulls (*Larus argentatus*) were applied. Eggs had been collected between 1988 and 2008 from three islands in the North and Baltic Seas. They were analysed for three diastereomers of HBCD (alpha-, beta- and gamma-HBCD).

Analyses were performed by HPLC-MS/MS analysis with electrospray negative ionisation after enantiomer-specific separation on a chiral column. As in most biomonitoring studies, alpha-HBCD diastereomers were predominant in all eggs investigated, although the technical product consists mainly of gamma-HBCD. For all eggs, so-called enantiomer fractions (EF) for alpha-HBCD showed a significant deviation from the racemic mixture (EF 0.34–0.48 instead of 0.5 for the racemic mixture of both enantiomers). For eggs from the Baltic Sea island Heuwiese, the EF values were higher than those for eggs from both North Sea sites. The determined contents of total HBCD (sum of all three diastereomers) were in the range 13.8–74.8 ng/g lipid weight (lw) and 4.17–107 ng/g lw for eggs from the two North Sea islands and between 25.1 and 98.7 ng/g lw for the eggs from the Baltic Sea island. At all sites an increase of HBCD levels was observed until about 2000. Afterwards, levels decreased significantly (e.g., by about 60 percent for the gull eggs from the Baltic Sea site). For the Trischen North Sea site (influenced by the Elbe estuary) HBCD concentrations of eggs in 2008 were in the same range as in the period 1988–1994. The corresponding decrease at the Mellum site in the western part of the North Sea was delayed; it took until 2008 for HBCD egg burdens to decrease to levels of about 50 % of the peak concentration measured in the year 2000.

The observed declining HBCD burdens may be regarded as a result of the implemented emission control measures for HBCD production plants or of a reduced use of this flame retardant in recent years.

#### OUTLOOK

The presented studies are examples of how ESBs can contribute exposure data for the risk assessment of emerging substances (e.g. for the assessment under REACH or the Stockholm Convention on

POPs). An additional impetus to use ESB data for this purpose may come from the further implementation of the Global Monitoring Plan under the Stockholm Convention. In the revision of the Guidance for a Global Monitoring Programme (current version: UNEP 2004), specimen banking will be covered in more detail in a separate chapter (based on Decision SC-4/31 of the Conference of the Parties; UNEP 2010).

Even in the current version of the UNEP Guidance it is recommended to store the remaining homogenised tissue samples after analysis to permit retrospective analyses for the later determination of environmental trends and other purposes. Although environmental specimen banks are currently established mainly in developed countries, developing countries may also use ESBs as monitoring tools in future. A symposium on this topic was held at Ehime University in Matsuyama (Japan) in December 2009. The symposium proceedings with selected papers from the meeting are available online (Isobe et al., 2010).

The potential use of ESBs for the risk management of chemicals in Europe was the topic of a recent workshop. In collaboration with NORMAN, the German Environmental Agency organised a first Conference on European Environmental Specimen Banks which was held in Berlin in June 2010.

About 70 participants from European ESBs, EU institutions of chemical safety management, EU Member State government bodies and other interested parties joined the meeting. The scientific programme of the workshop included presentations on the EU ESB programmes from different views (geographic: north, central and south Europe; ecosystems: marine, limnetic, terrestrial). Further contributions reviewed different aspects of European ESBs in the context of chemical safety management. Results from studies of emerging substances were also presented as posters.

Finally, the potential for harmonisation between ESBs was explored in two discussion groups. These sessions covered the questions “What chemical?” and “What specimen?”. The final discussion also covered the possible co-operation of NORMAN with ESBs. Most participants agreed that the retrospective analysis of chemicals in archived samples can yield important information on the exposure of wildlife to potential emerging substances. These data may also be used to identify a compound as emerging substance (e.g., if environmental concentrations increase).

For broader usage of such data it would be helpful to add results from such studies to the NORMAN EMPDAT database. On the other hand, NORMAN could give input to ESBs on compounds relevant for monitoring. For example, the results of the NORMAN activity on prioritisation of emerging substances will be helpful for ESBs to identify new target compounds. The participants recommended that a proposal on future co-operation should be drawn up by a working group.

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## Current concerns related to wastewater reuse and xenobiotics

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### XENOBIOTICS AND WASTEWATER UTILISATION

The need for additional water sources due to the intense drought periods in many regions of the world is apparent and wastewater utilisation for irrigation or the replenishment of water bodies is now standard practice in various countries.

Wastewater treatment and reuse has been the focus of numerous studies whose main objective has been the establishment of quality criteria for reuse taking mainly into consideration conventional pollution parameters such as Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD), pH, total suspended solids, heavy metals and the microbiological load. During the last fifteen years though, chemicals have become a major concern, and the number of parameters that need to be evaluated for the safe reuse of wastewater has increased.

The wide range of micropollutants persisting in sewage after conventional treatment includes inorganic compounds, heavy metals, endocrine disrupting compounds, pharmaceutically active compounds, disinfection by-products and many other complex organic compounds. In the list of compounds that can persist, nanoparticles cannot be excluded, at least on the basis of what is currently known. The release of heavy metal-containing nanoparticles into the environment through wastewater reuse applications may be harmful to the efficacy of beneficial microbes that function in element cycling, pollutant degradation and plant growth. Nanoparticles of Ag, CuO and ZnO are of interest as antimicrobials against pathogenic bacteria. Gajjar et al. (2009) for example, have demonstrated their antimicrobial activity against the beneficial soil microbe, *Pseudomonas putida* KT2440. However, there is still a big gap in knowledge of the behaviour of nanoparticles during wastewater treatment, and this topic will not be dealt further within this brief review.

### RELEVANT REGULATIONS AND LIMITS, AND THE NEED FOR RISK ASSESSMENT

Many of the above-mentioned compounds are known or suspected causes of effects adverse to human health and/or the environment. As Bolong et al. (2009) mention, the industrial and technological advances in the production of chemicals have outpaced regulatory practices. A major concern is the absence of limit regulations, especially for new compounds, as related to water and wastewater treatment. One example

of the few actions that have been taken by the European Commission, related to the development of strategies to deal with endocrine disrupting compounds, is the amendment of the European Community Directive on Risk Assessment and Directive on the classification of dangerous substances (Europa, 2006). In the US, the FDA requires ecological testing and evaluation of pharmaceuticals when environmental concentration exceeds 1 µg/L (Snyder et al., 2003).

This small sample of regulatory practices indicates that there is no coordinated ordinance that is accepted by the global community. Furthermore, limits on pharmaceuticals and personal care products (PPCPs), and other recently detected compounds have not yet been determined for water and wastewater treatment criteria. Environmental Risk Assessment (ERA) has been used in recent years to evaluate risks from chemical pollutants, but the focus has primarily been on the risk to the aquatic compartment (e.g., Water Framework Directive). For risks to the terrestrial compartment, some ERA studies have included risks to the soil compartment due to applying wastewater sludge to soil (Lindberg et al., 2007). In addition, the release of pharmaceutical compounds through wastewater releases is to some extent dealt with by the EMEA guidelines, since these are concerned with the release to the environment of medicinal products for human use (EMEA, 2006). According to the latter, the terrestrial environmental fate and effects analysis for medicinal products is required within Tier B - Phase II. However, in general, environmental risks from organic micropollutants to the soil compartment have been much less studied. As for wastewater irrigation, there is a general lack of knowledge in relation to the associated environmental risks. In addition there is a methodological gap in ERA of wastewater irrigation, since guidelines (E.C., 2003) consider only two possible routes for pollutants to enter the soil compartment (i.e. aerial deposition and application of wastewater sludge).

### WASTEWATER REUSE FOR IRRIGATION AND IMPACTS ON SOIL AND PLANTS

The use of reclaimed wastewater for irrigation is an important route for the introduction of xenobiotic compounds into the environment. There are a number of studies, for example, indicating that pharmaceutical residues that are adsorbed to soil may be taken up by plants. In laboratory experiments it has been demonstrated that the uptake of sulphadimethoxin in sorghum, pea and corn influence their development. Hydroponic culture plants incorporated sulphamide up to a final concentration of 180 to 2000 mg/kg. Roots of corn and sorghum accumulated much more active ingredients than the shoots. Similar results were obtained for rye, carrot, corn, sorghum and pea in field trials. Enrofloxacin was also accumulated in µg/g amounts (Schneider, 2008).

Plant uptake of pharmaceuticals may also influence plant development. It is in part not clear whether the negative effects on plants originate

from the direct damage to the plant by the pharmaceuticals themselves or the antimicrobial action of pharmaceuticals on soil microorganisms is responsible for the damage by affecting the plant–microorganism symbiosis (Chander et al., 2005). The latter is attributed to the fact that antibiotics in the soil may influence plant development indirectly by disrupting soil communities: the decay in the number of soil bacteria leads to a lack of feed for soil fauna (protozoa, nematodes, micro arthropods) and finally influences soil functions: plant residues are decomposed more slowly, denitrification is slower, and therefore nutrients are recycled more slowly (Migliore et al., 1998). Risk assessment for the uptake of pharmaceuticals in edible portions of crops suggests that with the allergenic potential and long-term effects of antibiotics, the risk cannot be neglected (Kumar et al., 2005).

In a study by Chefetz et al. (2008), the mobility and sorption–desorption behavior of carbamazepine, naproxen and diclofenac were studied in soil layers sampled from a plot irrigated with both freshwater and secondary-treated wastewater (STWW). Carbamazepine and diclofenac were significantly retarded in the 0–5 cm soil sample rich in soil organic matter (OM). Carbamazepine was not affected by the water type (freshwater versus STWW), whereas diclofenac exhibited a higher retardation factor in the freshwater system. Naproxen exhibited significantly lower retardation factors than diclofenac but with a similar trend, i.e. higher retardation in the freshwater versus STWW system. In the 5–15 cm soil sample containing low OM, naproxen was highly mobile while carbamazepine and diclofenac were still retarded. In the 15–25 cm sample, all compounds exhibited their lowest retardation factors.

Sorption data suggested that OM governs the studied pharmaceuticals' interactions with the soil samples. However, higher carbon-normalised sorption coefficients were measured for the pharmaceuticals in the 15–25 cm sample, suggesting that both quantity and the physico-chemical nature of OM affect sorption interactions. This study suggests that carbamazepine and diclofenac can be classified as slow-mobile compounds in OM-rich soil layers. When these compounds pass this layer and/or are introduced into OM-poor soils, their mobility increases significantly. This emphasises the potential transport of pharmaceuticals to groundwater due to intensive irrigation with reclaimed wastewater in OM-poor soils.

In a study performed by Kong et al. (2007), a series of experiments were conducted in a hydroponic system to investigate the uptake of oxytetracycline (OTC) and its toxicity to alfalfa (*Medicago sativa* L.). OTC inhibited alfalfa shoot and root growth by up to 61 % and 85 %, respectively.

The beneficial symbiotic relationship between most plant species and arbuscular mycorrhizal fungi is a primary determinant of plant health and soil fertility. There is therefore increasing recognition of the need to study the impacts of anthropogenic stressors on plant–microbe interactions in soil ecotoxicology studies and risk assessment. A case study exploring the use of root-organ cultures to evaluate the effects of 12 common veterinary and human-use pharmaceuticals on the arbuscular mycorrhizal fungus, *Glomus intraradices*, grown on *Daucus carota* root-organ cultures is presented. The bioassays were conducted over a 28-day exposure period at concentrations up to 1000 µg/L. Root length and the fungal endpoints of hyphal growth and spore production were evaluated weekly during the study. Sulphamethoxazole and atorvastatin were the most phytotoxic compounds with EC<sub>50</sub> values of 45 µg/L and 65 µg/L, respectively.

Three compounds exhibited selective mycotoxicity, whereby the fungal symbiont was adversely affected at concentrations significantly less than that calculated for root length. The EC<sub>50</sub> for *G. intraradices* hyphal length was 45 µg/L for doxycycline, while carbamazepine and 17- $\alpha$ -ethynylestradiol targeted spore production with EC<sub>50</sub> values of 113 and 116 µg/L, respectively. The assay results indicated that the root lengths responded quickly to the presence of phytotoxic pharmaceuticals in the culture medium. Hyphal length was found to be a sensitive endpoint after 21 days' exposure, while spore production required 28 days' exposure before significant differences could be detected.

The phytotoxicity of enrofloxacin on crop plants *Cucumis sativus*, *Lactuca sativa*, *Phaseolus vulgaris* and *Raphanus sativus* was determined in a laboratory model where the effect of 50, 100 and 5000 µg/L was evaluated after 30 days' exposure by measuring post-germinative growth of primary root, hypocotyl, cotyledons and leaves by Migliore et al., (2003). Concentrations between 50 and 5000 µg/L induced both toxic effect and hormesis in plants, by significantly modifying both length of primary root, hypocotyl, cotyledons and the number/length of leaves. A toxic effect was induced by high concentration (5000 µg/L), while hormesis occurred at low concentrations (50 and 100 µg/L). A continuum between toxic effect and hormesis was found in the four plant species. Both toxic effect and hormesis could be related to an efficient plant drug uptake, in the order of µg/L. Plants were able to metabolise enrofloxacin into ciprofloxacin, as also happens in animals; *Cucumis*, *Lactuca* and *Phaseolus* biologically converted about one quarter of stored enrofloxacin. Phytotoxicity of enrofloxacin on plants generates both toxic effect and hormesis, related to plant drug uptake. Enrofloxacin, and its metabolite ciprofloxacin, as terrestrial environment contaminants must be monitored due to the high risk associated with their presence. The possible effects of this hitherto unconsidered cause of contamination include not only toxicity and selection of resistant strains, as happens with other antibiotics, but also damage to the genetic structure of non-target populations.

An example of the accumulation of phthalate esters in agricultural soil is provided by a thorough study made by Zeng et al., (2008) that concerns the evaluation of the existence of such compounds in land irrigated by wastewater in China. In many peri-urban areas of Southeast Asia, land use has been transformed from rice-based to more profitable vegetable-based systems. Phthalates were detected in all soil samples in this study with the concentrations ranging from 0.195 to 33.6 µg/g dw, mainly originating from sewage and industrial wastewater irrigation and sewage sludge application. However, excessive accumulation of such compounds in agricultural soils may not only result in environmental contamination as mentioned in the study, but also lead to elevated phthalates uptake by crops, which may affect food quality and safety.

The residues of polynuclear aromatic hydrocarbons, polychlorinated biphenyls, chlorinated benzenes and phenols were investigated in soil, wastewater, groundwater and plants in a study undertaken by Al Nasir and Batarseh, (2008). The uptake concentration of these compounds was comparatively assessed using various plant types including *Zea mays* L., *Helianthus annuus* L., *Capsicum annum* L., *Abelmoschus esculentus* L., *Solanum melongena* L. and *Lycopersicon esculentum* L. which were grown in a pilot site established at Mutah University wastewater treatment plant, Jordan. The concentration levels of all targeted compounds (such as naphthalene, acenaphthylene, acenaphthene, fluorine, phnanthrene, anthracene, pyrene, chrysene, o-cresol, p-cresol, 2,4-dim, 2,6-dichl, 2,3,5-trichlo, 2,3,4,6-tetrachloro, etc) found in soil irrigated with wastewater were much higher than for the reference site, indicating a source of contamination due to irrigation with wastewater. The different plant types showed different uptake concentrations of various organic compounds. Roots were found to be the most contaminated plant part, while fruits were found to be the least contaminated. Generally, organic pollutants might be transferred from the soil irrigated with wastewater to different plant parts. The uptake ratios are dependent on the plant type and the physico-chemical properties of organic compounds.

## WASTEWATER REUSE AND RELEASE OF ANTIBIOTIC-RESISTANT GENES IN THE ENVIRONMENT

The introduction of antibiotics into the environment via wastewater discharges and/or reuse applications is of particular interest because exposure of virulent bacteria to antibiotic residues could induce resistance (Chee-Sandford et al., 2001). It is known that the activated sludge system of wastewater treatment plants could be referred to as a genetic reactor where bacterial organisms from many different individuals have the opportunity to mix and genetically react. Moreover, the soil, surface and ground water environments also constitute genetic reactors, where the bacterial organisms originating from the wastewater treatment plants mix and counteract with environmental organisms (Baquero et al., 2008).

Antibiotic-resistant bacteria may be released directly into wastewater systems from patients medicated by antibiotics and may consequently be released into the environment through wastewater reuse schemes and/or disposal. Resistance can also be acquired through horizontal gene transfer through the uptake of resistance determinants via conjugation, transduction and transformation and therefore be spread beyond the habitat of the original hosts (Zhang et al., 2009). Both human and animal health control measures are at risk if pathogens cease to be treatable with antibiotics. During recent years, evidence has accumulated that exposure to antibiotics has brought about the resistance of bacteria in the environment.

Recently, antibiotic-resistant bacteria including *S. aureus* A1 mecAr and *E. Cloacae* A10 ampCr were taxonomically identified in hospital wastewater (Volkman et al., 2004). This is of particular importance since there are cases where hospital wastewater is used for irrigation as well. Antibiotic-resistant genes, within microbes or as naked DNA bound to clay particles, were found to persist in environmental compartments affected by urban or agricultural activity, such as river sediments, dairy lagoons, wastewater effluent and water treatment plants (Pruden et al., 2006). However, further understanding of how resistance is acquired and maintained in bacterial populations is needed before a link can be made between the presence of antibiotics in the environment and antibiotic resistance.

Zhang et al. (2009) recently reported on the impact of the wastewater treatment process on the prevalence of antibiotic resistance in *Acinetobacter* spp. and the possible spread of antibiotic resistance from wastewater treatment plants to their receiving water bodies and consequently, if wastewater is used for irrigation, to the general environment. Samples were taken from a treatment plant receiving domestic wastewater and limited amounts of industrial waste, with hospital wastewater comprising a very small percentage of the total flow. What they found is that the prevalence of antibiotic resistance was significantly higher downstream than upstream of the treatment plant. However, other studies gave con-

tradictory results and this divergence can be attributed to factors affecting the efficiency of removal of resistant bacteria at different plants (e.g. initial composition of sewage, type of treatment, plant operation, etc.), or differences in the materials and methods used for the assessment of antimicrobial resistance (e.g. type of medium, definition of the breakpoint value, etc) (Guardabassi et al., 2002).

Monitoring of the propagation pathways of the antibiotic-resistant bacteria and assessment of the environmental compartments with respect to their states of antibiotic resistance is certainly needed. This is the objective of the new European Cost Action TD0803 under the title, 'Detecting evolutionary hotspots of antibiotic resistances in Europe (DARE)'. The reduction of the introduction of antibiotic contamination requires the implementation of methods for wastewater treatment capable of removing these compounds.

## CONCLUSIONS

There are currently several gaps in knowledge of: the potential effects of wastewater reuse practices; identification of the compounds present in treated effluent organic matter; degradation mechanisms; and transformation products. Moreover, questions are only now being focused on: the risks associated with non-target organisms in the environment; plant and crop uptake; and the fate and behaviour of various compounds in mixtures. Furthermore, knowledge is greatly lacking on the possibilities of pharmaceutical residues reaching humans through biomagnification in the food chain. Risk assessment protocols for antibiotics and resistant bacteria in water systems, based on better systems for antibiotics detection and antibiotic resistance microbial source tracking are also starting to be discussed.

In conclusion, whilst wastewater reuse brings a number of benefits to water balances and management, it also raises a number of questions. Intense research effort must therefore be devoted to this area, so as to secure human health and the ecological systems.

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## Futher reading

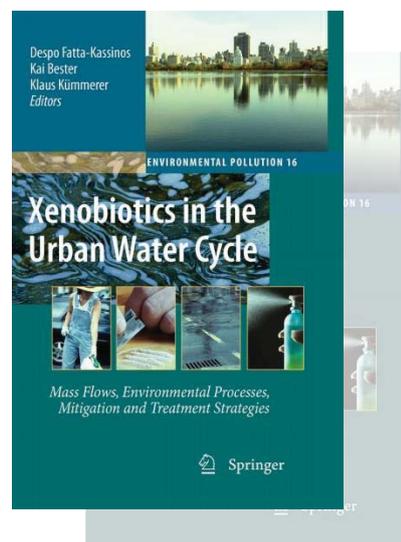
### XENOBIOTICS IN THE URBAN WATER CYCLE- MASS FLOWS, ENVIRONMENTAL PROCESSES, MITIGATION AND TREATMENT STRATEGIES

**Springer Environmental Series: Environmental Pollution, Vol. 16.**  
**Fatta-Kassinos, Despo; Bester, Kai; Kümmerer, Klaus (Eds.). 1st Edition., 2010, XIV, 507 p., ISBN: 978-90-481-3508-0.**

The book examines compounds that have only recently been investigated – such as illicit drugs, scents and toxins – and stimulates the discussion of the causes of, and solutions to, the problem by including 25 chapters written by international experts. The presence of xenobiotics in the aquatic environment is seen as one of the biggest challenges for a sustainable water future. There is therefore a need to understand, in an integrated manner, the sources, flow paths, fate and effects of xenobiotics in the urban water cycle. This book is an authoritative and comprehensive reference source covering:

- Occurrence, sources and fluxes of xenobiotics in urban waters
- Processes concerning the fate and transport of xenobiotics, mass flows and transformation products
- Mitigation, treatment methods and systems for the removal of xenobiotics
- Risk assessment methodologies and risk management
- Information on source control and mitigation measures.

The book contains a wealth of information on some of the compounds most frequently found in urban water systems, and of special interest will be the chapters dealing with compounds that have only recently been investigated, such as illicit drugs, scents, and toxins.



# Organophosphorus flame retardants

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Because of their persistent nature and toxicity, some brominated flame retardants (BFRs), such as pentabromo diphenyl ether, applied in a wide range of commercial products, are restricted in use or are being phased out. As a result, the search for and use of alternative flame retardants (FRs) is increasing, and alternatives based on e.g. metal-, phosphorus- and nitrogen-based compounds are currently on the market.

Phosphorus FRs have been used for over 150 years, and can be divided into three main groups: inorganic, organic and halogen-containing FRs. The organophosphate esters (OPFRs) have been since the 1960s, mainly in polymers, where the halogenated OPFRs are mainly applied as a flame retardant, and the non-halogenated compounds as a plasticiser. Some OPFRs are listed as high-production-volume chemicals, and were found in the environment in the '80s (Muir et al., 1981, 1983). Since the late '90s much more attention has been given to these compounds, as they were found at high levels in indoor environments (Carlsson et al., 1997; Marklund et al., 2003; Stapleton et al., 2009; Covaci et al., 2011), and some are on the list for risk assessment by the European Union. Certain OPFRs are carcinogenic or potentially carcinogenic, genotoxic or neurotoxic, and have high toxicity. Persistency varies widely within the group of OPFRs, but several are persistent in the abiotic environment.

Occurrence data are mainly restricted to TPP (triphenyl phosphate), TCEP (tris(2-chloroethyl)phosphate), TDCPP (1,3-dichloro-2-propyl phosphate), and TCPP (tris(chloropropyl)phosphate). These compounds are found in air, water, snow and sediment (Marklund et al., 2003, 2005, 2010). In an effect-directed analysis (EDA) study of sediment from the Scheldt river basin, TCPP and TEHP were found as possible key-pollutants, but they exhibited weak-to-moderate anti-androgenic activity in an in vitro assay (Weiss et al. 2011). Recent data in biota showed that TPP and TCPP were found in fish and mussels from Swedish lakes in

concentrations from 21–180 and 170–770 ng/g, respectively (Marklund et al., 2010). OPFRs were found both in background locations and near emission sources.

Sources of OPFRs are sewage treatment plants, traffic and airports. TPP and TCPP have been linked to traffic, where it is assumed that TPP leakage from motor oils, and TCPP was related to the ventilation systems of cars by emission from the car interior (Marklund et al., 2005). Another compound, tributyl phosphate (TBP) was linked to aircraft hydraulic fluids, as high levels of TBP were found in a motor oil and in snow collected at airports (Marklund et al., 2005).

It is assumed that sewage treatment plants are a main source of OPFRs for rivers. Various compounds, TCPP, TCEP, TPB, TPP, TDCP (tris-(2-chloro-, 1-chloromethyl-ethyl)-phosphate), and TBEP (tris-(butoxyethyl)-phosphate), have been found in STP effluents in concentrations up to 500 ng/L (Andresen et al., 2004; Martinez-Carballo et al., 2007). Large variations in elimination rates from STPs (Ruhr/Rhine area) were found, ranging from 57 to 86 % for TBP and TBEP, and incomplete elimination of TCPP, TDCP and TCEP (Meyer and Bester, 2004). Aeration of the STP water was the major treatment step to remove the non-halogenated OPFRs.

TCPP, TDCPP, TPP, TBP, and TBEP are the most abundant OPFRs in indoor dust, and concentrations are in the µg/g range (Stapleton et al., 2009; Van den Eede, 2011). In a Belgian study, the levels of OPFRs were found to be at least 20 to 30 times higher than PBDEs and HBCD, and estimated exposure from dust ingestion ranged from <1 to 50 ng/kg body weight for adults and toddlers (Van den Eede, 2011). The exposure scenarios showed that the body burdens were 100 to 1000 times below the reference values, although for a high dust ingestion for toddlers the intake was only 5 times below the RfD.

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# Position Paper on Passive Sampling of Emerging Pollutants in the Aquatic Environment: State of the Art and Perspectives

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## EXECUTIVE SUMMARY

Passive samplers represent an innovative monitoring tool for the time-integrated measurement of bioavailable contaminants in water and sediment. Passive sampling technology is proving to be a reliable, robust and cost-effective tool that could be used in monitoring programmes across Europe. These devices are now being considered as part of an emerging strategy for monitoring a range of priority and emerging pollutants.

Passive sampling is based on the deployment in situ, or use in the laboratory, of non-mechanical devices of simple construction capable of accumulating contaminants dissolved in water or sediment pore water. Such accumulation occurs via diffusion, typically over periods of days to weeks. Contaminants accumulated in exposed samplers are subsequently extracted and their concentration levels measured, allowing the quantification of time-weighted average (TWA) concentrations in water or equilibrium pore water concentrations in sediment. These devices can be deployed in most aquatic conditions (fresh and saline) and associated water treatment facilities, thus making them ideal for monitoring across the entire water cycle and even in remote areas with minimal infrastructure. Passive sampling can also be employed in batch sediment extractions to provide estimates of contaminant concentrations in pore water or assessment of bioavailable concentrations of contaminants in sediment.

In 2009, the NORMAN association organised a meeting of experts in the field of passive sampling. As a result of this meeting a position paper was produced, which reflects the view of the experts on the topic of passive sampling and its application in the monitoring of emerging pollutants in the aquatic environment and indicates future research and development needs in this area.

The position paper discusses functional principles of passive samplers and problems associated with the effects of environmental variables (temperature, water turbulence and sampler fouling) on their performance. Further, it lists the established or expected/potential performance of passive samplers for monitoring of the most discussed groups of emerging substances (such as cyanobacterial toxins, antifouling agents, brominated flame retardants, endocrine disrupting compounds, fluorinated surfactants, organosiloxanes, pharmaceuticals, polar pesticides, sunscreen filters etc.) and availability of calibration data that enable estimation of TWA concentrations. The document also shows the applicability of the passive sampling concept in risk-oriented monitoring of emerging substances in sediments and in determination of the bioaccumulative exposure of organisms. The great potential of this technology in combination with toxicological assays

to determine the biological relevance of mixtures of toxicants with specific modes of action, and present at low concentrations, is also demonstrated.

If passive sampling is to become accepted and used in a regulatory context for monitoring water quality across Europe, then there is a need for the development of improved validation methods and setting-up of the appropriate quality control and quality assurance schemes for the technology. Successful demonstration of the performance of passive samplers alongside conventional sampling schemes, and inter-laboratory studies that demonstrate reproducibility of data produced by different designs of passive samplers, are urgently needed to facilitate the acceptance of passive sampling in routine regulatory monitoring programmes in the future.



# Workshop on Engineered Nanoparticles in the Environment : Analysis, Occurrence and Impacts

19-20 October 2010, Koblenz, Germany

Organisers: Thomas Ternes (BfG, D), Carsten Prasse (BfG, D) and Corinna Brinkmann (BfG, D)

## INTRODUCTION

Nanotechnology has become an important part of our everyday life, and nanoparticles, i.e. particles with dimensions smaller than 100 nm, are already used today in a large number of consumer products such as personal care products, clothing and sports equipment. Furthermore, their use and application is expected to strongly increase with nanotechnology being one of the most promising future technologies. However, there are still many uncertainties about the potential adverse effects of nanoparticles, especially when considering that these particles, owing to their size, even have the potential to penetrate into living cells or to cross the blood-brain barrier. There are also still major gaps in our current knowledge of their environmental behaviour. Because they are produced in such large quantities (~2 million tonnes of TiO<sub>2</sub> in 2009) and applied so widely, nanoparticles are discussed as a new emerging group of environmental pollutants.

The NORMAN workshop "Engineered Nanoparticles in the Environment – Analysis, Occurrence and Impacts" addressed, amongst others, issues related to analytical techniques for nanoparticles in environmental matrices, the fate of engineered nanoparticles in the aquatic environment and during wastewater treatment, their interactions with inorganic and organic pollutants, and their potential ecotoxicological impacts on biota. The main objective of the meeting was to discuss and evaluate the future requirements with regard to a profound environmental assessment of engineered nanoparticles.

The following central questions were discussed during the workshop.

## ANALYSIS: ARE THERE APPROPRIATE ANALYTICAL METHODS FOR ENVIRONMENTAL MATRICES?

For specific questions appropriate analytical methods are available, especially for laboratory systems with a limited number of substances. However, for complex environmental matrices with high quantities of natural particles it is still a challenge, and comprehensive methods to quantify engineered nanoparticles (ENPs) are lacking to date. It is therefore absolutely crucial to use several independent analytical methods for the determination of ENPs in the environment. However, there is still an enormous need for concepts and analytical developments to enable the determination of ENPs in environmental matrices.

## BEHAVIOUR OF ENPS IN THE ENVIRONMENT: TO WHAT EXTENT ARE THEY MODIFIED IN THE ENVIRONMENT? DO THEY PASS "NATURAL AND TECHNICAL" BARRIERS?

ENPs discharged into the environment are already modified by chemical, physical and biological processes. For instance, ENPs tend to agglomerate with each other and with naturally occurring particles, forming particles with larger sizes in the µm- or even in the mm-range. Furthermore, chemical processes such as oxidation or hydrolysis are likely to alter their surfaces, which have been specifically designed for certain applications. Others may completely dissolve and precipitate again as is the case for Ag<sub>0</sub>-ENPs which transform mainly into Ag<sub>2</sub>S. Finally, the formation of biofilms at the ENP surfaces might alter the properties of ENPs. The interaction with the surrounding media of the surface of the ENP, which can be functionalised at will, will largely control the fate of the ENP in the environment.

All these factors have to be considered when assessing and determining the potential of ENPs to pass natural barriers (e.g. hyporheic zones, soil) and technical barriers (e.g. bank filtration, wastewater treatment pro-

cesses). On the basis of current knowledge, the barriers are passed only under special conditions and to a limited extent. However, the knowledge gaps with respect to this topic are huge.

## POLLUTANT CARRIERS: ARE ENPS EXPECTED TO BE RELEVANT CARRIERS FOR INORGANIC/ORGANIC POLLUTANTS?

ENPs are prone to adsorb or absorb organic and inorganic pollutants because they have a large surface area in relation to their small sizes and because of their specific surface properties. But one crucial question for the relevance of ENPs as carriers for pollutants is whether the proportion of ENPs is high enough to compete as sorbent with natural particles which are already present in environmental samples. Preferential flow might have a major impact, although it is difficult to assess. On the other hand there are pollutants which might be sorbed to ENPs already during their application such as in sunscreens. Since the desorption of pollutants is frequently a rather slow process, ENPs might carry at least these pollutants, since during application the competition of other sorbents might be much lower than under environmental conditions.

## ECOTOXICITY: DO ENPS HAVE SEVERE IMPACTS ON BIOTA?

The number of ecotoxicological studies in the literature is increasing. However, the design of these studies is extremely challenging because of the rapid chemical, physical and biological modification of their surfaces, which might significantly differ between laboratory and environmental conditions. These modifications have a significant influence on the ecotoxicological results. Furthermore, there is frequently a lack of proper characterisation of nanoparticles, both before and during the tests applied. However, even though the knowledge gaps are much higher than the number of available studies, there are already a few scientifically sound ecotoxicological studies indicating that severe impacts are likely to occur. There is a crucial need to invest much more effort in the reproducibility and the validation of the results, as well as on the proper selection of test organisms and end points. Furthermore, it will be very challenging to transfer the results from lab-scale to environmentally relevant conditions. Also the size effect has to be investigated in greater detail: it is vital to assess whether the observed effects are caused by the size-related physico-chemical properties (e.g. higher specific surface area) or whether there is a real 'nano-effect' which cannot be explained just by the increased surface of the equivalent mass of smaller particles compared to larger ones.

## OVERALL CONCLUSIONS

In total, 70 participants from all over Europe and the USA attended the workshop. All participants agreed that a NORMAN working group on 'Nanoparticles in the aquatic environment' should be initiated, with regular meetings every year and an extended workshop every two years. The primary goal of this working group will be to design the future directions of research in the exciting and emerging field of the environmental impacts of nanoparticles on a European level.

# TransCon2010 Environmental Transformation of Organic Compounds: Towards a Joint Perspective on the Importance of Transformation Products as Environmental Contaminants

**12-17 September 2010, Ascona, Switzerland**

Organisers: Juliane Hollender (Eawag, CH), Kathrin Fenner (Eawag, CH), John Sumpter (Brunel University, UK)

Transformation products of organic contaminants formed in the environment might be – and in some cases are known to be – more persistent, bioaccumulative and/or toxic than their parent compounds. They are therefore considered an emerging issue in environmental chemistry and toxicology. Since consistent methodologies for their assessment are lacking, and environmental toxicology and chemistry data on transformation products are in most cases sparse, an international conference on the topic, TransCon2010, was convened at Monte Verità, Ascona, Switzerland, in September 2010. The conference brought together about 75 academic, regulatory and industry participants from different countries to develop a common understanding of how much transformation products contribute to the overall chemical risk in the environment and of how to deal with transformation products in chemical risk assessment and environmental quality assessment.

## DEFINING THE SCIENTIFIC STATE OF THE ART

In the opening keynote lecture John Sumpter (Brunel University) set the basis for discussing the importance of transformation products by pointing out that the overall goal of our research should be to protect the environment and that therefore our focus should be on those transformation products that are of most ecotoxicological concern. Over the course of the conference, several cases of known, problematic transformation products were presented, including well-known cases such as the transformation of DDT to its toxic and persistent transformation product DDE, but also some more recently discovered issues such as the photodegradation of triclosan to toxic products (Kris McNeill, ETH Zurich) or formation of drinking water disinfection by-products linked to carcinogenic effects in humans (Susan Richardson, U.S. EPA).

Sessions on Monday and Tuesday on analytical tools for the identification of transformation products, reconnaissance and field studies and laboratory-based studies on the chemical and biological formation of transformation products demonstrated that current research on transformation products is heavily focused on assessing exposure to transformation products. Specifically, analytical approaches to identify transformation products including high-resolution mass spectrometry, and 1- and 2-dimensional NMR techniques were pointed out by Thomas Ternes (BAFG). Juliane Hollender (Eawag) presented an overview of quantitative analyses of transformation products present in the aquatic environment in trace concentrations, thus demonstrating that highly sensitive and temporally and spatially resolved monitoring of transformation products is possible and ongoing at different institutions. Further, sessions on Wednesday discussed models to predict environmental exposure to transformation products (Kathrin Fenner, Eawag) and structure-based approaches to predict rates and pathways of different transformation processes (Gerrit Schüürmann, UFZ Leipzig), thus emphasising the diversity of ongoing exposure-related research. Presentations on attempts to predict biotransformation pathways of micropollutants were nicely contrasted by Perry McCarty's (Stanford University) historical perspective on microbial transformations of chlorinated solvents, which also enumerated some challenges in predicting these transformations considering general principles of microbiology.

Sessions on Thursday were dedicated to effect- and risk assessment and featured experimental and model-based approaches to assess ecotoxicological and human health effects of transformation products relative to their parent compounds (Beate Escher, University of Queensland). These sessions clearly demonstrated the large data gaps on the effect side, and also emphasised the uncertainties concerning transformation product data and the resulting difficulties in their inclusion in chemical risk assessment that regulatory authorities (Mark Bonnell, Environment Canada) and chemical and pharmaceutical industry (Jason Snape, Astra Zeneca) are confronted with. Finally, ongoing research on the transformation of nanoparticles in the environment was presented by Joel Pedersen (University of Wisconsin-Madison) and identified as another very complex scientific field that has only just started being investigated in a systematic manner.

## RESEARCH OPPORTUNITIES

Besides the keynotes and regular conference contributions as poster or platform presentations, there were four concurrently run workshops aimed at deepening the discussion on specific topics and particularly pointing out promising new research opportunities. The four groups addressed novel analytical tools, opportunities to predict transformation products and rates, effect assessment, and risk assessment of transformation products. They were chaired by Michael Radke (University of Bayreuth), Christian Zwiener (University of Tübingen), Martin Hansen (University of Copenhagen), and Carla Ng (ETH Zürich). The three most important visions that came out of the working groups were (i) establishing a closer link between exposure and effect assessment of transformation products through the concept of effect-driven transformation studies, (ii) a more extensive usage of a number of databases to develop tools that predict the probability and likely routes of chemical and biological transformations through co-operation of those who use the data (regulators), those who own it (industry) and the researchers developing the models, and (iii) developing methods to read across from existing experimental data on the parent compound to facilitate property prediction for the transformation products.

## ENFIRO project, Life Cycle Assessment of Environment-Compatible Flame Retardant – Prototypical Case Study

Co-ordinator: Pim Leonards  
Institute for Environmental Studies, VU University, de Boelelaan 1085m 1081 HV Amsterdam, The Netherlands  
<http://www.enfiro.eu>

Flame retardants are applied in a wide range of commercial products, such as electronics and plastics, to inhibit or resist the spread of fire. Owing to their persistent nature and their toxicity, some brominated flame retardants (BFRs), such as pentabromo-, octabromo-, and decabromodiphenyl ether, need to be substituted by non-toxic substitutes, and will be or are being phased out because of their environmental hazards. Less toxic alternative flame retardants appear to be available already, but comprehensive information on their possible toxicological effects, exposure and performance are often lacking.

The ENFIRO project is a research project that evaluates viable substitution options for a number of BFRs for better, safer alternatives. A practical approach is followed, based on the chemical substitution cycle (Fig. 1) in which the alternative flame retardants are evaluated regarding their environmental and toxicological properties, their flame retardant properties, and their influence on the function of products once incorporated.

The major objectives of ENFIRO are i) to deliver a comprehensive dataset on viability of production and application, environmental safety, and a life cycle assessment of the alternative flame retardants (FRs), and ii) to recommend certain flame retardant/product combinations for future study based on life cycle analysis (LCA), life cycle costing (LCC) and risk assessment studies. The project is financially supported by the EU in FP7 and a unique consortium of 12 partners from universities and industries/SMEs with extensive knowledge of a wide range of technologies in the fields of fire safety, environmental pollution analysis, chemistry, toxicology, end product requirements and socio-economy. It will produce results necessary for defining sustainable alternatives for BFRs.

The project carries out three levels of assessment by which the alternative FRs are compared to the BFRs:

- Hazard and exposure of the flame retardant
- Material performance (fire and application)
- Impact assessment of the product.

ENFIRO follows a two-phase strategy in which the first step is a prioritisation and selection of alternatives, followed by a broad screening to further select viable alternative FRs. The selection and prioritisation phase showed that only limited information exists on fire performance, toxicity, physico-chemical properties, exposure and economic aspects of alternative FRs. In total, 15 commercially available halogen-free FRs (HFFRs) were selected from the groups of inorganic, organophosphorus & salts, nitrogen, nanoclay, and intumescent FRs. These FRs cover five major applications: printed circuit boards, electronic components, injection-moulded products, textile coatings, intumescent paint.

In all studies the HFFRs are compared to TBBP-A, decabromo diphenyl ether, and brominated polystyrene. Currently, the screening studies of the HFFRs and BFRs are carried out on the fire performance, hazard characterisation and exposure. Based on these results, the second phase will further select 3 to 4 FR/product combinations to study in more detail the hazard, exposure, fire performance and technical applications. Finally, the results will be used to perform risk assessment, LCA, LCC and social life cycle assessment studies.

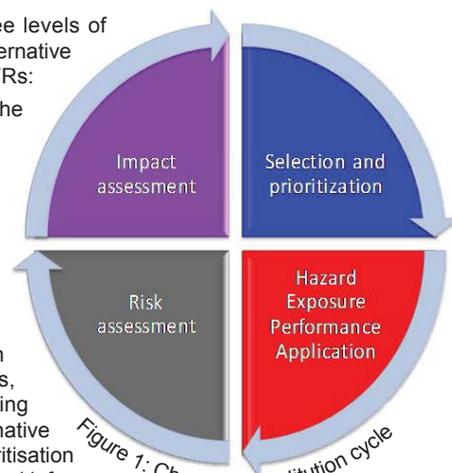


Figure 1: Chemical substitution cycle

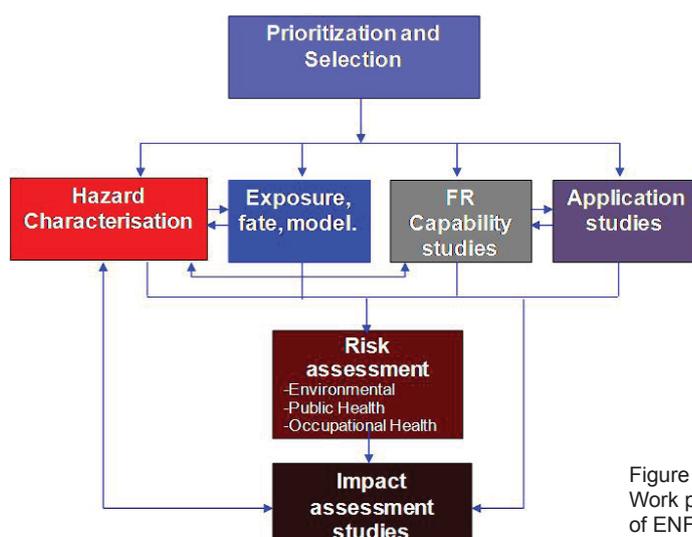


Figure 2:  
Work packages  
of ENFIRO

# PHARMAS project, Ecological and Human Health Risk Assessments of Antibiotics and Anti-cancer Drugs found in the Environment

## FP7-ENV-2010- ENV.2010.1.2.2-2

Project coordinator: J. Sumpster, Brunel University

Scientific coordinator: B. Roig, Ecole des Hautes Etudes en Santé Publique (EHESP)

In the PHARMAS project (a website will soon be available) a consortium of scientists from both academia and industry has been assembled to assess the risks to wild animals and humans posed by environmental exposure to pharmaceuticals.

Besides the coordinating institutes, members of the project consortium are: Goteborg University, Leuphana University, NERC, Institute for Environmental Studies, Radboud University, IVL Svenska Miljöinstitutet, ISOE, Ecologic, Armines, Danmarks Tekniske Universitet, Veolia, Environment Research and Innovation.

The project will concentrate on two classes of human pharmaceuticals, namely antibiotics and anti-cancer drugs, because there are good reasons for thinking that these could be of particular concern.

Among the main actions that will be performed:

- Human and animal exposure to pharmaceutical molecules will be assessed by measuring and modelling the concentrations found from the resource (mainly surface water) to the tap (drinking water)

- The missing data on ecotoxicological and toxicological thresholds of concern will be provided via the implementation of targeted ecotoxicological experiments and the compilation of all available literature, with a specific focus on the evaluation of adverse effects on embryos/newborns to determine whether they are more susceptible than adults to adverse effects of pharmaceuticals.
- The project will go beyond the typical substance-by-substance risk assessments by investigating the toxicity of realistic mixtures involving antibiotics and anti-cancer drugs in several dedicated case studies.
- PHARMAS will produce probabilistic estimates of the risk caused by the exposure of wildlife and humans to the selected pharmaceuticals by analysing the uncertainty and variability in the exposure estimates.
- PHARMAS will evaluate the usefulness of ecological effect data for the assessment of human effects. These will be evaluated on the basis of a comparison of the toxicokinetic and toxicodynamic processes involved.
- PHARMAS will explore options to develop a common effect endpoint for human and ecological risks.

## Life of the network, NORMAN Activities

*The NORMAN Network operates in accordance with an Annual Joint Programme of Activities defined by the Steering Committee in consultation with the members of the Association. This section of the bulletin summarises the activities carried out so far and points up forthcoming results. More information on each of these activities is provided on the network website [www.norman-network.net](http://www.norman-network.net).*

## Milestones and achievements in 2010

### DATABASES

The NORMAN EMPODAT database has been significantly upgraded, and now contains about 120 000 occurrence data on 307 substances in more than 20 European countries. A battery of statistical tools has been developed, allowing for a rapid overview of the distribution of substances in the different matrices, countries and data quality categories.

A customised statistics module allows for personalised substance / parameter searches. Automatically updatable "Substance fact sheets" have been created for each substance, also providing information on the performance of the analytical techniques used.

The information will be used for future prioritisation of substances directly in the database, according to the prioritisation methodology which is currently under development in WG-1 (see below).

Further reprogramming and maintenance of EMPOMASS and EMPOMAP modules was carried out during 2010. As regards mass spectral information, a significant step forward is planned for 2011 where

UFZ, Leipzig will take the lead in the implementation of a server of the MassBank database (Horai et al., 2010; [www.massbank.jp](http://www.massbank.jp)) as a platform for the collection and exchange of mass spectral data within NORMAN and from NORMAN to the scientific and regulatory community worldwide. Indeed, it is expected that this improvement in the NORMAN mass spectral database will allow significant progress in the identification of unknowns in non-target screening and effect-directed analysis (EDA) – see WG-3 description below.

### WORKING GROUPS

- Working Group 1 – INERIS, FR: Prioritisation of emerging substances

The objective is the identification of those emerging substances that warrant priority attention (including priority needs in terms of improvement of existing data), based on criteria such as their occurrence in the environment, spatial and temporal distribution, usage pattern, level of consumption, (eco)toxicity, persistence and bioaccumulation potential.

The difference compared to the other prioritisation methodologies and the justification for this study is that, for emerging substances, there are by definition some knowledge gaps in the risk assessment process (e.g. insufficient information on the effects of the substance, insufficient performance of the analytical method necessary to quantify the level of occurrence of the substance in the environment). These knowledge gaps do not allow the substance to be correctly evaluated and may lead to the substance being discarded or overlooked if conventional prioritisation methodologies are applied.

The NORMAN methodology for prioritisation of emerging substances is therefore based on two main steps:

1. A first classification of substances in a defined number of action categories;
2. Subsequent ranking / prioritisation of the substances within each action-category.

Six specific types of action categories have been identified as prioritisation objectives, representing the actions to be taken by the research community and public authorities to cover the current knowledge gaps, and which will be part of future NORMAN actions.

The methodology aims to cover emerging substances in all environmental compartments. However, in this first stage priority indicators are being developed for the aquatic compartment only.

The candidate substances for this prioritisation exercise are the substances on the current list of NORMAN emerging substances (update 2010) which consists of more than 700 substances (available on the NORMAN website [www.norman-network.net](http://www.norman-network.net) >> About us >> List).

A first draft of the methodology for the definition of the prioritisation framework was prepared and discussed at the first meeting of the WG in February 2010 in Brussels. Further to the comments received, a second draft of the working document was prepared and discussed at the second WG meeting in November, in Paris. A first-run test of the methodology is under way. The first results (prioritised lists for the different action categories) will be available in 2011.

- Working Group 2 – INERIS, FR: The value of bioassays and biomarkers in water and sediment quality monitoring programmes: strategies for the interpretation of results

In 2010 the coordination of the WG (previously the responsibility of RIVM) was taken over by INERIS.

An inventory of biological test tools and strategies for interpretation of the results, plus bioassays and biomarkers currently available, is in preparation and is planned to be finalised by June 2011.

## QA/QC ACTIVITIES; INTERLABORATORY STUDIES

- Use of passive sampling for emerging substances

Intense preparatory work was performed in 2010 under the leadership of the Water Research Institute – WRI (Slovak Republic) – for the organisation of an international interlaboratory calibration study on passive sampling applied to emerging contaminants, which will be executed in spring–summer 2011.

The study of the applicability of these monitoring tools to emerging substances has been part of the NORMAN network's activities since 2009. Further to the Expert Group meeting organised by WRI at IPSW 2009 in Prague, a Position Paper on "Passive sampling of emerging pollutants in the aquatic environment: state of the art and perspectives" was published in summer 2010. This paper represents an important piece of information since it provides an exhaustive overview of the state of the

In September 2010, the group was invited to participate in an intercomparison study on two sites in France including fish and invertebrate biomarkers and bioassay in water and sediments. Six laboratories participated in the study. Results from the participants are expected by June 2011. The evaluation and interpretation of the results will be the basis for the preparation of a second exercise led by INERIS at different sites in Europe in 2011.

- (Working Group 3 – UFZ, Leipzig, Germany: Effect-directed analysis for hazardous pollutant identification

2010 saw the launch of a new Working Group on effect-directed analysis (EDA) for identification of hazardous contaminants.

The justification for this WG stems from the added value offered by field-based approaches (and in particular, EDA) to identify hazardous compounds. This type of approach should be an integral part of investigative monitoring programmes, and the results may be used to provide an additional line of evidence to conventional prioritisation methodologies for identification of relevant toxicants. In this respect, this WG represents the bridge between the activities of WG-2 on bioassays and WG-1 on prioritisation of emerging contaminants.

The kick-off meeting of the WG took place in Leipzig on 19–20 October. During the meeting there was a general consensus on the fact that acceptance of the effect-based approaches by public authorities has increased in recent years. However, participants concluded that in order to achieve application of EDA in monitoring, a strategy to approach authorities is needed, which should comprise: i) a position paper to approach authorities and bring a clear message, ii) a simplified EDA protocol ready to be used in monitoring and iii) pilot studies in order to demonstrate the operational applicability of the simplified protocol. One of the first outcomes of the meeting was the preparation and submission in January 2011 of a project proposal – EDA-EMERGE – under Marie Curie Initial Training Networks (ITN).

Tasks planned for 2011 include:

- Publication of a book on EDA in the book series Handbook of Environmental Chemistry
- Development and implementation of a high-resolution, accurate Mass-Bank for NORMAN
- Organisation of a workshop on new aspects of EDA in the identification of emerging candidate compounds, based on adverse effects in field samples (planned for autumn 2011)
- Organisation of the WG-3 annual meeting (autumn 2011)
- Planning of a Demonstration Programme which could take place in 2012.

art for the different types of application of passive samplers not only for monitoring of emerging contaminants in water, sediment and biota, but also for ecotoxicity assessment (e.g. use of passive samplers as mimics for bioconcentration, etc.). The paper is available on the NORMAN website [www.norman-network.net](http://www.norman-network.net) >> workshops >> Expert Group meetings and a summary is provided in this Bulletin.

The interlaboratory calibration exercise which will take place in 2011 will be organised as "Chemical Monitoring On Site" (CM Onsite) by the NORMAN Association and JRC in support of the Chemical Implementation Strategy of the Water Framework Directive (CIS WFD). The objective of the intercomparison exercise, which will be open to participants from commercial, academic and regulatory laboratories, is to present the variability in data by comparing results from various passive samplers sent by participating laboratories exposed to water at a single (reference) site. The target substances will include polar pesticides, pharmaceuticals, biocides, steroid hormones and brominated flame retardants.

- **PT (proficiency testing) on metabolites of pesticides in drinking water (IWW, Germany)**

This interlaboratory comparison study on metabolites of pesticides and glyphosate was provided in the context of the AQS Baden-Württemberg drinking water PT scheme, in collaboration with IWW Water Centre (Mülheim an der Ruhr). Given the significance of metabolites of pesticides as emerging contaminants at the European scale, the scope of the exercise was extended beyond the national level under the NORMAN umbrella, thus giving an interesting opportunity to European laboratories working to increase the quality and comparability of analytical data for this category of emerging pollutants. Thanks to the considerable number of laboratories – 82 – participating in the study, it was possible to include a method-specific evaluation of the results (an overview of the comparability of results obtained by different methods across European Member States). This evaluation showed that in most cases there is no significant difference between methods, with a tendency towards “better” values for methods including standard addition or internal standards.

- **Interlaboratory study on perfluorinated alkyl substances in environmental samples**

The final report of the interlaboratory study on perfluorinated alkyl substances in environmental samples has now been completed and sent to the participants (and will soon be available on the NORMAN website). The study was performed in 2009 by the Institute for Environmental Studies (IVM) in collaboration with NORMAN, INERIS and QUASIMEME and in conjunction with a study on human materials organised by Prof. Bert van Bavel (MTM, Orebro University). As a result, the study consists of

## WORKSHOPS IN 2010

- **Workshop on “WFD River Basin-Specific Pollutants (RBSP) Monitoring – Identification and Monitoring” (JRC)**

The workshop took place on 10–11 June in Stresa, Italy and was organised as a NORMAN annual workshop in collaboration with JRC IES. The objective of the workshop was to provide a common forum for MS and interested groups for presenting, discussing and streamlining approaches for harmonised selection and monitoring of RBSP in the WFD context. Particular attention was given to emerging contaminants, as their prioritisation and monitoring are particularly challenging. The workshop aimed to produce clear recommendations to MS on how to proceed. In order to plan the workshop according to MS’ needs, a questionnaire was distributed to MS representatives, which allowed the collection of exhaustive information about the procedures applied by Member States for the selection of River Basin-Specific Pollutants. In addition, four different working sessions with specific topics were prepared on data availability; identification of RBSP candidate substances; selection of RBSP; monitoring of RBSP.

The conclusions of this workshop included:

- Exchange/consultation of concentration data at EU level is envisaged (i.e. shared monitoring data through a database at EU level). The NORMAN database for emerging pollutants was identified as a tool to improve the overview of the status of contamination.
- Common data format (concentration + metadata) is needed to improve interoperability of databases and enhance exploitation of available monitoring data. To this purpose, a common DG ENV–EEA data collection template is already available. It was used during DG ENV EU-wide data collection, and is also adopted by NORMAN. Its implementation at MS level is needed.
- Collaboration at EU-level is useful for efficient use of resources in investigative monitoring.
- EU-wide monitoring programmes are useful exercises to improve use of resources in investigative monitoring. MS should be directly involved in the planning and setting-up of EU-wide monitoring programmes.

two parts: a human part (organised by MTM) and an environmental part (organised by IVM).

For the environmental part, the samples provided were surface water, marine fish (pike-perch) and sludge. Participants from laboratories worldwide were allowed to apply their own in-house methods and calibrants. The results were collected and statistically evaluated using Cofino statistics. Z-scores were allocated to individual laboratories’ results.

The large number of laboratories participating in this international interlaboratory study confirms the high level of interest in analysis of PFCs in both human and environmental matrices. This study showed that the performance of labs participating in the human part of the study was better than the performance in the environmental part. This may partly be caused by the low levels of PFCs in the non-fortified samples. However, there are probably other sources that have contributed to the high variance of the results in this study, and this is explained in detail in the report. It is also worth commenting on the analysed matrices: for the first time, sewage sludge was included in the study. The variance for the results in this matrix was substantial, showing that more effort is needed to improve methods for sludge.

- **Implementation of the NORMAN protocol for methods validation in European standardisation**

A New Work Item Proposal based on the NORMAN protocol for methods validation was prepared by IWW in July 2010 and is now going to be submitted by France to CEN TC230.

- An exchange of experiences at EU level about the use of non-target screening techniques for investigative monitoring is desired by MS. (Activity will be launched by JRC and NORMAN in WFD chemical monitoring group).

More details can be found in the workshop report, which is published as a “JRC scientific and technical report” and available on the [www.norman-network.net](http://www.norman-network.net) >> Workshops.

- **Workshop on “Environmental specimen banking (ESB) and emerging substances (UBA, Germany)**

The workshop took place on 21–22 June in Berlin. EU ESBs are not yet organised as a network; each of them has its own characteristics and work programmes. The scientific programme of the workshop included: 1) presentation of the EU ESB programmes; 2) two discussion groups on harmonisation on the following issues: “What chemical?” and “What specimen?”.

NORMAN chaired the two discussion groups in order to investigate the potential for closer collaboration between NORMAN and ESBs for the analysis of emerging contaminants.

There is obvious mutual benefit to NORMAN and ESBs in working together. ESBs can add spatial and time trend data to the NORMAN prioritisation process. NORMAN, on the other hand, can give recommendations to ESBs when it comes to analysing contaminants that were not measured in the past and which are today regarded as substances of emerging concern. For institutional co-operation between EU ESBs and NORMAN, however, EU ESBs need to make progress towards the creation of an ESB network before the establishment of formal links with NORMAN,

A letter of intent is currently being drafted by members of the ESB community. The letter will communicate willingness to co-operate with EU Chemical Safety Management (CSM).

The report of the conference is not yet available. For more details on this conference, see also in the Bulletin the science note by Heinz Ruedel – Fraunhofer Institute, Germany.



