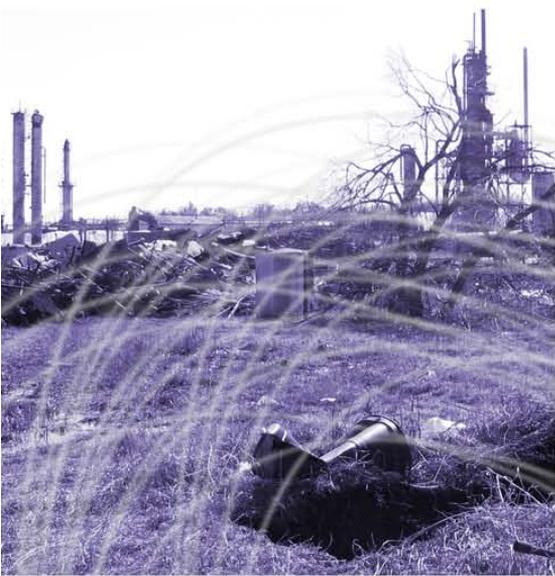


Proceedings

Workshop on

Emerging Environmental Pollutants



Key Issues and Challenges

Stresa, Italy
19-20 June 2006



Network of reference laboratories
for monitoring of emerging
environmental pollutants

EUR 22806 EN

Proceedings

Workshop on

Emerging Environmental Pollutants



Key Issues and Challenges

Stresa, Italy
19-20 June 2006



Network of reference laboratories
for monitoring of emerging
environmental pollutants

EUR 22806 EN

MISSION STATEMENT

The mission of the JRC is to provide customer-driven scientific and technical support for the conception, development, implementation and monitoring of EU policies. As a service of the European Commission, the JRC functions as a reference centre of science and technology for the Union. Close to the policy-making process, it serves the common interest of the Member States, while being independent of special interests, whether private or national.

European Commission

DG Joint Research Centre
Institute for Environment and Sustainability (IES)
I-21020 Ispra (VA), Italy
www.jrc.ec.europa.eu

www.norman-network.net

Editor:

Valeria Dulio, Norman project coordinator
INERIS
Parc Technologique ALATA – B.P. N°2
F-60550 Verneuil-en-Halatte
E-mail: valeria.dulio@ineris.fr
Tel.: +33 3 44 55 66 47
Fax: +33 3 44 55 66 00

JRC contact:

Georg Hanke
E-mail: georg.hanke@jrc.it
Tel.: ++39-0332-785586
Fax: ++39-0332-786351
<http://ies.jrc.ec.europa.eu>

Cover: José-Joaquín Blasco

Legal Notice

Neither the European Commission nor any person acting on behalf of the Commission is responsible for the use that might be made of the following information.

A great deal of additional information on the European Union is available on the Internet. It can be accessed through the Europe server: <http://europe.eu/>

EUR 22806 EN

ISBN 978-92-79-06227-8

ISSN 1018-5593

Luxembourg: Office for Official Publications of the European Communities

© European Communities, 2007

Reproduction is authorized provided the source is acknowledged

Printed in Italy

Editor:

Valeria Dulio, INERIS

Scientific Committee:

Valeria Dulio, INERIS
Georg Hanke, EC JRC IES RWER
David Westwood, UK EA
Pim Leonards, RIVO
Jaroslav Slobodnik, Slovak EI
Rod Robinson, NPL
Damia Barceló, CSIC
Monika Herrchen, FHG

Meeting organisers:

Valeria Dulio, INERIS
Georg Hanke, EC JRC IES RWER
Robert Loos, EC JRC IES RWER
Madeleine Rizzi, EC JRC IES

Key Note Speakers:

Thomas Ternes, BFG
Frank Lamé, TNO
Dimitrios Kotzias, EC JRC IHCP
Pim de Voogt, University of Amsterdam
Eva Brorström-Lundén, IVL
Walter Giger, EAWAG/ Giger Research Consulting
Richard Owen, UK EA
Steven Eisenreich, EC JRC IHCP ECB
Nick Cartwright, UK EA
Norbert Theobald, BSH
Jürgen Volz, KIWA
Claudio Carlon, EC JRC IES RWER
David Briggs, Imperial College London
Hans Løkke, NERI
Martin Holt, ECETOC
Anne Marie Fouillac, BRGM
Jaroslav Slobodnik, Slovak EI
David Schwesig, IWW
Damià Barceló, CSIC

Parallel sessions chairs and rapporteurs:

Session 1 – Data sources for emerging pollutants
Jaroslav Slobodnik, Slovak EI
Heather Leslie, IVM
Session II – Prioritisation criteria for emerging pollutants
Nick Cartwright, UK EA
Marina Coquery, CEMAGREF
Session III – Monitoring tools and analytical methods
Peter Lepom, UBA
Georg Hanke, EC JRC IES RWER
Session IV – Models and prediction methods
Willie Pejinenburg, RIVM
Michael McLachlan, Stockholm University

Workshop venue: Hotel La Palma, Stresa, Italy

CONTENTS

<i>I. Introduction</i>	7
<i>II. Purpose and objectives</i>	7
<i>III. Workshop organisation</i>	8
<i>IV. Summary of presentations: key issues</i>	9
IV.1. Introduction to the NORMAN project	9
IV.2. The current concerns from different scientific communities regarding emerging substances	
IV.3. Focus on some emerging topics	12
IV.4. The stakeholders in the management of emerging pollutants	13
IV.5. Meeting the science needs for emerging pollutants: current work areas in EU	18
IV.6. NORMAN working tools and activities	21
<i>V. Conclusions from the parallel sessions</i>	23
V.1. Session 1 – Data sources for emerging pollutants	23
V.2. Session II – Prioritisation criteria for emerging pollutants	25
V.3. Session III – Monitoring tools and analytical methods	29
V.4. Session IV – Models and prediction methods	32
<i>VI. Conclusions and recommendations</i>	33
<i>VII. Extended abstracts of the presentations</i>	35
<i>VIII. List of participants</i>	111

I. Introduction

Since the 1970s the impact of chemical pollution has focused almost exclusively on lists of conventional priority pollutants, especially those referred to as PBT (fulfilling criteria of Persistence, Bioaccumulation and Toxicity) or POPs (Persistent Organic Pollutants). The number of regulated, conventional pollutants, however, represents only a small part of the total number of potential pollutants. Emerging pollutants pose increasing threats to public health and ecosystems. Emerging pollutants are not necessarily new chemicals, and some of them have often long been present in the environment, but their presence and significance are only now being elucidated.

How are emerging pollutants identified? How do emerging pollutants become regulated pollutants? What investigations should be undertaken when an emerging pollutant is identified? What are the substances that are being identified as emerging pollutants today, and what information is currently missing or required in terms of monitoring and assessment of their associated risks?

Information on these substances is often difficult to obtain and the methods used are often at a research and development stage, or not appropriate for harmonisation at the European level. This makes comparison and interpretation of data very difficult, and represents a major difficulty for decision-making by the authorities.

To discuss these issues from a wide perspective a workshop on 'Emerging environmental pollutants: key issues and challenges' was held in Stresa, Italy on 19-20 June 2006 as part of the activities of the EU-funded NORMAN project (Network of reference laboratories, research centres and related organisations for monitoring of emerging environmental pollutants)¹. The workshop was organised with the collaboration of:

- INERIS - Institut National de l'Environnement Industriel et des Risques (France)
- JRC-IES – Joint Research Centre – Institute for Environment and Sustainability (EC)
- EA – Environment Agency for England and Wales (UK).

II. Purpose and objectives

The specific objectives of the workshop were:

- To inform participants interested in NORMAN activities about the project's goals
- To discuss the state of current knowledge and to review demand for the analysis of emerging pollutants for the purpose of risk assessment and risk management programmes (including identifying gaps in the information currently available)
- To enable an overview of the main issues and priority needs as regards additional monitoring activities for emerging pollutants and the requirements of method validation and dissemination of information
- To facilitate an exchange of views with 'future customers' of the NORMAN network, relating to its organisation and scope of work.

¹ The NORMAN project is funded by the European Commission under the 6th Framework Programme – Priority 1.1.6.3: Global Change and Ecosystems. The aim of the NORMAN network is to enhance the exchange of information on emerging environmental pollutants, 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 served. To find out more about NORMAN, visit our website at <http://norman-network.net>

III. Workshop organisation

The workshop involved a two-day programme. The first day gave a general overview of the current issues, with presentations on specific topics and projects under the 5th and 6th Framework Programmes dealing with monitoring and risk assessment of emerging pollutants. Special attention was paid to the views of users and key stakeholders (policy-makers, regulatory bodies, organisations in charge of risk assessment and risk management) regarding the current gaps in, and needs for, risk assessment and management.

The second day focused on how NORMAN should operate, in collaboration with other existing initiatives and research projects, and how it should establish a long-term co-ordination programme to address the identified current and future needs in the field of emerging pollutants. After a plenary session where the main activities and working tools of the NORMAN project were presented, the workshop participants broke out into four working groups, each of which addressed a specific aspect of emerging pollutants analysis and prioritisation:

- Parallel Session I: Data sources for emerging pollutants
- Parallel Session II: Prioritisation criteria for emerging pollutants
- Parallel Session III: Monitoring tools and analytical methods
- Parallel Session IV: Models and prediction methods

Detailed questions were prepared for open discussion in each parallel session. The workshop ended with a plenary session where the rapporteurs presented the feedback from the four parallel sessions and the final conclusions were set out.

All presentations are available on the Norman webpage:

<http://www.norman-network.net>

Summary of presentations: key issues

III.1. Welcome and introduction to the NORMAN project

Giovanni Bidoglio (JRC-IES) opened the workshop and welcomed all participants. He presented a general overview of the JRC's activities in support of EU policies and co-operation with international bodies. Giovanni Bidoglio stressed that one of the main roles of JRC is to explore the cost-benefit trade-offs of the various policy strategies: this requires investigators to compare threats posed by multiple contaminants, including emerging contaminants, released to multiple media and to multiple organisms.

Valeria Dulio (INERIS) introduced the NORMAN project and pointed out that for more effective identification of future emerging contaminants and prevention of their release to the environment, systems of risk identification, assessment and management need to be based on results that are comparable, reproducible and accepted by the scientific community. NORMAN has a role in this process as a network designed to foster the exchange of data and information on emerging substances and the validation and harmonisation of common measurement methods and monitoring tools. Since NORMAN's ultimate objective is to become a permanent network beyond the EC funding, input from this workshop will be extremely helpful for the definition of the future strategy of the network.

III.2. The current concerns from different scientific communities regarding emerging substances

Water: Thomas Ternes (Federal Institute of Hydrology) presented an overview of emerging chemicals in water. The focus of environmental research in the water compartment has recently been extended from more classical pollutants, such as PCBs, DDT, dioxins and pesticides, to pollutants such as pharmaceuticals, hormones, cosmetics, biocides, polyfluorinated compounds, PCBE, HBCD, phosphoric ester flame retardants, etc. This is partly due to the enormous progress made in chemical analysis in the last 10-15 years, in which the increasing use of LC-MS now allows the identification of extremely polar organic substances without derivatisation at ng/L levels.

Several studies in Europe and North America report the presence of pharmaceuticals (human use) and other polar emerging contaminants in rivers, lakes and groundwater in the µg/L range. For most of the substances identified today as emerging pollutants, the route into the environment is via private households and then via the municipal wastewater treatment plants (WWTPs). Compounds that are not readily (bio)degradable enter the receiving waters either as dissolved pollutants or adsorbed onto suspended matter. The WWTPs' removal efficiency is therefore crucial for the contamination of the receiving water bodies. Other categories of emerging compounds, such as veterinary pharmaceuticals, can contaminate farmland when manure is used as fertiliser, and are likely to enter the rivers as a result of run-off from the fields. Another source of contamination is leakage into groundwater that may originate from the disposal of household products as domestic waste in landfills.

Occurrence of these micropollutants in drinking water has also been reported at waterworks using groundwater resources with an unexpected wastewater content (unintended wastewater reuse).

One further remark is about the occurrence of transformation products (TPs) from micropollutants, which are mostly unknown and polar. They include, among others:

- ✓ Metabolites excreted by humans and animals (e.g. clofibric acid from pharmaceuticals for human use)

- ✓ TPs formed by microorganisms in the environment, such as ketopiperazines
- ✓ Oxidation by-products formed during ozonation or chlorination, such as BQD
- ✓ Disinfection by-products (e.g. THMs, haloacids, NDMA).

And it should be remembered that our knowledge of 'micro(nano, pico)pollutants' is limited to those which are part of monitoring programmes.

As regards the toxicological risks associated with drinking water, the detected residues are unlikely to cause effects, even though there is a dearth of long-term studies. Additionally, most of the transformation products have never been identified and their toxicity is totally unknown.

As regards ecotoxicological risks, it is very likely that severe environmental effects will be found for more micropollutants or for mixtures.

In conclusion, although adverse effects have been identified on biota in only a few cases, it can be expected that in future more concerns will arise over 'emerging substances' or even 'groups of substances'. Because there are so many compounds, the goal should be to select indicator substances regulated under the WFD in order to represent different kinds of pollution sources.

For more details about this presentation, see the extended abstract by Thomas Ternes (Section VI.).

Soil: Soil pollution and degradation are a result of population growth and technological development. Within the water cycle, soils act as the key zone for storage, filtration and transport of water and associated pollutants. If the accumulation of pollutants exceeds the buffer capacity, then soils or sediments can become the source of diffuse pollution of adjacent compartments such as groundwater and surface waters. A wide range of man-made chemicals - designed for use in industry, agriculture, pest control and consumer goods - and emissions from the combustion of fossil fuels are the main sources of diffuse pollution.

Knowledge of the occurrence of emerging substances (e.g. veterinary pharmaceuticals from the application of manure to farmland), and their potential (adverse) effects are of major importance for a sustainable environment. Nevertheless, it seems that knowledge of the more 'common' substances in the soil compartment is still at too low level and is therefore a priority.

Frank Lamé presented two studies performed in the Netherlands. The first was aimed at the definition of the background levels for 252 compounds in soil. The term 'background level' is interpreted here not as the level of concentration related to the natural – undisturbed – environment, but rather as the concentration level of a compound when there is expectation of direct or local soil pollution. 100 sampling locations were selected and at each location samples were taken over an area of 2500 m² from the top-soil, the intermediate layer and the underlying layer. The results of the study will be used for the determination of the new target levels to be implemented in the Dutch Soil Policy in 2007. (In general the target levels will be set at the 95-percentile value of the distribution of the compounds as found in the top-soil). But knowing the background levels for 252 compounds in more or less undisturbed soils does not mean that all these compounds are regularly measured when looking at soil quality on a routine basis (Not all these compounds are part of the routine soil quality monitoring programmes). In general, only 11 compounds are monitored. A second study was therefore conducted to define the list of compounds that should routinely be measured when determining soil quality. Arsenic, barium, cadmium, cobalt, copper, mercury, lead, nickel, zinc, cyanide, chloride, mineral oil, sum-PAH and EOX were identified as parameters to be included in such list. This study showed that soil quality investigations tend to focus on the same limited number of compounds. As result, competent authorities may overlook not only the more 'exotic substances' but even the more common compounds and sources of soil contamination.

For more details about this presentation, see the extended abstract by Frank Lamé (Section VII).

Air: The Clean Air for Europe Programme reviewed potential emerging pollutants in ambient air. In general, ambient air is not as critical an exposure pathway for emerging pollutants, although there are some notable exceptions, e.g. nanoparticulates and some chemical components of particulate matter. There are emerging air pollutant concerns relating to near-source concentrations, e.g. airborne pesticides and other agrochemicals and emissions from landfill, including biological pathogens. Assessment and measurement in these areas tend to be the subject of individual research projects within the universities. In addition these areas often relate to occupational exposure rather than environmental hazards to the general population. Government departments and health regulatory bodies have roles to play in the assessment of the health risk from emerging pollutants in these areas.

Indoor air is a significant area of 'emerging concern'. Across Europe, people live and work in indoor environments. On average, people spend 85-90% of their time indoors (homes, workplaces, cars, public transport means etc.). In indoor environments (buildings, homes) people are exposed to a complex mixture of chemicals at concentration levels which are often up to five times higher than outdoors. The presence of these chemicals in indoor air is the result of infiltration of polluted outdoor air and of emissions from various indoor sources, including building materials, activities of the occupants, consumer products, smoking etc. Research on emerging pollutants in indoor air is carried out by a number of different sectors, including building, construction products, furnishing materials, chemicals, transport (in-cabin air) and workplace, rather than the environmental sector. The term 'emerging pollutants' is not commonly used in these sectors, though the same methodology, of identification, risk assessment and evaluation as a potential target for regulatory action is followed.

It is worth noting that in the environmental sector the focus is still on conventional pollutants with identified and reasonably well understood health effects (e.g. ozone or benzene gases, or particulate matter). These pollutants still represent a current focus of EU-funded projects, and there are a number of activities to harmonise measurements across the EU, for example within the AQUILA network.

The presentation given by Dimitrios Kotzias (JRC-IES) focused on two EU-funded projects, INDEX and AIRMEX, launched in December 2002 and October 2003, respectively. The main objective of the INDEX project was to propose a list of priority compounds which should be considered for regulation in indoor environments. On the basis of:

- ✓ the overall population risk caused by indoor sources
- ✓ toxicological properties, including hypersensitivity for allergy and asthma,
- ✓ known health effects and
- ✓ considerations of comfort,

the INDEX project decided to define and prioritize the main indoor air pollutants as follows:

Group 1 (high priority): benzene, formaldehyde, carbon monoxide, nitrogen dioxide, naphthalene

Group 2 (low priority): m&p-xylenes, o-xylene, acetaldehyde, styrene, toluene

Group 3 (chemicals requiring further research with regard to human exposure and dose/response): NH₃, d-limonene, a-pinene.

The AIRMEX study dealt with the measurements of indoor/outdoor air and personal exposure to pollutants in various European cities.

For more details about this presentation, see the extended abstract by Dimitrios Kotzias (Section VII).

III.3. Focus on some emerging topics

After this general overview of the current concerns and perception of the different scientific communities as to the issue of 'emerging environmental pollutants', four examples of emerging topics were presented.

Polyfluorinated contaminants: there is an increasing concern over PFCs due to the upward concentration trends found for several PFCs in environmental matrices such as sediments and biota. Pim de Voogt presented the results of the PERFORCE project, which was funded by the European Commission with the aim of making an exposure assessment of perfluorinated organic compounds in the European environment. Analytical methods for water, sediment, air and biota were developed and validated. A worldwide interlaboratory study was organised using fish tissue, fish liver extract and water samples. The results revealed large variations in the between-laboratory results, showing that there are still difficulties in generating comparable results. A Europe-wide monitoring campaign was carried out, including sampling of surface water, sediment, air and biota and wastewater treatment plants. The results of the sampling campaign, which show that PFCs are widely present in the European environment, improved our knowledge of spatial and temporal trends in Europe and possible sources of PFCs. There is still a need to improve our understanding of PFC transfer to, and removal from, the atmosphere and, the oceanic transport routes, and of the mechanisms of bioaccumulation / biomagnification and bioelimination of PFCs.

For more details about this presentation, see the extended abstract by Pim de Voogt (Section VII).

Siloxanes: Volatile Methylated Siloxanes (VMS) are used in large quantities in a vast number of industrial and household products, including fuel, car polish, cleaners, anti-foaming agents, car waxes and various personal care products. The widespread use of siloxanes, as well as their high volatility, has increased concern about these compounds and a joint study was performed by IVL, the Swedish Environmental Research Institute and NILU, the Norwegian Institute for Air Research, with funding from Swedish EPA and the Nordic Council of Ministers. The results of these research initiatives were presented by Eva Brorström-Lundén (IVL). Siloxanes (VMS) are present as common pollutants in many different matrices in the Nordic environment. They seem to be emitted through diffuse pathways and they enter the aquatic food chain. They are also present in samples of human breast milk. No Observed Effect Concentrations (NOECs) and estimated Chronic Values (ChV) were exceeded only in samples of water entering sewage treatment plants, with levels significantly reduced in the outgoing water from the same treatment plant. This leads to the conclusion that the current emission levels do not pose any risk to the environment at the moment, because of quick removal mechanisms. Nevertheless, these compounds deserve some attention since the NOECs and ChV are available for only two substances belonging to the category of siloxanes, (the octamethylcyclotetrasiloxane - D4, and the decamethylcyclopentasiloxane - D5) and were estimated from a limited amount of data. The possibility of effects in the local environment close to emissions should not be excluded.

For more details about this presentation, see the extended abstract by Eva Brorström-Lundén (Section VII).

Benzotriazole anticorrosives: The complexing agents benzotriazole (BT) and tolyltriazole (TT, a mixture of 4- and 5-methyl isomers in the benzene ring of BT) are widely used as anticorrosive agents, as chemical intermediates for dyes, pharmaceuticals and fungicides, as antifogging constituents in photographic applications and as ultraviolet stabilizers. Walter Giger (EAWAG) presented the results of research studies investigating the environmental occurrence of BT and TT in rivers, lakes, bank filtrates and groundwater in Switzerland. The investigated contaminants

occur at quantitatively measurable but varying concentrations in municipal wastewaters and rivers, reflecting their ubiquitous input into wastewaters and their different behaviour during biological wastewater treatment. They are only partly removed in mechanical-biological wastewater treatment because of their high polarity, i.e. high solubility in water, and their resistance to biodegradation. Thus, residual amounts of BT and TT are widely distributed in the receiving ambient waters. In particular, BT is - after EDTA – the second most abundant individual contaminant in many natural waters. BT can be tracked back to its use as an anticorrosive agent in dishwasher detergents. However, it is currently not clear how TT gets into municipal wastewaters, because most of its applications are not directly connected to municipal wastewaters. Additional questions of concern are how BT and TT behave during bank filtration and how they are affected by the various processes of drinking water treatment plants using lake water as a water resource.

For more details about this presentation, see the extended abstract by Walter Giger (Section VII).

Engineered nanoparticles: Richard Owen (UK Environment Agency) gave an overview of engineered nanoparticles as an issue of emerging concern. Engineered nanoparticles are an important sector of nanotechnologies, representing a diverse range of substances currently on the market, from metal and metal oxide based nanoparticles to carbon-based nanotubes and fullerenes. While engineered nanoparticles offer significant potential benefits, there are also considerable uncertainties with regard to potential risks to the environment and human health. The fate, behaviour and toxicity of these materials in the environment are largely unknown and, while there are likely to be current releases, the ability to measure their presence is also currently limited. Addressing the data gaps for risk assessment of engineered nanoparticles requires both fundamental research and more applied work, including the evaluation of the appropriateness of current test methods for assessing hazard, development of reference materials and technologies for detection and measurement of engineered nanoparticles in the environment. In the UK, research is being co-ordinated through a body established by the UK Government (the Nanotechnologies Research Co-ordination Group). A number of research publications and research programmes are now beginning to address the environmental risks of manufactured nanoparticles. Included in this is the UK Environmental Nanosciences Initiative (ENI), which has been established specifically to address this issue, acting as a hub for environmental nanosciences research in the UK.

For more details about this presentation, see the extended abstract by Richard Owen (Section VII).

III.4. The stakeholders in the management of emerging pollutants

The way in which the scientific findings are received and taken into account by policy makers and regulatory bodies will directly affect the management of emerging substances. It is therefore crucial to analyse how the issues related to emerging pollutants are integrated in the chemicals policy (REACH) and in the current environmental policies in the various environmental compartments.

Emerging substances and REACH

This presentation provided by Steven Eisenreich (ECB) covered the essential features of REACH, explaining the differences between current legislation and REACH, and the data needs for chemical risk assessment under both current legislation (sans REACH) and anticipated under REACH. The role of monitoring data and process information in evaluating PBT criteria under REACH were also discussed.

Management of Emerging Substances and the Water Framework Directive

Nick Cartwright (UK Environment Agency) presented the perspective of the UK Environment Agency as a competent authority dealing with the water framework directive (WFD).

As part of the analysis of pressures and impacts in the implementation of WFD Article 5, Member States need to draw up risk maps and identify the specific pollutants responsible for the identified pressures and impacts. These substances, identified at the river basin and water body level, form part of the classification for good ecological status of a water body and may also include emerging substances.

The first risk maps were submitted in 2004 for the first planning cycle (2009-2015) and at that stage the pressures identified in UK, and most probably in all other MS, were from traditional pollutants, not from emerging pollutants. From 2009 the risk maps will have to be revised for publication in 2013 (to allow for extensive public consultation before the plans can be put in place in 2015).

For any possible inclusion of emerging substances as 'relevant substances' in the next river basin management plans (RBMP) the information on emerging substances will have to be made available by 2008.

But how are emerging substances identified? The Environment Agency has adopted a Chemical Strategy to help prioritisation of activities on chemicals. There are three approaches to priority setting:

- screening of individual substances
- reviewing groups of substances with similar properties
- looking for signals in the environment (e.g. work on steroids following the identification of feminised fish in rivers).

The substances identified via screening activities are then ranked on a risk basis (combination of hazard rating and exposure rating). The substances that are classified as relevant substances need to be monitored and an EQS has to be established for each of these substances.

One major difficulty encountered with emerging substances is that very precautionary EQS values may be derived for these substances because of the high level of uncertainty and poor knowledge of their effects. There is no mechanism to obtain additional data from industry when deriving EQS under the WFD, and compliance checking with very low EQS represents a significant analytical challenge, as sound monitoring requires a limit of quantification of at least 30% of the EQS. As a result, competent authorities are likely to be quite reluctant to set EQS for emerging substances for which there are significant data uncertainties.

Estimating exposure may be even more difficult since monitoring data and emission information on emerging substances are limited. REACH does still not address these issues. It will be important that the EU chemicals legislation complement the WFD. REACH is likely to be important in controlling chemicals at source to tackle diffuse inputs.

Another remark made by Nick Cartwright regarding the inclusion / identification of emerging substances as 'relevant substances' is that once a substance is identified as a 'relevant substance' in a water body, extensive requirements need to be met in terms of monitoring (which is highly expensive). So it is necessary to make sure that only the substances for which there is a real environmental risk are added to the list of relevant substances if competent authorities are to retain any capacity for investigative monitoring.

For more details about this presentation, see the extended abstract by Nick Cartwright (Section VII).

Management of emerging substances in the marine environment

Norbert Theobald (Federal Maritime and Hydrographic Agency) provided the perspective of a national monitoring authority. As concentrations are 2 to 3 orders of magnitude lower than on land for nearly all new compounds, the development of new methods - or at least the improvement of existing procedures (e.g. using larger samples, additional clean-up and more selective detection systems) - is necessary.

Marine monitoring is very expensive and it is therefore necessary to prioritise the substances to be monitored. So how are these emerging pollutants selected for monitoring in the marine environment?

Following a scientific approach one should start from structural considerations about substances (looking for homologues of known pollutants), combined with toxicological investigations and non-target screening or a combination of the two (i.e. toxicity directed analysis). All these are innovative and valid approaches but they are expensive, since experimental studies need to be carried out.

An economical approach towards prioritisation would start from products which are suspected of posing possible environmental problems, either because of their biological effects or because the compounds are produced in large volumes. However, it is often very difficult to get information such as production volumes from private companies, since this information is often considered as confidential.

The last approach, which is also the most frequently implemented, is the administrative approach, which starts from a compilation of the lists of priority pollutants of the various international organisations (EU-WFD, OSPAR, HELCOM, etc.). Prioritisation procedures adopted within these commissions are used to help rank the numerous compounds.

Since only 10% of the resources are available for implementing additional emerging substances into the survey programmes, it is crucial when carrying out new investigations in new pollutants to optimise the efficiency of all processes and find ways to get free resources (by benefiting from collaborative activities).

First of all, the quality of the monitoring and the effort can be adjusted during the monitoring life cycle. In the first part of an investigative programme a limited screening is necessary mainly to understand what the concentration range is and where the compounds are that detectable. This preliminary phase can be followed by a more intensive stage where spatial distribution and temporal trends are analysed. Then, when the processes are known or when changes / trends are constant, the effort can be reduced. It is also possible that a substance does not need to be monitored any longer (this is the case of substances for which the concentration decreases to zero or when negative trends are confirmed).

In addition to this improvement in efficiency of the monitoring process, co-operation with other institutions and participation in collaborative research projects is crucial for the investigation of emerging substances for which there would otherwise not be sufficient resources.

A core of parameters (classical pollutants) will represent the routine monitored parameters, integrated by a number of new pollutants which are measured as part of other research projects or types of collaborative initiatives with other institutes.

For more details about this presentation, see the extended abstract by Norbert Theobald (Section VII).

How the drinking water industry deals with emerging pollutants

Jurgen Volz reported the experience in the Netherlands by KIWA (the joint R&D institute of the Dutch drinking water industry).

The EU drinking water directive and the Dutch drinking water ordinance require the drinking water suppliers to guarantee

- a) compliance with drinking water standards (MAC = Maximum Admissible Concentration) for several dozen substances
- b) that drinking water does not contain any unregulated substances (e.g. emerging environmental pollutants) in concentrations which may be harmful to human health.

One of the most serious problems with emerging substances for drinking water suppliers is that regulators tend to develop purely ecotoxicological EQS for these substances without taking drinking water aspects into account.

Historically, two main groups of emerging substances have created many problems for the drinking water industry: disinfection by-products and pesticides. But both these groups were regulated at a relatively early stage of their emergence, which makes the problem easier to deal with for water suppliers because there are mandatory drinking water standards to be complied with.

The main difficulties stem from the huge number of emerging pollutants that are unregulated and whose presence or absence in drinking water needs to be checked. For technical and financial reasons it is impossible to monitor all these substances and a pragmatic case-by-case approach needs to be applied to evaluate the need to carry out further investigative work. On the other hand, experience shows that the detection of a new substance in drinking water in one part of the world very quickly becomes a global issue and drinking water suppliers need to be on the alert at all times and try to keep up to date with what is going on in the world in order to anticipate unjustified alerts and convince their regulators and customers that the drinking water that they supply is free of these 'unwanted substances'.

Another remark is about unknown peaks which are often identified when broad screening methods are applied in monitoring. Techniques for identification and quantification of the compounds at the origin of these peaks are indeed improving. However, even the most sophisticated techniques of chemical analysis will not be able to cover all the territory. Fundamental support will come from biomonitoring systems which target the combined toxicity of all compounds in the extremely complex water matrix. These systems are already widely implemented by water suppliers in the Netherlands as early warning systems to detect any unreported toxic spills that may have occurred upstream and trigger a river water intake stop. Moreover, only on very rare occasions has it been possible to isolate and identify a single compound which was responsible for the biomonitoring alarm.

In conclusion, one of the main problems faced by drinking water suppliers is that national and EU authorities fail to consider that the Drinking Water Standards (DWS) is much lower than the Environmental Quality Standard (EQS) for most regulated pollutants and in particular for pesticides. This means that a water utility using ecologically safe river water (meeting the EQS) would have to achieve 99.9 % treatment efficiency, which is practically impossible. It is important to consider here the interpretation of Article 7 of the WFD which states that MS *'shall ensure the necessary protection for the bodies of water identified with the aim of avoiding deterioration in their quality in order to reduce the level of purification treatment required in the production of drinking water'*.

For more details about this presentation, see the extended abstract by Jurgen Volz (Section VII).

Management of emerging pollutants in soil

Claudio Carlon (JRC-IES) explained in his presentation that there are still several open questions about the emerging substances that may be considered relevant in soil, their occurrence and effects. As a result, regulatory systems are not prepared yet to address emerging pollutants in soil.

When discussing the assessment and management of emerging pollutants in soil, a distinction can be made between the management of local and diffuse contamination.

As regards local contamination which can be associated with e.g. landfills or industrial facilities, concerns were raised some years ago about petrol additives such as Methyl-tert-butyl ether (MTBE). The EC Risk Assessment Report published in 2002 concluded that MTBE is not carcinogenic according to the criteria set out in the EU Directive on Dangerous Substances. However, there is still high uncertainty about the proper regulation of MTBE in soil and groundwater, as it is evident that there is a large variation in the environmental quality criteria proposed by the different European countries. There is also a concern over the disposal of electronic equipment (e-waste) which may leach toxic chemicals into the leachate of lined landfills or contaminated groundwater near unlined landfills. Lead is a major potential contaminant, but the leaching of brominated flame retardants (BFR) such as Polybrominated diphenylethers has also led to their identification as potential relevant pollutants.

As regards the management of local contamination, the regulatory systems address the contaminated media (the soil), and the remediation burden is on the polluter. However, emerging pollutants are not usually analysed, or it is difficult to prove the responsibility of the polluter. As a matter of fact, concentration thresholds (based on screening risk assessment) are not provided for these substances and a site-specific risk assessment (SS-ERA) might be necessary. A TRIAD approach, based on bioassays, is applied to this type of risk assessment. However, even when the TRIAD protocol outlines eco-toxicological and/or ecological effects, in most cases these effects can hardly be related to the occurrence of specific substances in the soil (the cause-effect relationship is hard to prove). Moreover, the SS-ERA methodology applied to contaminated soil is far from being a standardised approach and is still in the domain of the scientific research.

As to diffuse soil and groundwater contamination, one example is the contamination by endocrine disruptors and pharmaceuticals caused by amendments of soil by sewage sludge and manure produced by animal excreta. The application of polar pesticides in agriculture is also a concern for diffuse contamination of soil and water.

Emerging pollutants might have effects on humans at population level and on the ecosystem at a larger scale. However, few data are available on the occurrence and bioavailability of emerging pollutants in soil.

In conclusion, as regards the risk assessment of soil contaminants, large uncertainties and needs for harmonisation of risk assessment methodologies still exist even for the most common chemicals. In this context, the problem of emerging pollutants in soil has been mainly considered in relation to the potential leaching to groundwater and human exposure by drinking use.

Claudio Carlon also mentioned the HERACLES project (Human and Ecological Risk Assessment for Contaminated Land in European Member States) which has been launched to

improve harmonisation in the application and outcomes of risk assessment for contaminated land across Europe. HERACLES is a long-term research framework co-ordinated by JRC, in collaboration with several other European research institutes. The project addresses three levels of risk assessment: Relative Risk Assessment, Screening Risk Assessment and Site Specific Risk Assessment, and encompasses both human health and ecological risk assessment.

For more details about this presentation, see the extended abstract by Claudio Carlon (Section VII).

Management options for indoor air pollutants

The presentation given by Dimitrios Kotzias (JRC-IES) focused on the results of the INDEX and AIRMEX projects (already mentioned in his previous presentation) with particular regard to the recommendations and management options for substances identified as priority indoor air pollutants (see previous presentation by Dimitrios Kotzias in Section IV.2).

For more details about this presentation, see the extended abstract by Dimitrios Kotzias (Section VII).

III.5. Meeting the science needs for emerging pollutants: current work areas in EU

The management of emerging pollutants is directly related to their risk assessment. Two EU FP6 projects were reported on: INTARESE and NoMIRACLE, both dealing with assessment of risks.

EU FP6 project INTARESE: Integrated Assessment of health Risks of Environmental Stressors in Europe

David Briggs – project co-ordinator from Imperial College of London – gave an outline of this integrated project. INTARESE was launched in November 2005 in order to support the implementation of the European Environment and Health Action Plan, by providing the methods and tools essential to integrated assessment of health risks from environmental stressors.

Integrated assessment demands the ability to analyse and compare different aspects of the environment, human populations and health, at different spatial and temporal scales, and to produce coherent information on the combined and cumulative risks and impacts of environmental stressors in ways that can improve decision-making and enhance policy.

Integrated risk assessment requires linkage and use of a wide range of data, scientific knowledge and methodologies, including:

- monitoring technologies (including ground- and space-based environmental monitoring, biomonitoring and health surveillance)
- risk and impact assessment methodologies
- methods and tools for risk characterisation and risk communication.

In recent years, major scientific advances have been made in each of these areas. The need now is to bring these advances together, identify and fill key gaps in existing knowledge and methodologies, and develop the tools needed to make the knowledge and technologies operational.

The aim of the INTARESE project is to achieve this integration. To this end, the project will:

1. develop a conceptual framework for, and systematic approach to, integrated risk assessment;
2. review and assess the adequacy of the monitoring systems needed to support such assessments;
3. test and apply the approach through a series of integrated assessments of exposures and health risks in a number of specific policy areas, including transport, housing, agriculture, water, wastes, household chemicals and climate;
4. develop and bench-test a computer-based system and decision support tool for applying this approach on a routine basis.

For more details about this presentation, see the extended abstract by David Briggs (Section VII).

EU FP6 project NoMIRACLE, Novel methods for integrated risk assessment of cumulative stressors in Europe

Hans Lokke (NERI, DK), in his capacity as project co-ordinator presented NoMIRACLE's main goals and activities.

The objectives of this integrated project include a) developing new methods for assessing the cumulative risks from combined exposures to several stressors, including mixtures of chemical and physical/biological agents; b) achieving more effective integration of the risk analysis of environmental and human health effects.

NoMIRACLE is not specifically dealing with emerging pollutants, but the array of methods from the project may be useful in the assessment and evaluation of the risks posed by emerging pollutants.

For example, the multi-criteria ranking methods allowing for assessment of the uncertainty could be very useful in the identification and prioritisation of emerging chemicals from complex databases.

For more details about this presentation, see the extended abstract by Hans Lokke (Section VII).

How is industry contributing to developing science-based evidence for tackling emerging pollutants?

Martin Holt (ECETOC) focused his presentation on the work being done within ECETOC, which is the body in charge of commissioning task forces and workshops aimed at reviewing current scientific knowledge, identifying data gaps and priority research needs which are often then funded by the CEFIC Long range Research Initiative (CEFIC LRI).

Martin Holt stressed during his presentation that the chemical industry approach is that the management of chemicals should be based on a risk assessment that considers both hazard and exposure.

Another second key principle applied by industry is that a tiered iterative approach to risk assessment should be used in order to ensure that the level of refinement and detail of the information required for a risk assessment is proportional to the potential risks of a chemical, based on consideration of both hazards and exposures, in combination.

This approach is the basis of the 'targeted' risk assessment methodology that ECETOC has developed for the prioritisation of the substances to be submitted to the process of risk assessment under REACH.

The sources of uncertainty which exist in the risk assessment procedure can be reduced through generation of more detailed information (higher tier), through the use of more sophisticated models and by developing greater scientific knowledge of the aspects related to exposure and effects assessments.

ECETOC have had a memorandum of agreement to manage the strategic research programme on human health and the environment funded by CEFIC LRI. The programme has two main themes:

- Exposure: development and validation of fate and distribution models to improve predictions of exposure and to develop databases and tiered model systems.
- PBT and long-term risk to ecosystems, with:
 - the development of an understanding of the significance of the factors that affect bioavailability and ecotoxicity
 - the development of methods to measure degradation and improvements in the extrapolation from laboratory studies to the prediction of environmental half-lives
 - tools for modelling bioaccumulation and understanding of biotransformation in food chains
 - improvement of the understanding of mode of action and critical body burden.

Various projects were funded as part of this programme. The presentation gave some insight on GREAT-ER and MonitoringBASE projects.

GREAT-ER is a programme aimed at developing and validating a powerful and accurate chemical exposure prediction tool for use within the EU environmental risk assessment schemes. Various steps to improve the first exposure assessment tool have already been made and several lessons have been learned. As regards the application of the tool to currently discussed emerging pollutants, a pilot study in rural catchments was conducted in the UK to monitor and model the fate and concentration of pharmaceuticals and personal care products. The conclusions of the study were that the measured influent and effluent concentrations were consistently lower than predicted (typically an order of magnitude).

The second project described in more detail is MonitoringBase. The MonitoringBase database was developed as part of the LRI programme of CEFIC to facilitate retrieval of background concentrations and ranges of organic chemical concentrations in the European marine and freshwater environment. Besides measured concentrations, this database includes information, references and links to more than 160 planned, on-going and completed contaminant monitoring, survey and screening studies in the European and Arctic aquatic environment.

As concluding remarks from this presentation, it was stressed that monitoring and modelling play a major role in exposure assessment, but there is still much to do to improve the quality and applicability domain of higher-tiered models.

To improve the applicability of existing models there is a need to improve the use of measured data. As data are generated, they should be used to refine and develop existing models. To help increase accessibility to data, a dedicated data centre whose role is to co-ordinate data acquisition and dissemination (in order to harmonise monitoring and reporting formats) may be a cost-effective way of achieving this goal.

To improve the monitoring programmes, some lessons can also be learnt: attention should be given to identifying and involving regulatory authorities, local officials, trade organisations, laboratories, industry and academia in order to ensure that existing knowledge and practical

experience is used and that there is necessary acceptance of the results of the study (their endorsement is necessary). Monitoring programmes should integrate knowledge generated in the past and become more fit for purpose. Finally, there is a need to ensure that future programmes are 'information rich' and not 'data rich'.

For more details about this presentation, see the extended abstract by Martin Holt (Section VII).

III.6. NORMAN working tools and activities

NORMAN (Network of reference laboratories for monitoring and bio-monitoring of emerging pollutants; www.norman-network.net) is a coordination action project funded under the EU 6th Framework Programme (Contract N° 018486). The focus of NORMAN is on emerging environmental substances, for which data are often scarce and measurement methods are often at the research and development stage or have not yet been harmonised at the European level. This makes it difficult to interpret and compare the results and represents a major difficulty for regulatory bodies in their decision-making.

The NORMAN project was funded in order to promote the creation of a network of reference laboratories, research centres and related organisations in order to:

- improve the exchange of data / information on emerging substances
- foster the validation and harmonisation of measurement methods to meet the demands of risk assessors and risk managers.

The main activities of the network were presented by the various Sub-project leaders.

NORMAN networking activities (Sub-project leader: Anne-Marie Fouillac – BRGM, France)

The objective of this part of the project work plan is to organise the functioning of the future permanent network, i.e. designing its structure, identifying its members and activities.

As part of its current networking activities, NORMAN carries out a regular literature research in the field of emerging substances (scientific watch), which is used to feed its databases and as an input to the NORMAN newsletter (which contains a section dedicated to summaries / critical reviews of selected recent research publications)..

In addition, NORMAN maintains a network of NORMAN Contact Points in the different EU countries in order to facilitate gathering of information on emerging substances from national reports and research initiatives (i.e. the information that appears in the so-called grey literature).

Finally, NORMAN organises workshops and conferences. In total four events will be organised during the life of the EC contract.

NORMAN databases (Sub-project leader: Jaroslav Slobodnik – EI, Slovakia)

NORMAN facilitates international co-operation and access to the existing data via three databases: (i) EMPOMAP: a database of leading European experts, organisations and projects dealing with emerging substances, (ii) EMPODAT: a database of geo-referenced monitoring and occurrence data accompanied by the ecotoxicological information from bio-assays and biomarkers and (iii) EMPOMASS: a database of mass spectrometric information on provisionally identified and unknown substances.

NORMAN validation protocols (Sub-project leader: David Schwesig – IWW, Germany)

NORMAN is developing a common European approach to the validation of both chemical and biological methods for the respective monitoring and bio-monitoring of emerging pollutants (or their effects) in a broad range of matrices. This protocol addresses three different validation approaches, in increasing order of complexity:

1. intra-laboratory validation (research level)
2. basic external validation (transferability at expert level)
3. inter-laboratory validation (routine level)

After testing of the first protocol in three case studies designed to match the three levels of validation, the final version of the protocol will be prepared and the implementation of the protocols in the field of European Standardisation and European Legislation will be attempted. That will be done by initiating negotiations to launch New Work Item proposals at CEN level.

NORMAN case studies (Sub-project leader: Damià Barcelo')

As explained above, in order to test these protocols and the ability of the network to meet EU demands for monitoring emerging pollutants, three case studies are being undertaken, involving partners from a wide selection of Member States, including New Member States.

WP-C1: Oestrogens in sewage treatment effluents for the validation and harmonisation of an analytical methodology for research laboratories;

WP-C2: Non-steroidal anti-inflammatory drugs (NSAID) in water for the validation and harmonisation of an analytical methodology for reference laboratories;

WP-C3: Brominated flame retardants (DecaBDE) in dust for the validation and harmonisation of an analytical methodology for routine laboratories.

The final goal of the project is to extend the current consortium of partners and to implement a permanent network operating after the project finishes at the end of 2008. In the future, NORMAN could operate as a network in the field of emerging substances with possible activities of:

- Scientific watch (horizon scanning activities)
- Organisation of expert group meetings (to discuss specific topics at a more technical level) and more wide-scope conferences (aimed not only at scientists but also at competent authorities and other stakeholders)
- Preparation (as a result of these technical meetings) of position papers as a means of communicating with regulators;
- Provision of QA tools for the validation of measurement methods by:
 - identification of substances of high priority
 - checking of the availability of methods and status of validation
 - bringing together experts, PT providers or other bodies for rapid organisation of studies for method validation
- Maintenance of databases (with regular update and validation of the information) for sharing of information
- Identification of a list of priority issues on which to start research programmes.

The definition of the strategy for the implementation of the future network is part of the current work of the NORMAN partners.

IV. Conclusions from the parallel sessions

IV.1. Session 1 – Data sources for emerging pollutants

Chaired by Jaroslav Slobodnik (EI, Slovakia), Rapporteur Heather Leslie (IVM, the Netherlands)

The chairman gave a brief overview and demonstration of the three NORMAN databases, EMPOMAP, EMPODAT and EMPOMASS (see previous section). The ICPDR database (www.icpdr.org) was used as an example for EMPODAT, which was not yet online, as a basis for the discussions.

The discussion was aimed at identifying problems and gaining input to the design of the final databases. The workshop also served as an opportunity to disseminate information on the databases to the participants.

The following questions were put to the participants:

1. Who will be the user(s) of the NORMAN databases?
2. What do you want to get out of these databases?
3. How can the data producers be motivated to contribute their data to the NORMAN databases?
4. What should be the minimum QA/QC metadata information (next to the name of the compound and its concentration) for you to trust the data?

For clarity's sake, the main outcomes of the discussion with participants in Parallel Session I are summarised by database.

EMPOMAP

It is a great idea and is likely to contain a large percentage of the total number of emerging pollutants (EP) experts and will therefore be widely used.

Users would use it as a tool to find other experts (worldwide if possible) working in the same field. If possible, the EMPOMAP database should be interlinked with EMPODAT.

EMPODAT (the discussion focused on the chemical monitoring part, less on the biological monitoring module)

The database is likely to be used by people looking for:

- access to data in a fast and efficient way as an alternative to methods used pre-NORMAN database (currently, the approach to finding ES information is: internet search engines for grey literature reports and proceedings & abstracts from conferences and symposia, Web of Science for peer reviewed literature, ask colleagues and other contacts, visit conferences, symposia, workshops...)
- information about measured concentrations reported in other countries: is the substance widely detected or only detected in specific areas?
- indication of the concentration levels in different matrices and information about which matrices are the best ones to detect an ES in
- help define ESs that should be included in monitoring programmes (and therefore help the design of monitoring programmes)
- data to guide the risk assessment and risk management processes
- information about ES's (potential) toxicity, if available (e.g. even if it is only IAUC data on genotoxicity/carcinogenicity, or suspected mode of toxic action class)
- find basic physico-chemical data on the ES (although there may be other better or easier databases for that)

- information on the kinds of methods available to measure an ES and what the potential pitfalls are
- indication of whether there is a method already available using instrumentation to which they have access at their laboratory
- simply browse to check out 'what's new' on the ES scene; therefore it would be useful to be able to search according to some 'relevance/significance' or 'novelty' term (such as most recently added substances, substances already detected in all EU countries, highest number of reported detects in a matrix, known to be hazardous, etc., and combinations thereof).

As regards the information that users would like to get from the database, the preference for most users is for details and raw data over aggregated, integrated data.

Moreover, users would like to be able to judge the quality and reliability of the data in the database. For this to be easy to judge, QA/QC information could be included such as: level of blanks (most ESs are being detected at very low concentrations), whether blanks are subtracted from the reported value, LOD and LOQ, uncertainty and how it is estimated (top-down or bottom-up approach), the use of CRM or RMs, control charts, ¹³C labelled internal standards and whether samples were pooled.

In any case, as regards the minimum QA/QC information to be included in the database, it can be concluded from the discussion that one of the major challenges for the EMPODAT database will be to find the right balance between 'keeping it simple and uncomplicated' and including a lot of QA/QC and metadata to make the database more useful and reliable. Data should always be associated with the data provider to enable database users to decide for themselves how reliable and usable the data are. This should be very clear to the database user (it could be a scientist, regulator, NGO, industry, policy maker, general public) through a warning/disclaimer with a clear explanation of what to look for in terms of data quality. Some fields should be made compulsory (e.g. LOD, uncertainty, analytical instrumentation). The ICES database is an example of one containing a high degree of metadata, but at a significant cost.

Representatives of several countries expressed willingness to supply data for the NORMAN monitoring database, but, each country supplies data in its own format. This is currently not a drawback because there are personnel available to convert the formats. However there is reluctance to provide detailed data: aggregated data are commonly reported. No one foresees problems with entering previously published data into the database. The strength of commitment to voluntarily supplying (and certainly to voluntarily entering) data in the database is not clear, however. The time factor for volunteer data entry is critical.

Regulators suggested that they will use the database only superficially if the data provided are unreliable or lack supporting QA/QC information. They suggested avoiding duplication of effort by linking as much as possible to other databases dealing with emerging substances and their ecotoxicity (e.g. MODELKEY).

Industry is wary of databases containing only measured ES concentrations because of the lack of control over the interpretation of the data in them. And defining their products as 'emerging pollutants' is dangerous/difficult for industry to endorse, because the word 'pollutant' strongly implies 'harmful' and in many cases this is not (yet) proven for ESs. Industry is willing to supply data that are already published in its own databases.

EMPOMASS

This database will be useful to laboratories, but the time needed to enter MS data may inhibit the voluntarily uploading of MS information. The database will be considerably more straightforward for GC-MS spectra than for LC-MS(MS) spectra. There is an on-going debate on

what to do about LC-MS(MS) data – characterised by high variability in spectra and low comparability (different voltages generate different numbers of ions).

In this context a question was raised: Do we want varying spectra or nothing at all? It has been concluded that it is useful to include both MS-MS (parent and main daughter ions) and exact mass measurement data accompanied with the detailed information how the mass spectra were obtained (type of instrument, mobile phase, voltage settings etc.). The collection of exact mass determination data was strongly recommended as it significantly narrows down the number of potential candidate substances for unambiguous identification.

Environmental screening using MS techniques shows typically several tens (water) or hundreds (sediments) compounds in each analysed sample, 40-60% of which are provisionally identified based on a mass spectral library search. Unfortunately, there are a lot of unreliably “identified” compounds” – first hit from library is often (erroneously) reported as an ES without any additional support information. It was suggested to collect in the database also the raw mass spectra of provisionally identified compounds next to the extracted numerical information on major ions in the spectra. This will enable to use one’s own tools/software to judge the quality of the mass spectral interpretation or to interpret them independently.

Next to the provisionally identified substances there are numerous unknown substances present in samples. It was agreed that storing mass spectral information on these unknowns in the same way as for provisionally identified substances is useful. A proposal was made to link EMPOMASS with MODELKEY database of mass spectra and to use AMDIS (software developed by the US Defence Ministry) for spectral search and interpretation.

Question arose as to what actions are triggered by detecting an unknown substance – in most cases NO action is taken. Constant large peaks in the chromatograms are not necessarily associated to the presence of toxic compounds (e.g., could be degradation products of leaves in the water), whereas the small peaks may be causing the greatest problems. With regard to the various research projects on toxicity of individual fractions of samples (e.g., MODELKEY), the database should include a possibility to store/interpret data from fractionation analyses.

IV.2. Session II – Prioritisation criteria for emerging pollutants

Chaired by Nick Cartwright (Environment Agency, UK), Rapporteur Marina Coquery (Cemagref, France)

The following questions were put to the participants:

1. How do we select the chemicals to prioritise?
2. What are sufficient criteria and data to prioritise for a) investigation or b) action?
3. What examples illustrate the main deficiencies in current approaches?
4. What are the main data gaps?
5. How do we deal with uncertainties & data gaps?
6. How should we rank relative priorities?
7. How should we validate the ranking?

1- How do we select the chemicals to prioritise ?

The most pragmatic approach to the selection of candidate substances is the one that starts from a compilation of the existing priority lists. This approach, however, is not sufficient if emerging pollutants are to be taken into account, and should be complemented by taking into account:

- newly detected substances (results from research studies, e.g. non-target screening studies, with new peaks detected)
- metabolites of parent compounds,
- substances with low persistence but continuous emissions (e.g. steroids, glyphosate, triclosan),
- substances with low K_{ow} but that could bioaccumulate (e.g. nanoparticles, PFOS),
- (eco)toxicological effects, with particular attention to long-term, chronic effects,
- use patterns, e.g. low-volume but highly toxic substances with diffuse usage,
- structural characteristics, i.e. infer from a known group of substances the inclusion of substances with similar physico-chemical properties.

2- What are sufficient criteria and data to prioritise a) for investigation or b) for action?

The first step is to clearly identify the purpose (aim) of the prioritisation process. For this purpose, two levels of prioritisation could be considered in time:

- investigation (screening/spot monitoring),
- action (surveillance/regulatory monitoring for emissions reduction, risk reduction, etc.)

General comments:

- Before running a prioritisation it is important to keep in mind what the protection goal is (e.g. Protection of the environmental ecosystems or protection of human health? What are the environmental media addressed and what is the specific target?)
- The criteria for prioritisation need to be set so that the final list of prioritised chemicals is 'manageable'. There is therefore the need to include a sufficient number of criteria.
- There is a very large number of possible criteria for deciding whether a new substance should be included in a monitoring programme, so criteria should be chosen depending on the purpose of prioritisation and availability of data.

a) Prioritisation for investigation:

When prioritisation of contaminants has to be carried out for investigation purposes, the ultimate aim is to identify and prioritise areas where there is a knowledge deficit and where there is high potential risk that should not be overlooked (e.g., pharmaceuticals are measured in the environment, we have documented acute effects but limited information is available on chronic effect => investigation is needed in order to obtain more data to prove/discard potential risk).

Possible criteria for prioritising substances for investigation purposes are:

- For exposure considerations:
 - Occurrence: information on the use pattern and volume, release of substances; production volume; environmental concentrations if available
 - Properties of substances (physico-chemical properties, PBT, CMR, ...);
- For hazard considerations:
 - Biological effects, properties of substances.

Additional comments made about prioritisation of chemicals for *investigation purposes*:

- There is value in the diversity of approaches to prioritise substances for investigation as this gives a wider overall coverage; But the approach taken needs to be documented so it can be evaluated.
- A more precautionary approach is recommended: some degree of false positive is acceptable. But the screening criteria need to produce a realistic list of chemicals that can be evaluated within the resources available. It can be an iterative process to get criteria/thresholds that select a realistic number of chemicals.
- Surrogate data are acceptable to collect information on criteria, whenever data are missing (e.g. K_{ow} instead of actual bioaccumulation data).
- The prioritisation methodology should get to conclusions in a short time.
- Establish criteria to exclude substances from the list (e.g., NO high-volume chemicals,...).

- Public concern can trigger the studies: e.g. pharmaceuticals, lots of data available already, more work done because of the public and public authorities interest.
- The greater the severity of the risk – even if high uncertainty – the higher the prioritisation.
- For risk assessment: the fact that nothing is known on the substance is a criterion.

b) Prioritisation for *action purposes*:

Prioritisation for action refers to the selection of chemicals to be included in routine monitoring programmes carried out by the public authority.

When going from investigative to action purposes (e.g., surveillance monitoring) it is considered crucial:

- to have full understanding of the regulatory regime that is going to be used (e.g. WFD for water).
- to reduce uncertainty about data (and therefore a tiered approach should be applied in order to determine where effort should be invested initially in order to reduce uncertainty)
- to get a good prioritisation in order to save resources in the future.

3- *What examples show the main deficiencies of current approaches?*

As regards current prioritisation approaches, one important weakness of current prioritisation methodologies is that mixture effects are not taken into account. However, the main deficiencies are mainly related to the data used rather than to the methodology itself (methodology criteria).

Some examples were discussed:

- Limited ecotoxicity data: in many cases it is necessary to use acute ecotoxicity data because there are no chronic toxicity data available (e.g. for pharmaceuticals, they exist but are not available, not public; there is no classification and labelling for environmental toxicity for pharmaceuticals)
- Spatial and temporal information on occurrence of the candidate substances: it is crucial to ensure that use/exposure data are used at the right geographic scale, but the source of the information is not always sufficiently known.
- The low concentration levels in the environment typical of emerging substances lead to significant analytical challenges which can influence the quality and reliability of those data.
- The information on metabolites (degradation of parent compounds; conjugates for pharmaceuticals) is not always sufficiently known and/or not fully taken into account in the prioritisation methodologies.

It was also stressed that it is very important to document accurately the way in which the prioritisation process was carried out, i.e. clearly explaining the criteria applied, databases used, etc. This is very important to allow reference back to the choices made.

4- *What are the main uncertainties and data gaps?*

Some of the considerations made above also apply here. Moreover, the group made some additional remarks, focusing on the current uncertainties and gaps associated with monitoring data. For risk assessment at the European scale, there is a need for good comparability of datasets available from the different European countries. Monitoring data for emerging substances are often not comparable from one country to another and sometimes from one laboratory to another, and this represents a major gap today.

The quality of the data and the knowledge of the QA/QC information associated with the data are also considered important issues in the selection / use of valid data in the prioritisation process. This QA/QC information about the data is typically not sufficiently known and/or not used in the prioritisation process.

Regarding uncertainty of monitoring data, one should not forget that the uncertainty associated with spatial distribution is usually higher than the analytical uncertainty.

However, an important consideration about the quality of the data is that the required quality criteria should depend on the purpose of the prioritisation. Quality criteria should in fact be different for screening and for routine monitoring (associated with compliance checking purposes): it is reasonable to accept higher uncertainties at the beginning of the process (screening), whereas there is a need to reduce uncertainties when moving on to regulatory monitoring, for instance.

5- Methods of ranking

Criteria can be set for different targets, but how should individual rankings be aggregated? Various methodologies were discussed.

Prioritisation of pharmaceuticals: starts with an assessment of sales data / consumption patterns (TGD model) + considerations about behaviour / properties of the substances, then compares the calculated results with measurement data for selected contaminants.

For drinking water, the following items are considered in the ranking process: toxicity data + occurrence in the source and drinking water + efficiency of drinking water treatment + media attention.

For the definition of the list of priority substances under the Water Framework Directive, the COMMPS (combined monitoring-based and modelling-based priority setting) procedure started with a compilation of existing lists of PS. The COMMPS methodology is currently under revision and it is too early to make firm statements. A proposal was made for separate use of Exposure and Effect data => leading to two ranks to identify potential risks (based either on exposure or on effects). However, a risk approach based on a combination of hazard and exposure is favoured.

In general a final stage of expert judgement for ranking is needed and applied in most prioritisation methodologies.

6- Validation of prioritisation procedure

The validity of a prioritisation process is limited in time; there is a need to go back to the results and check whether substances that have emerged since the prioritisation exercise would have been identified by the application of the proposed methodology.

How would one know whether the procedure was successful?

- External criteria of success: the recognition that the procedure delivered an outcome
- Internal criteria: feedback from experts proposing the procedure;
- Should include the possibility of 'proving' the prediction by lab experiments.

IV.3. Session III – Monitoring tools and analytical methods

Chaired by Peter Lepom (UBA, Germany), Rapporteur Georg Hanke (JRC-IES, EC)

The aim of Parallel Session III was to discuss items relating to the approaches and analytical techniques for detecting and quantifying emerging pollutants in the environment.

Two main groups of questions were prepared for the participants in order to promote discussion of:

- ✓ the IDENTIFICATION of emerging pollutants in the environment by monitoring efforts and
- ✓ the QUANTIFICATION of emerging pollutants in order to assess exposure and thus provide the necessary concentration data for risk assessment.

The questions and main outcomes of the discussion with the participants of parallel session III are summarised below.

1- How can new emerging pollutants be identified?

The strategies for monitoring emerging pollutants comprise different approaches, including:

- hot-spot search at sites which, according to impact assessments, are most likely to emit pollutants
- composite sampling (daily/weekly, depending on substance characteristics) in order to obtain temporal coverage
- from source-to-environment approaches (WWTP surface water drinking water), following known pathways
- add-on to existing monitoring stations, by extending the range of monitored substances in routinely taken samples
- monitoring areas with only background concentrations
- accumulation in ecosystems: sewage sludge, biota
- monitoring human exposure: e.g. through mother's milk, food.

The applied monitoring strategy is dependent on the available funding!

- Can emerging contaminants be detected by chance?

In the past, several important groups of contaminants in the environment have been discovered by chance, i.e. as by-product of other investigations. Examples are Alkylphenols and PCBs, which were detected by researchers actually looking for other substances.

Regulators have recently been obliged to identify emerging risks associated with chemical pollutants, e.g. for the aquatic environment within the Water Framework Directive, through the identification of river basin-specific pollutants. Concepts are therefore needed in order to prioritise efforts/resources and allow the application of the most effective measures for protection of the environment.

The assessment of production data, usage patterns and estimates of losses plays an important role in the identification of substances of possible concern to the environment. The REACH concept will help in obtaining this information.

Other unexpected substances might occur through the importation of products from countries in which no strict chemical policy is in place. These can be e.g. substances used in tanneries in non-EU countries.

Naturally occurring substances, such as algal toxins, can also be of relevance and their frequent occurrence in environmental samples might lead to investigations of their toxicological properties.

The Toxicity Identification Evaluation (TIE) approach can also help in identifying emerging pollutants in the environment. For further TIE considerations, see below.

- What is the practical significance of screening methodologies (GC/MS, LC/MS) in the identification of EP?

Analytical methods that allow the measurement of a large number of pre-defined target analytes in a single analysis ('target analysis') or those that perform a mass spectrometric full scan detection of all substances that exit from a gas- or liquid-chromatography separation ('non-target analysis') are most promising in analysing environmental samples for emerging pollutants.

While target analysis is now routinely done, including for larger numbers of substances, the applicability of non-target analysis depends on current technical developments. For non-polar substances, analysed by GC/MS, the availability of good spectra libraries is essential; but data evaluation is very time consuming.

For polar compounds, non-target screening (LC/MS) has just recently become possible with new instrumental developments (the so-called 'Q-trap' instrument generation).

Libraries for LC/MS are not readily available and matrix effects, particularly in matrix-rich samples, make non-target analysis difficult. Further development is expected, as until now the 'Universal detector' has so far been lacking for LC/MS.

- What are new promising analytical techniques for EP identification?

Linked to the previous discussion item, the most promising analytical techniques are:

- Target screening by LC/MS/MS (ion-trap) for 200-300 compounds has recently become possible, although sophisticated instruments are needed.
- Multiclass/multicompound screening allowing combination of substance groups with different physico-chemical properties in a single analytical run. Examples include e.g. pos./neg. ion mode switching in LC/MS and programmed temperature injection techniques in GC/MS.
- Multidimensional gas chromatography with time-of-flight mass spectrometric detection (GCxGC-TOF-MS) is a powerful new instrumentation. It allows the chromatographic separation of very complex mixtures and their identification by the mass spectral fingerprint. Huge amounts of data are created and further development of instrument and data evaluation algorithms is necessary prior to routine application.

- What is the significance of effect-based measurement techniques in EP identification?

Toxicity Identification Evaluation (TIE): fractionation of a sample and testing for toxicity after fractionation can be combined with chemical analysis to identify the cause of toxic effects.

At the concentration levels of chemical substances occurring in the major European rivers the acute toxicity cannot be measured by standard testing, as these tests are not sensitive enough.

Moreover, toxicity in the environment cannot be completely explained by summing the detected pollutants that are known to be toxic.

As toxicity tests often do not detect chronic effects and bioaccumulation, they cannot be used for detecting substances that occur in the environment at lower concentrations and which can

lead to adverse effects only after biomagnification and -concentration in the food chain. In these cases only the chemical analysis can act as an early warning for upcoming risks.

The approach used in the Modelkey project (fractionation and analysis) can be of benefit in that respect.

2- How to monitor (quantify the concentration levels of) new emerging pollutants?

Once specific emerging contaminants have reached a certain degree of attention, there is need for comparable concentration data in order to assess the related risk. Often the first datasets are produced by research groups and are published in the scientific literature.

- Can we really trust published data on EPs?

Not always. They should be interpreted with care, as QA/QC information is often insufficiently documented. It is essential that QA/QC data should be provided along with analytical results and studies. An increasing level of QA/QC metadata is currently required for publication (e.g. by Environmental Science and Technology).

- How to get valid data on emerging pollutants?

The following practical limitations on obtaining good quality data have been identified:

- Availability of standard compounds with a certified quality
- Availability of isotope labelled standards and reference materials
- Availability of proficiency testing schemes for emerging pollutants
- It is important that an intense exchange of methods under development and samples for comparison purposes between laboratories occurs, in order to improve performance and share experiences.

- What are the mechanisms for the user to check data quality?

Data quality can only be assessed if metadata on QA/QC are provided along with the data. For use of the data in first assessments for an emerging pollutant it can be accepted that the level of QA/QC measures applied and documentation of QA/QC is lower than for compliance monitoring.

- How can knowledge from expert laboratories be transferred to others?

Analytical methods and approaches are commonly being developed in research laboratories. At that stage the methods can sometimes demand high skill levels. Instruments and equipment used might not be readily available or might even have been developed by the laboratory for that specific purpose.

Within the Norman project and during the discussions, the terminology of an expert laboratory describes an institute that performs monitoring, not necessarily with standard approaches and at a high level of sophistication.

Routine laboratories instead demand methodologies which are highly automated, easy to insert into an existing laboratory, with fully developed QA/QC procedures, validated and tested in interlaboratory trials, which demands mostly routine skills from the operators.

Routine laboratories aim for the most cost-efficient operation, often performed in a competitive economic context. At this level, methods standardised at EU level via CEN (European Committee for Standardisation) are used in most laboratories.

Knowledge transfer from research to expert lab can be facilitated by:

- Distribution of developed methods through workgroups
- Analysis of samples in parallel
- Use of non-certified reference materials
- Common participation in research projects.

Knowledge transfer from expert to routine laboratories can be facilitated by:

- Hands-on courses/workshops
- Obligation for accreditation
- E-learning (to be developed).

IV.4. Session IV – Models and prediction methods

Chaired by Willie Peijnenburg (RIVM, the Netherlands), Rapporteur Michael McLachlan (ITM, Sweden)

Working Group 4 discussed the role that models can play in the field of emerging pollutants, with a particular focus on identifying pollutants, developing analytical methods, and applying these methods in monitoring programmes. After establishing some general guidelines on the use of models in this context, the group went on to address four specific questions.

The following list of questions was put to the participants:

1. How can models help identify potential environmental pollutants? Examples?
2. When developing analytical methods for emerging pollutants, what questions can models help answer?
3. When setting up monitoring programmes (or conducting an initial screening) for emerging pollutants, what questions can models help answer?
4. How can monitoring data be used to improve models? Examples?

The results of the discussion with participants in parallel session IV are summarised below.

General comments:

As the fundamental guiding principle when using models, it is important to realise/acknowledge that models are always wrong, as they can only represent a part of reality. However, this does not prevent models from being extremely useful for certain applications. It is important to ascertain and communicate the usefulness and the limitations of a model.

Another important issue in modelling is the level of model complexity. Models can have widely varying levels of sophistication, whereby more complex models can as a rule describe more aspects of the system being modelled. However, the most sophisticated model may not always be the best solution for a given problem. Sophistication generally comes at the cost of more detailed model input requirements, which can put a considerable burden on the model users and – in the worst case – prevent use of the model if the required information is not available. Furthermore, the added sophistication in a more complex model may address behaviour of a part of the modelled system that is not relevant for the question being addressed or that does not reduce the overall model uncertainty. To achieve an appropriate level of model complexity, one must find a balance between minimising model uncertainty and minimising data requirements. Since models of the environmental behaviour of emerging pollutants typically contain many sources of large uncertainty (e.g. physical chemical properties, emissions), the models applied in this field are typically quite simple.

1- How can models help identify potential emerging pollutants?

Models can be used to predict the levels of chemicals in the environment based on their emissions, their physical chemical properties, and the characteristics of the environment. The spectrum of useful modelling techniques is broad, ranging from simply ranking production/emissions estimates through material flow analysis to multimedia fate and transport models. Models (in particular QSARs) can also be used to predict the toxicity of chemicals on the basis of their structure. Hence, models are potentially potent tools for identifying potential emerging pollutants, even in the complete absence of environmental measurements or toxicological data.

The group was not, however, aware of any past or current emerging pollutants that have been identified via models. Other approaches, such as non-target analysis of environmental samples or observations of effects have been responsible in the past.

The group was convinced that this is now changing. Models have now reached a standard and achieved a level of acceptance in the scientific and regulatory community that has resulted in them being increasingly applied for chemical screening processes. One example is the Existing Substances Evaluation by Environment Canada in which 23000 chemicals are being prioritised for further study. Another is the Swedish Environmental Monitoring Programme, in which models are used to select chemicals for target analyte screening. Decamethylcyclotrisiloxane (D5) is an example of a potential emerging pollutant where models have played a significant role in stimulating the investigation of a chemical's occurrence in the environment.

Despite the blossoming potential of models, the group was also keenly aware of their limitations. One weakness that should be emphasised is the inability of current modelling tools to identify emerging pollutants where the problematic chemical is a metabolite. In addition, there is a need for better integration of the modelling tools available so that e.g. models for predicting physical chemical properties from molecular structure, for predicting chemical fate, and for predicting chemical toxicity are in a common package. The group was also of the opinion that models will not replace the other techniques for identifying emerging pollutants, but that they will be a useful additional tool.

Finally, there was a plea for a trigger to induce a generalised theory that allows one to assess that a chemical has the potential to become an emerging compound. It was concluded in this respect that there is a need for new ways to learn from experience.

2- When developing analytical methods for emerging pollutants, what questions can models help answer?

The group was also of the opinion that models are very useful in the analytical method development process, once a potential emerging pollutant has been identified.

A model assessment of an emerging pollutant's distribution and behaviour in the environment can identify which environmental media are most important for the chemical's fate and where the highest concentrations can be expected. This information can be used to select the matrix for which the analytical method will be developed. Chemical fate models also calculate the expected distribution of the chemical amongst different phases in a given medium (e.g. in the gas phase vs. associated with aerosols in the atmosphere), which can be decisive in developing both the sampling and the analytical methodology. Furthermore, the model predictions of the expected concentrations in the selected medium can assist the analytical chemist in selecting the limit of detection required if the method is to be useful. If information is available on the formation of transformation/metabolism products, models can also predict whether the native

species or the product will be the dominant form in the environment and thus more amenable to analysis/monitoring.

Another kind of model, namely models of sorption, can be useful in assessing the manner in which a chemical is bound in a given matrix. This can help the analytical chemist in designing extraction methods for emerging pollutants.

Genomics and bioinformatics are also expected to open up new possibilities in method development in the near future. It is expected that these techniques will be useful for developing / identifying methods to measure chemical effects.

3 - When setting up monitoring programmes for known emerging pollutants, what questions can models help answer?

The group also elaborated on the ways in which models can help to develop monitoring programmes. In analogy to the discussion above, chemical fate and transport models can be used to identify the matrix that is most suitable to meet the goals of a monitoring programme (e.g. if the goal is time trend monitoring, this may be the matrix expected to react most quickly to changes in pollutant emissions). Furthermore, they can indicate which phase of a matrix should be sampled (see above) or, in the case of biological monitoring, which species, sex, age class, etc. The model predictions of the variability of the pollutant levels in the matrix in space and time can help in choosing where to sample and when to sample, and what spatial and temporal integration is optimal. Models can also be invaluable in assessing whether the available analytical methods have quality assurance parameters (e.g. precision, limits of quantification) that are sufficient to meet the goals of the monitoring programme. Also, not to be forgotten, models can indicate when monitoring programmes can be stopped, for instance when no further useful information is expected.

In summary, it was concluded that applying models in setting up and running monitoring programmes can significantly reduce the costs and improve the programme's effectiveness. This tool can also reduce the level of unneeded sampling, which may have important benefits, not only with regard to optimal utilisation of available financial resources, but e.g. also in reducing the pressure on sensitive or endangered species. Examples of where models are already used in developing monitoring programmes are in combating oil spills, in assessing VOCs in the indoor air environment, in cases of groundwater contamination, and in the monitoring of emissions around chemical production facilities. The group felt that there is great potential to extend this tool to other applications. However, they noted that an essential prerequisite in designing monitoring programmes, namely the clear definition of a programme goal, is just as vital for the application of models in this context.

4 - How can monitoring data be used to improve models?

There was unanimous agreement on the importance of monitoring data for improving models. It is only with field data that models can be effectively evaluated, and model evaluation is the key for building trust in the models. Hence, modellers and environmental analysts / scientists running monitoring programmes have a common interest, namely in working together.

To extract the potential benefits inherent in co-operation between these groups, communication is the key. The group recommended that both analysts and modellers should be involved in planning monitoring programmes. A minor change in a monitoring programme can make a huge difference in the value of the data for model evaluation, and (as noted above) the input of modellers can result in better and more economical monitoring programmes. Examples of where such collaborations have been successful include the assessment of the fate of detergents in European rivers (GREATER) reported by Martin Holt at the workshop and the work of EMEP in studying long-range atmospheric transport of POPs. The group expressed the hope that this kind of co-operation would increase in the future.

V. Conclusions and recommendations

The following concluding remarks can be made as a result of the presentations made and the discussions in the parallel sessions.

1) In the past research priorities have focused on priority pollutants such as POPs, pesticides, toxic metals and radionuclides. Only recently has the attention of the scientific community started to shift to emerging contaminants. Therefore a major challenge will be to identify the chemicals which have the potential to become dangerous in the future. The criteria of persistence, bioaccumulation and toxicity which are used as primary factors to estimate the risks of chemicals to humans and ecosystems, need to be revised to improve our capability of predicting the potential of a chemical to become an 'emerging contaminant'. For example: contaminants that are continuously released to the environment can behave as "pseudo-persistent" substances, regardless of whether they are structurally stable (because their degradation is offset by their constant emission).

2) It is noted that the 'emerging compounds' issue is at a more advanced stage in the water field than in the other fields. This is mainly due to the specific focus on emerging pollutants within the Water Framework Directive which has required Member States to address this issue. There is also an increased number of exposure routes in the water field.

Nevertheless, the 'emerging substances' issue should be looked at as a 'global issue'. Because substances have different sources and pathways and can transfer from one compartment to the other, it is logical and scientifically correct to consider all environmental compartments and follow the whole environmental cycle of a substance.

3) For most of the occurring emerging contaminants, risk assessment and ecotoxicological data are not available and it is therefore difficult to predict which health effects they may have on humans, terrestrial and aquatic organisms and ecosystems. Information about sources, entry routes, and fate is also of high importance. Since only limited resources are available for including additional emerging substances in the survey programmes, it is crucial to:

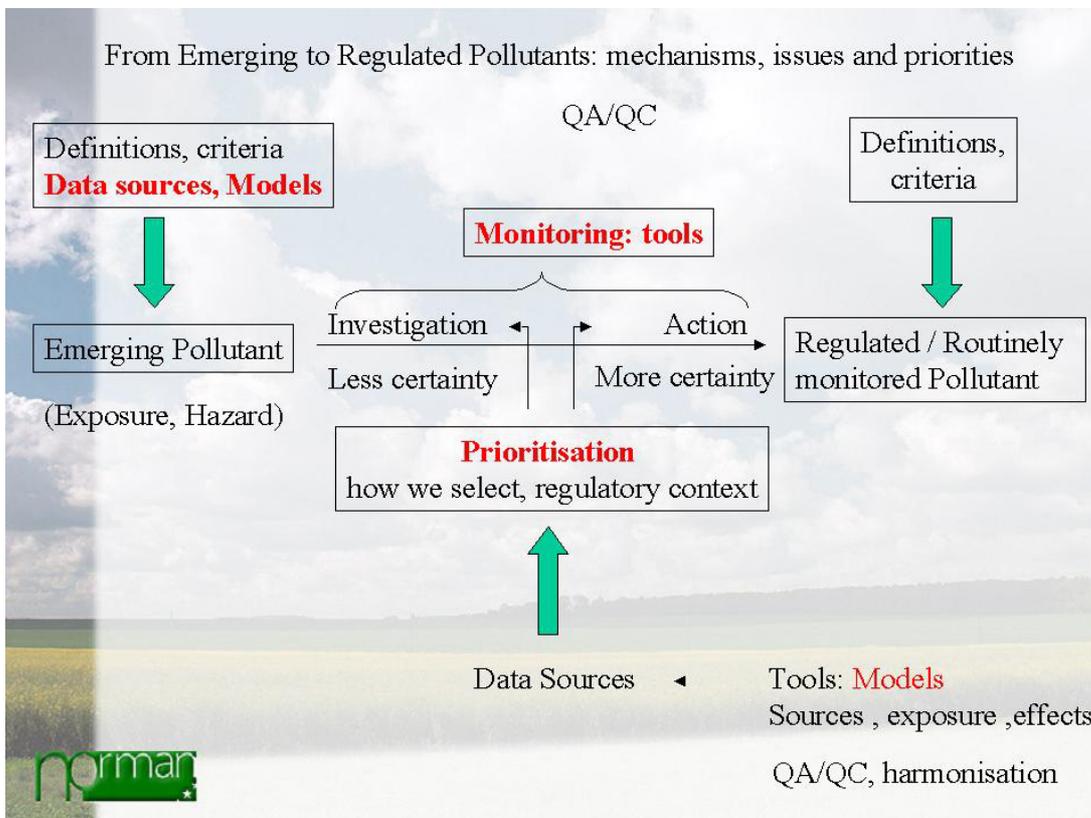
- optimise the efficiency of all processes and find ways to get free resources by benefiting from collaborative activities
- improve collaboration between research institutes for a more efficient exchange of data and information already available on emerging contaminants (development of common databases and common data reporting formats);
- improve collaboration between modellers and environmental analysts / scientists running monitoring programmes: communication is the key to realising the potential benefits inherent in co-operation between these groups;
- develop and improve harmonisation of techniques that combine chemical analysis and detection of biological effects.

In conclusion, it is crucial that we start looking at the overall system, making better use and integration of all the tools available (see picture below):

- monitoring tools (analytical and biological methods to allow identification of emerging substances and quantification of their level of occurrence and their effects)
- modelling tools in synergy with the monitoring tools (for prediction purposes and more effective use of resources)
- QA/QC tools to ensure that the data are reliable, comparable and fit for purpose
- databases for collection and comparison of data / benchmark values with a set of relevant metadata to understand the significance of the data, accessibility and use of QA/QC information.

All these items should be the input to the prioritisation tools, which should support the process of identification of a substance as an 'emerging substance' to the point where we have sufficient and commonly accepted information for sound decision-making (about a substance moving

from 'emerging status' to 'regulated status'). All these components are currently developed more or less separately: one way to reduce the gaps in the overall process would be to integrate these component parts more closely.



VI. Extended abstracts of the presentations

Emerging substances in water

Thomas Ternes
Federal Institute of Hydrology (BFG)
Am Mainzer Tor 1, 56068 Koblenz, Germany

E-mail: ternes@bafg.de

INTRODUCTION

The focus of environmental research has recently been extended from the more “classic” environmental pollutants such as PCBs, DDT, dioxins and pesticides to the so called “emerging compounds” which have detected very recently in the environment, but are released in the environment for a longer time. Emerging pollutants are pharmaceuticals, hormones, cosmetic ingredients, biocides which enter the environment mainly via regular domestic use (Daughton and Ternes, 1999). Furthermore, compounds are recently detected leaching out of electric products such as flame retardants or used in products to create inert surfaces such as perfluorinated compounds. Since GC is to some kind restricted to uncharged, nonpolar compounds, polar compounds can be analysed by GC/MS only after they are transformed to more volatile derivatives. Within the last 10-15 years the increasing use of LC Tandem MS has led to a “revolution” in environmental analysis, providing a new analytical tool which enables the identification of extreme polar organic pollutants such as pharmaceuticals without derivatisation down to ng/L levels in all kinds of water bodies (wastewater, surface water, ground water, drinking water). Hence, the LC tandem MS offers a new window to determine polar organic compounds in drinking water processes and in the final drinking water itself. More than 2800 different substances are used only as pharmaceutical ingredients in North America and the EU today, including painkillers, antibiotics, antidiabetics, betablockers, contraceptives, lipid regulators, antidepressants, antineoplastics, tranquillisers, impotence drugs and cytostatic agents. Many of these compounds are transformed in the body. A combination of unchanged pharmaceuticals and degradation products are therefore present in raw and treated wastewater. Personal care products comprising the ingredients of shampoos, liquid bath admixtures, skin care products, dental care products, soaps, sun screen agents, hair styling products etc. are used in enormous quantities throughout the world. In the end of 1990s their annual production exceeded 500000 t for Germany alone. Fragrances, UV blockers and preservatives are known to be present in the environment. They enter the wastewater via their regular use during showering or bathing.

Routes into environmental waters

For most human pharmaceuticals, hormones, biocides, ingredients of personal care products and food ingredients private households are the main source to enter municipal wastewater. Hospital wastewater also contributes to the total loads of pharmaceuticals and biocides to a significant but not major extent. Compounds that are not readily (bio)degradable enter the receiving waters either as dissolved pollutants or sorbed onto suspended matter via the discharges of wastewater treatment plants (WWTP). Therefore, the removal efficiency of WWTPs is crucial for the contamination of the receiving water bodies with these compounds. Veterinary pharmaceuticals more likely contaminate farmland when manure is used as fertiliser and rivers when afterwards a run-off from the fields took place. Another route into the

environment is represented by point-source discharges from manufacturing plants which may cause locally elevated levels of contamination. Leakage into groundwater from landfill sites may lead to groundwater contamination, since the disposal of household products via domestic waste is very common. In addition to the infiltration of polluted river water and the use of manure or dung as fertiliser on agricultural lands, leakage from sewer drains, WWTPs and manure storage tanks are potential routes for groundwater contamination. Other pathways for soil and groundwater contamination include spray irrigation of raw and treated wastewater onto agricultural land as well as contamination from leaking septic tanks. In cases of unintended water reuse, wastewater is generally much less treated as compared to planned indirect potable reuse where advanced technologies are applied to upgrade the wastewater by a multi-barrier system, intentionally avoiding the break through of bacteria, viruses or parasites as well as inorganic and organic pollutants. Hence, persistent pharmaceuticals and their metabolites are being found in drinking water, demonstrating *unintended* indirect potable reuse. Most polar and persistent compounds used in appreciable quantities can be detected in aqueous environmental matrices. Although, only in a few cases adverse effects on biota have been identified, it can be expected that in future more concerns will be elucidated for “emerging substances” or even “groups of emerging substances”. Due the high number of compounds, the goal should be to select *indicator substances* regulated in the Water Framework Directive representing different kind of sources for pollution.

Occurrence in drinking water and evaluation of risks for drinking water consumers

In recent years several studies in Europe and North America reported the identification of these “emerging compounds” in wastewater, surface water, ground water and final drinking water (e.g. Barcelo, 2005; Kolpin et al., 2000; Ternes and Joss, 2006; Glassmeyer et al., 2005; Richardson and Ternes, 2005; Daughton and Lepp, 2001). In surface waters the concentrations of these compounds ranged up to a few $\mu\text{g L}^{-1}$. Even in ground water and drinking water residues of organic emerging pollutants were detected up to the $\mu\text{g L}^{-1}$ level. Eventually, there are concerns that other pharmaceuticals designed for special biological effects are also hazardous to the environment. Estrogenic effects (Routledge et al., 1998) and renal alterations (Triebkorn et al., 2004) at environmental concentration ranges were already reported for the contraceptive 17α -ethinylestradiol (EE2) and the antiphlogistic diclofenac, respectively. A recent article in Nature (Oaks et al., 2004) highlighted that residues of veterinary used diclofenac are probably responsible for renal failure of vultures, which led to a dramatic decline (> 95 %) of the vulture population in Pakistan.

In surface waters the concentrations of these compounds ranged up to a few $\mu\text{g L}^{-1}$. Even in ground water and drinking water residues of organic emerging pollutants were detected up to the $\mu\text{g L}^{-1}$ level. The question arises whether these residues pose risks for drinking water consumers.

A recent EUROPEAN study (Wenzel et al., 2003) investigated the risks for drinking water consumers caused by endocrine disrupting compounds (EDCs) present in drinking water. The aim of this study was to provide information on the exposure to EDCs through water intended for human consumption, using existing data from the various EU Member States as well as literature studies. Furthermore, a monitoring study was designed and executed to draw a more complete picture of the actual occurrence of EDCs and the potential exposure of humans through drinking water. Synthetic and natural estrogens, alkylphenol, alkylphenol ethoxylates, alkylphenoxy acetic acids, bisphenol A and organotin compounds were analysed in raw and drinking water sampled at 4 accurately selected European waterworks with limit of quantifications (LOQs) down to 0.050 ng/L. Pesticides were not analysed in the monitoring study, since those data were already known.

The following results can be summarised, based on i) the monitoring of the 4 waterworks, ii) the literature survey and iii) the evaluation of questionnaires filled in by in total 84 European waterworks:

Pesticides which have the potential for endocrine disrupting activity can be present in groundwater and raw water used for drinking water production at varying frequencies and concentrations. Based on the available data, drinking water samples with concentrations exceeding 0.1 µg/L were reported only in a few cases. Comparable to surface water and groundwater, most information for drinking water were available for the pesticides atrazine, simazine, diuron, isoproturon and lindane. Since the limit values of the drinking water directive for pesticides (0.1 µg/L in EU) are in general lower than potential guidance values based on human health, direct health hazards via the reported concentrations in drinking water are not expected. However, these guidance values are not available for all pesticides.

Organotin compounds and bisphenol A: Of all the organotin compounds investigated TBT is of most toxicological concern. TBT was detected in surface waters up to 0.05 µg/L and bisphenol A was even present up to the upper ng/L range. In raw water and drinking water bisphenol A was reported to be present in a few cases in the lower ng/L range. In the monitoring study of the 4 waterworks, monobutyltin, dibutyltin and dimethyltin were found in the raw water of the waterworks, while TBT and bisphenol A were not detected, neither in final drinking water nor in tap water investigated. Since these compounds are typically used as stabilisers (tin organics) or monomers (bisphenol A) in plastics, leaching from plastic products such as pipes might lead to TBT or bisphenol A contamination in the treated water. Due to its physico-chemical properties TBT sorbs onto particles and should generally be removed by passage through soil or sediment to groundwater and by the respective drinking water treatment processes.

Alkylphenols were frequently detected in surface waters. Nonylphenol occurs in the µg/L-range, octylphenol was detected at lower concentrations in the ng/L range. The presented data imply a great variation of nonylphenol concentrations in European surface waters due to varying efficiencies of the purification processes in WWTPs. The reported concentrations for nonylphenol and octylphenol in drinking water are in the ng/L range; only in one study 2 µg/L of nonylphenol were reported to be found. Tap water samples analysed in the monitoring study of the waterworks contained neither nonylphenol nor octylphenol above the limit of quantification of 4 ng/L and 0.5 ng/L, respectively. Based on the current assessment concerning effects on humans, the nonylphenol quantity consumed via drinking water seems to be unlikely to pose adverse health effects. However, in order to determine drinking water standards and to evaluate the relevance of the presented nonylphenol concentrations for humans, more toxicological data as well as more reliable drinking water concentrations of nonylphenol are essential.

The synthetic estrogen 17 α -Ethinylestradiol (EE2) was detected in surface waters at concentrations up to a few ng/L. There are limited data regarding the occurrence in groundwater. In drinking water EE2 was neither found at waterworks of the questionnaire nor in the samples of the monitoring study, although a low limit of detection with 0.05 ng/L was attained in the case study. Low concentrations around 1.4 ng/L reported in the literature (Adler et al. 2001) seems to be an outlier, thus further confirmation is needed. The contribution of drinking water to the exposure of humans towards EE2 seems to be very low. However, since EE2 is one of the most potent synthetic estrogenic compounds unintentional exposure of the population, especially developing embryos or prepubertal boys and girls, should strictly be avoided. For an assessment of the exposure of humans via drinking water in Europe and North America, more reliable data down to the pg/L range on the concentrations in raw water and drinking water are required.

The **natural estrogens 17 β -estradiol and estrone** can be present in surface waters in the lower ng/L range and in groundwater below 1 ng/L. In the monitoring of the 4 waterworks generally no 17 β -estradiol and estrone were detected. In literature and questionnaires from waterworks estrone concentrations in drinking water up to 1 ng/L were reported. Due to the treatment train of the waterworks investigated, this high concentration is not plausible and

needs confirmation. Compared to an average dietary intake of natural estrogens via food, the roughly estimated ingestion of estrogens with drinking water using a worst case scenario seems to contribute with a maximum of around 4 % to the total exposure of an adult via mixed diet. Based on this knowledge, effects on humans due to the intake of steroid hormones in drinking water are not expected. However, for a profound evaluation more reliable data are required.

The following résumé can be drawn:

- The raw water of waterworks can be contaminated by EDCs. This is especially the case if surface water is used as water resource.
- Depending on the water treatment the drinking water might contain EDCs at low concentrations.
- Efficient drinking water treatment trains are appropriate to avoid a drinking water contamination by EDCs (e.g. using ozonation, activated carbon, bank filtration).
- Even if the raw water of waterworks is free of EDCs, drinking water/tap water might be contaminated by individual EDCs due to leaching from materials used in waterworks and water pipes.
- *Even if the highest concentration of an individual EDC reported for drinking water is considered for the assessment of effects on humans, based on the current knowledge, endocrine effects via the consumption of drinking water are rather unlikely.*

Removal options of emerging compounds preventing the contamination of drinking water resources (summary of the results from the EU project POSEIDON) (<http://poseidon.bafg.de>; Ternes and Joss, 2006)

The EU project POSEIDON established a basic knowledge on the removal of pharmaceuticals and personal care products (PPCPs) in wastewater and drinking water treatment. These results can be transferred to other organic chemicals to some extent as long as their physico-chemical properties are comparable. Both wastewater technology and drinking water technology optimised for the removal of domestic chemicals can be applied world-wide for indirect water reuse. Based on the POSEIDON outcome, a form of BAT (Best Available Technology) for water treatment concerning PPCP removal was proposed and will provide a basis to implement administrative measures with regard to persistent domestic chemicals as contaminants of reclaimed wastewater treatment plant (WWTP) discharges. Many PPCPs have limited biological degradability. On passing through WWTPs therefore, these compounds are generally only partly eliminated. Most polar PPCPs are discharged into the bodies of receiving water, while polar PPCPs with specific sorption properties as well as nonpolar PPCPs are mainly sorbed onto sludge and consequently lead to soil contamination when digested sludge is used as fertiliser. A permanent solution to this problem appears to be possible for the majority of compounds with acceptable costs by considering measures taken at the source (source control and source separation). However, these require political decisions, have to be accepted by the population and need decades for their implementation.

Concerning wastewater treatment processes it could be shown that

- the removal of PPCPs by sorption onto suspended solids is an important mechanism for hydrophobic compounds and compounds with positively charged functional groups (e.g. amines).
- sludge retention time (SRT) has major influence on biological degradation efficiency, mainly due to its influence on the diversity of the microbial population and on the multitude of degradation pathways being expressed; a SRT of ≥ 10 days is recommended
- due to first order kinetics of biological PPCP degradation the removal in a single completely stirred reactor is significantly lower as compared to the same total volume subdivided into cascaded compartments
- ozonation of treated effluent substantially reduces the PPCP concentrations at feasible cost with the exception of iodinated contrast media

- post-filtration leads to partial degradation of some antibiotics not degraded at 10-15 d SRT in the biological step
- stripping is not relevant for PPCP removal in state-of-the-art municipal wastewater treatment
- estrogens can be eliminated in WWTPs by applying a nitrification/denitrification step (SRTs ≥ 15 days), or by effluent ozonation or nanofiltration or activated carbon
- anaerobic sludge digestion leads to a degradation of some PPCPs
- for most of the PPCPs such as antibiotics only advanced technologies (effluent ozonation, nanofiltration or activated carbon) lead to an efficient removal
- source control (e.g. ecolabelling) and source separation (e.g. urine or rain water segregation) are important measures for reducing the PPCP load entering the environment (e.g. exfiltration or storm overflow) and improving the wastewater treatment efficiency (i.e. reducing dilution).

Concerning indirect potable water reuse it was revealed that

- planned indirect potable reuse of municipal wastewater is a feasible option concerning PPCP removal
- irrigation and soil passage leads to the removal of most PPCPs (>80%) either by sorption or by degradation
- direct infiltration of wastewater into groundwater should be avoided due to PPCP contamination of the groundwater.

Concerning drinking water treatment processes it could be shown that

- ozonation is a very effective process to oxidise PPCPs. Currently, there is no indication that the formed oxidation products are toxic.
- disinfection with chlorine and chlorine dioxide does not lead to a general oxidation/removal of PPCPs. The transformation products are currently unknown.
- activated carbon is a powerful process to remove PPCPs. Only very few PPCPs such as iodinated contrast media and the antibiotic sulfamethoxazole show insufficient affinity to activated carbon.
- nanofiltration and ultrafiltration/PAC are powerful processes to remove PPCPs.
- coagulation and flocculation are inappropriate to remove most PPCPs.
- PPCP contamination of drinking water produced from surface water is quite unlikely in most European facilities, which have complete treatment trains (activated carbon, ozonation, membrane filtration).
- contamination of drinking water is likely for small waterworks with pharmaceuticals residues in their raw water but lacking the more advanced technologies described above.

Measures at the source

Separate treatment of hospital wastewater (source control): Hospital waste water is heavily loaded with pharmaceuticals, antibiotic-resistant bacteria and biocides. Separate treatment of hospital wastewater, such as using ozonation of the effluent, should be considered. These measures could also be beneficial to the hospital since such treated wastewater could be reused for flushing toilets and gardening or directly discharged, thus reducing associated drinking-water fees and avoiding wastewater fees.

Labelling of products (source control): Environmental labelling of products could significantly reduce the use of environmentally harmful chemicals. For instance, the introduction of an environment label for pharmaceuticals is being discussed in Sweden with the cooperation of the pharmaceutical industry. This enables physicians and patients to select the most environmentally friendly pharmaceuticals (Wennmalm, 2003).

Disposal of products (source control): The disposal of products releasing emerging compounds should be controlled and supervised. For instance, it should be general practice to collect outdated (expired) or superfluous products containing environmental hazardous

compounds and to destroy them (e.g. by incineration) or possibly reuse them under controlled conditions.

Urine and wash water separation (source separation): Pharmaceuticals are excreted to a great extent with the urine (Ternes and Joss, 2006). Personal care products and surfactants are mainly present in the wash water of households. Separation and separate treatment of the urine and the wash water would significantly reduce the loading of the wastewater and may even allow recycling of the nutrients (Larsen and Gujer, 1996).

ACKNOWLEDGEMENTS

This study was part of the EU Poseidon project (EVK1-CT-2000-00047) which was financially supported by grants obtained from the EU Commission within the Energy, Environment and Sustainable Development Program of the Fifth Framework.

REFERENCES

Adler, P., T. Steger-Hartmann, W. Kalbfuss (2001): Vorkommen natürlicher und synthetischer östrogen Steroide in Wässern des süd- und mitteldeutschen Raumes. *Acta hydrochem. hydrobiol.* 29 (4), 227-241.

Barcelo, D. (ed.) Emerging organic pollutants in wastewater and sludge. *Trends Anal. Chem.* 22 (1), 2003.

Boxall, A.B.A., Fogg, L.A., Blackwell, P.A., Kay, P., Pemberton, E.J., Croxford, A. (2004) Veterinary Medicines in the Environment. *Rev. Environ. Contam. Toxicol.*, 180, 1-91.

Calamari, D., Zuccato, E., Castiglioni, S., Bagnati, R., Fanelli, R. (2003) Strategic survey of therapeutic drugs in the rivers Po and Lambro. *Environmental Science & Technology* 37, 1241-1248.

Daughton, C.G., Jones-Lepp, T.L. (2001) Pharmaceuticals and Personal Care Products in the Environment: Scientific and Regulatory Issues. Washington DC: ACS Symposium Series 791, American Chemical Society.

Daughton, Ch.G., Ternes, T.A. (1999) Pharmaceuticals and Personal Care Products in the Environment: Agents of Subtle Change? *Environ. Health Perspect.* 107, 907-938.

Frick, E.A, Zaugg, S.D organic wastewater contaminants in the upper chatahoochee river basin, Georgia, 1999-2002. ga.water.usgs.gov/pubs/other/gwrc2003/pdf/Frick_wastewater-GWRC2003.pdf -

Glassmeyer, S.T., Furlong, E.T., Kolpin, D.W., Cahill, J.D., Zaugg, S.D., Werner, S.L., Meyer, M.T., Kryak, D.D. (2005) Transport of chemical and microbial compounds from known discharges: potential for use as indicators of human fecal contamination. *Environ. Sci. Technol.* 39, 5157-5169.

Heberer T. (2002) Occurrence, fate, and removal of pharmaceutical residues in the aquatic environment, a review. *Toxicol. Lett.* 131, 5.

Jensen, S., Johnels, A. G., Olsson, M., Olterlind, G. DDT and PCB in marine animals from Swedish waters. *Nature* 1969, 224, 247-250.

Kolpin, D.W., Furlong, E.T., Meyer, M., Thurman, E.M., Zaugg, S.D., Barber, L.B., Buxton, H.A.T. (2002) Pharmaceuticals, hormones, and other organic wastewater contaminants in U.S. streams, 1999-2000: A national reconnaissance. *Environ. Sci. Technol.* 36, 1202-1211.

Larsen, T.A., Gujer, W. (1996) Separate management of anthropogenic nutrient solutions (human urine). *Water Sci. Technol.* 34, 87-94.

Oaks, J.L., Gilbert, M., Virani, M.Z., Watson, R.T., Meteyer, C.U., Rideout, B.A., Shivaprasad, H.L., Ahmed, S., Chaudhry, M.J.I., Arshad, M., Mahmood, S., Ali, A. & Khan, A.A. (2004): Diclofenac residues as the cause of population decline of vultures in Pakistan. *Nature* 427: 630–633.

Richardson, S.D, Ternes, T.A. (2005) Water Analysis: Emerging Contaminants and Current Issues. Anal. Chem. 77, 3807-3838.

Ternes T.A, Joss A. Removal of PPCP during drinking water treatment Human pharmaceuticals, hormones and fragrances: a challenge for urban water management, IWA Publishing, London 2006, ISBN: 1843390930.

Ternes, T.A. (1998) Occurrence of drugs in German sewage treatment plants and rivers. Wat. Res., 32, 3245-3260.

Ternes, T.A., Joss, A., Siegrist, H. (2004) Pharmaceuticals and personal care products: wastewater practice under close scrutiny, Environ. Sci. Technol., 38, 393A.

Triebkorn, R., Casper, H., Heyd, A., Eilemper, R., Köhler, H.-R., Schwaiger, J. (2004) "Toxic effects of the non-steroidal anti-inflammatory drug diclofenac: Part II. Cytological effects in liver, kidney, gills and intestine of rainbow trout (*Oncorhynchus mykiss*)," Aquat. Toxicol., 68, 151-166.

Webb, S., Ternes, T.A., Gibert, M., Olejnicak, K. (2003) Indirect human exposure to pharmaceuticals via drinking water. Toxicol. Letters 142, 157-167

Wennmalm, A. A proposed environmental classification system for medicinal products. Envirpharma conference, Lyons, France, April, 2003.

Wenzel, A., Müller, J., Ternes, T.A. Study on endocrine disrupters in drinking water, European report, ENV.D.1/ETU/2000/0083, 2003.

Emerging Substances in Soil

Frank P.J. Lamé
TNO Built Environment and Geosciences, Business Unit Soil and Groundwater
P.O.Box 80015, 3508 TA Utrecht

E-mail: frank.lame@tno.nl

The list of emerging substances as provided on the Norman website is long and most of the components are 'exotic'. And indeed, living in a highly industrialized world, 'exotic' chemicals are now part of our daily life. Knowledge of the consequences of these substances and potential (adverse) effects are of major importance in order to live in a sustainable environment. Nevertheless, before getting to 'exotic', do we have sufficient knowledge about the presence of the more 'common' substances?

Looking from an environmental perspective, soil quality in the Netherlands is set by a long list of potential pollutants for which legislative levels are defined. The question whether legislative values are defined nowadays depends on the toxicological effects as well as the supposed occurrence of a component.

However, the occurrence of components was until recent basically unknown. Of course for the most common (heavy) metals and organics, there was sufficient knowledge in the Netherlands, but at the same time for a large group of the listed components, there was no systematic information available. Basically, these parameters were listed because there was interest from specific project during the period wherein the old 'A-, B- and C-values were defined in the mid nineteen eighties. At least for part of these parameters it might be concluded that they will only occur in very specific cases of soil pollution.

It is foreseen that early 2007 a new soil legislation will be published in the Netherlands. One of the important changes related to that new legislation is a re-evaluation of the list of parameters with legislative levels. General principle is that a component should have (major) toxicological effects in order to be listed. This is of course directly related to the concentration levels in which the component occurs. Additionally, when a component is listed, legislative values are to be defined on all newly defined levels. This without necessary toxicological effect on the lower concentration levels.

The lowest level is now known as the background level, for which – as the name already clarifies – the concentrations are based on the background concentrations in the Netherlands. And indeed, there is no reason to expect toxicological effects on this lowest level. However, in order to obtain a full set of legislative values, also these background levels are important and have a function in relation to the question if unrestricted reuse of soil is possible.

The second and third level are related to the use or function of the soil; either being for public housing and living or for industrial purposes. Finally, the old intervention values (however partly with new concentrations) are maintained. Soil that exceeds the intervention values should be remediated before it can be reused.

As mentioned, there was until recently little known about the occurrence of components in soil. This was true for both the background levels, as well as for the concentration levels of component in urban areas. Therefore two separate, but clearly linked, initiatives were started between 2002 - 2004 and finished only in 2006.

The first study, in the Netherlands well known as 'AW2000' (an abbreviation of background values 2000) aimed to determine the background levels for all – at that time – listed

components. This means that background concentration had to be determined systematically for the 113 components for which legislative values were defined. Additionally, as a part of these are in fact sum-parameters (like sum-PAH), more than a hundred additional components also were to be determined, in total adding up to 233 components for which, directly or indirectly, a legislative value was set.

These background levels are not the levels that are related to the natural – undisturbed – environment. We have to acknowledge the fact that the Netherlands are densely populated and that the Netherlands, as well as the surrounding countries, are highly industrialised.

Additionally, agricultural use of the land has also impacts on the soil quality; as for example heavy metals are used in food additives for cattle and pesticides are used for crop protection. Thus, the 'background levels' that were to be determined should be interpreted as the concentrations that occur when there is no expectation of direct or local soil pollution.

In order to find locations for sampling, a series of criteria were defined in order to exclude as far as possible this direct input. Based on these criteria 100 sampling locations were selected throughout the whole of the Netherlands, representing agricultural and natural grounds, common soil types and land use; however, excluding villages and cities in order to diminish the chance of encountering soil pollution. At each location, samples were taken over an area of 2500 m² for the top soil (0 – 0,1 m), the intermediate layer where influence from atmospheric input might still affect the soil quality (0,1 – 0,5 m) and the underlying soil (0,5 – 1,0 m). All of these samples have been analysed in a comprehensive analytical study, not only determining the concentrations, but also ensuring the correctness of the results. Finally, at the end of 2004, we ended up with concentration distributions for in total 252 components and soil characteristics.

These results were then taken into a policy discussion, where as a consequence, it was decided that the target levels in the Netherlands had to be changed. Apart from changing the legislative values, also the name of the level will be changed, now being the background levels. In general, the background levels will be set at the 95-percentile value of the distribution of concentrations for each of these components as found in the top soil. For some components this implies higher concentrations, but for a number of other components the background levels will be lower than the earlier target levels. Unfortunately, the policy discussions on the legislative values have until now (mid October 2006) not been finalised, and therefore it is not possible to list the legislative values in this document.

Knowing the background levels in the – more or less – undisturbed soils, this does not relate to the concentrations that might be found in soils when looking at soil quality on a routine basis. Most reuse of soil is of course not situated in the undisturbed soils and environments, but in the villages and cities. There, intensive use of the soil over the centuries, might have resulted in enhanced concentration levels representative for the urban areas. And indeed, in general we are aware of that fact when analysing soil quality for the more common components like arsenic, cadmium, chromium, copper, lead, mercury, nickel, zinc, sum-PAH, mineral oil and EOX. But what concentrations might be expected for other metals for which also soil quality criteria are defined? And what about the leaching behaviour of these metals in soil?

Neither the concentrations nor the leaching of components like antimony, barium, cobalt, molybdenum, tin, selenium and vanadium are measured on a regular basis – if even ever! If concentrations found in these more disturbed soils indeed exceed the background levels as defined in the first study, there is reason to determine these components on a regular basis. They are then to be included in the package of components that are routinely measured when determining the soil quality. This discussion is currently still running. However, it was already determined that the formerly mentioned routine package of components (11 components) is indeed too small. An indication of the components that should (at least) be measured on a

routinely basis are antimony, barium, cadmium, cobalt, copper, mercury, lead, nickel, molybdenum, tin zinc, chloride, PCB's, mineral oil and sum-PAH. This list will however surely change during the coming months when the policy discussion on the parameters for routinely analysis will be finalised.

Given the combination of the previously mentioned two studies, apparently there is more to know about soil quality, even for the more common parameters, than we might realise. We have done extensive soil investigation since the early nineteen eighties, but nevertheless, have only recently obtained the knowledge on the necessity of determining parameters like antimony, barium, cobalt and molybdenum.

This conclusions for the Netherlands might well be expanded to other European countries where – in general – soil quality investigations often tend to focus on the same limited number of components. Thus apart from the more 'exotic' components, we might well overlook what is happening to the soil due to the more common components and sources of (diffuse) soil contamination.

An additional second step for the future might then be to widen the list of potential contaminants even further, based on knowledge on the daily use and the potential input in soil, for components as listed on the Norman website.

Emerging substances in indoor air

Dimitrios Kotzias
European Commission-Joint Research Centre
Institute for Health and Consumer Protection
21020 Ispra (Va), Italy

E-mail: dimitrios.kotzias@ec.europa.eu

SUMMARY

All across Europe, people live and work in indoor environments. On average, people spend between 85 to 90% of their time indoors (homes, workplaces, cars and public transport means etc.). In the past decades a large number of studies have indicated the presence of a vast variety of chemical compounds in indoor environments (buildings, homes); thus people are exposed to a complex mixture of chemicals at concentration levels which are often up to five times higher than outdoors.

The presence of these chemicals in indoor air is the result of infiltration of polluted outdoor air and of emissions from various indoor sources, including building materials, activities of the occupants, consumer products, smoking etc. Emissions in indoor air include volatile organic compounds (VOCs), carbonyls (aldehydes and ketones) as well as other substances, which are often associated with particles.

For many of these chemicals, the impact on human health and comfort is almost unknown and difficult to predict because of the lack of toxicological data and of information on the dose-response characteristics in humans or animal models. On the other hand, a full toxicological testing as requested by the “existing chemicals” legislation is difficult to accomplish for these compounds, because it would involve the investigation of acute and sub-acute toxicity, mutagenicity, carcinogenicity and reproductive toxicity according to testing protocols that are complex, time-consuming and expensive.

Moreover, the EU policy on limitation of unnecessary animal testing further limits the possibility of advocating a generalized animal testing of these chemicals. The result of this situation is that there is an objective difficulty in regulating the presence of chemicals in indoor air principally because of the absence of adequate hazard, exposure and risk assessment.

The lack of information regarding human exposure to air pollutants (indoors/outdoors) makes it necessary, in line with the Commission’s Environment and Health Strategy and Action Plan (launched on June 9, 2004), to develop targeted strategies to evaluate the impact of air pollution on human health. This should include, apart from monitoring ambient air pollution levels, specific measurements in selected confined spaces (homes, schools, public buildings etc.) within the frame of monitoring campaigns, specifically designed to assess indoor and outdoor air quality and personal exposure to pollutants in combination with micro-environmental activity patterns. Information from these studies are considered crucial for a first evaluation of the overall situation in indoor and outdoor environments and the evaluation of possible sources and source strengths of pollutants to which humans are chronically exposed during working, commuting and rest time. The paper reports on a proposed prioritisation of compounds which should be considered for regulation in indoor environments (INDEX project) and on a study dealing with the measurements of indoor/outdoor and personal exposure to pollutants in various European cities (the AIRMEX study) [1, 2].

THE INDEX PROJECT

Scope and outcome

The INDEX project (Critical Appraisal of the Setting and Implementation of Indoor Exposure Limits in the EU) started in December 2002 and had a duration of two years. The project was financially supported by DG SANCO and it was coordinated and carried out by the JRC in collaboration with a Steering Committee of leading European experts in the area of indoor air pollution. Scope of INDEX was to identify priorities and to assess the needs for a Community strategy and action plan in the area of indoor air pollution by:

- setting up a list of compounds to be regulated in indoor environments with priority on the basis of health impact criteria
- providing suggestions and recommendations on potential exposure limits for these compounds and
- providing information on links with existing knowledge, ongoing studies, legislation etc. at world scale.

The main steps to be followed in the project as they have been defined by the Steering Committee were:

- literature review (step 1)
- setting up criteria to select compounds (step 2)
- review of exposure and dose/response data (step 3)
- risk characterization of the selected compounds (step 4)
- prioritization of the selected compounds (step 5) and
- recommendations on potential exposure limits (step 6)

Based on the overall population risk caused by indoor source strengths, toxicological properties including hypersensitivity for allergy and asthma, known health effects and relation to comfort, it was decided within the INDEX project to define and prioritize the main indoor air pollutants as follows:

Group 1 (high priority): benzene, formaldehyde, carbon monoxide, nitrogen dioxide, and naphthalene

Group 2 (low priority): m&p-xylenes, o-xylene, acetaldehyde, styrene, toluene

Group 3 (chemicals requiring further research with regard to human exposure and dose/response): NH₃, d-limonene, a-pinene.

Recommendations and management options (for high priority air pollutants)

Recommendations and management options for priority indoor air pollutants proposed for regulatory purposes, would - according to present knowledge - protect the general population and most individuals most of the time, but they will not prevent all cancer from indoor exposures nor protect the most susceptible individuals in all conditions, such as individuals with serious respiratory or cardiovascular disease, highly reactive asthmatics, genetically predisposed individuals developing haemolytic anaemia from naphthalene, etc.

In addition to specific recommendations reported below, the following general recommendations and management options apply to most or many indoor air contaminants in the high and low priority lists:

- Use of appropriate ventilation practices based on the well defined standards for indoor environments according to the recommendations of the relevant professional organisations.
- Ban tobacco smoking in all indoor spaces under public jurisdiction. Raise public awareness on the hazards of tobacco smoke, and discourage smoking in private residences, particularly in the presence of children.

- Develop building codes to restrict the construction of attached garages, and to isolate the garages from living and working quarters (closing the doorways, sealing the structures and ensuring proper air pressure difference between garage and other indoor spaces).

High priority compounds

Formaldehyde: The no-effect level (acute and chronic) is estimated to be at 30 µg/m³ as 30-minute average. Pending the outcome of the current IARC revision of the carcinogenicity of formaldehyde, a guideline value should be as low as reasonably achievable.

Management options:

- Restrict emissions of formaldehyde from building products, furnishings and household/office chemicals.
- Discourage the use of formaldehyde containing products.

Nitrogen Dioxide: A long term guideline value of 40 µg/m³ (1-week average) and a short term guideline value of 200 µg/m³ are proposed.

Management options:

- Apply the indoor air concentration guideline in the building design process
- Develop building codes, ventilation standards and equipment/appliance standards (design, maintenance and use) so that all indoor combustion equipment will exhaust to chimneys/hoods/vents leading outdoors.

Carbon Monoxide: The 1-hour average guideline value of 30 mg/m³ and the 8-hour average guideline value of 10 mg/m³ are recommended.

Management options:

- Apply the indoor air concentration guideline in the building design process
- Develop building codes, ventilation standards and equipment/appliance standards (design, maintenance and use) so that all indoor combustion equipment will exhaust to chimneys/hoods/vents leading outdoors
- Require regular mandatory inspections for indoor combustion equipment
- Recommend alarm systems responding to abnormally high concentrations (e.g. 50 mg/m³).

Benzene: As benzene is a human carcinogen, its concentration in the air should be as low as reasonably achievable. Indoor concentrations of benzene should not exceed outdoor concentrations.

Management options:

- Sources emitting benzene (tobacco smoking, etc.) should not be allowed in the indoor environment
- Lower the permissible benzene content in any building material and consumer product.

Naphthalene: A long term guideline value of 10 µg/m³ is recommended based on irritation/inflammation/hyperplasia. This level is at the lower extreme of the olfactory perception range.

Management options:

- Restrict the use of naphthalene containing household products, particularly mothballs.

THE AIRMEX APPROACH

In order to systematically evaluate the relationship between indoor/outdoor air pollution and human (chronic) exposure to pollutants, the JRC-Institute for Health and Consumer Protection

(IHCP) launched in October 2003 the AIRMEX project (European Indoor Air Monitoring and Exposure Assessment Study). In the frame of the AIRMEX project measuring campaigns in Catania (I), Athens (GR), Arnhem and Nijmegen (NL), Brussels (B), Milan (I), Thessaloniki (GR), Nicosia (CY) and Leipzig (D) were carried out to estimate indoor/outdoor relationships and personal exposure concentrations for selected volatile organic compounds (aromatics, carbonyls, terpenes).

In agreement with the overall scope of the project, the measuring objects included public buildings (town halls, guild halls), schools and kindergartens. Personal exposure measurements were conducted with volunteers, employers and/or teachers, working in the pre-selected working environments.

Efforts were made to apply for all measurements in the different cities similar criteria for the selection of persons for personal exposure estimations e.g. division between smokers and non-smokers and/or for the working environment (offices with non-smokers/smokers, entrance hall or waiting room/area) and building locations (urban, sub-urban). A particular asset of the project, especially during this first phase of execution, was the obligation from the JRC-Institute for Health and Consumer Protection (IHCP) in close collaboration with local partners (scientific institutions and authorities) to assist by the installation of the samplers inside and outside the buildings and for personal monitoring and to carry out the chemical analysis of all samplers used during the measuring campaigns and sent from the local authorities and the other partners to JRC-IHCP. Moreover, a questionnaire was prepared for the volunteers to get additional information on micro-environmental activity patterns and personal habits (e.g. smoking etc.).

All measurements were carried out by means of passive samplers (Radiello, charcoal type for VOCs and DNPH-covered for carbonyl compounds). Personal exposure monitoring was performed for VOCs in all campaigns.

Duration of the measuring campaigns was basically one week, including the weekends. For personal exposure monitoring the time of the measuring period i.e. the time of bearing the personal passive samplers by the selected persons, it was agreed, to be up to three days for the convenience of the exposed individuals.

Taking into consideration the suggestions made in the INDEX project, as a first approach the following compounds were monitored:

VOCs

Hexane
Benzene
Toluene
Ethylbenzene
m/p-Xylene
o-Xylene
1,3,5-Trimethylbenzene
a-Pinene
d-Limonene

Carbonyls

Formaldehyde
Acetaldehyde
Propanal
Hexanal

CONCLUSIONS

On the basis of the results from the first phase (October 2003-April 2005) of the AIRMEX project the following conclusions can be drawn:

- Personal exposure concentrations to priority pollutants e.g. benzene, formaldehyde are in most cases higher than the respective indoor/outdoor concentrations
- In reference to the EU ambient air limit value for benzene of 5 µg/m³ (annual mean) by the year 2010, preliminary results indicate that about 25% of the outdoor concentrations, 30% of the indoor concentrations, and 45% of the exposure concentrations exceeded this limit value.
- In Southern European cities indoor/outdoor as well as personal exposure concentrations are higher than in cities of Central Europe. In Athens and Catania in buildings located in the city centre there is almost no difference between indoor and outdoor pollutant levels.
- Concentrations in schools and kindergartens are generally lower than in public buildings and offices with public access.
- True personal exposures cannot be determined directly from measurements pertaining from fixed ambient background monitoring stations. This implies, that in order to evaluate possible health effects associated with the presence of pollutants indoors and outdoors the best way for this will be to estimate personal exposure concentrations taking into consideration micro-environmental activity patterns and personal behaviour.

REFERENCES

D. Kotzias et al.: The INDEX project (Critical Appraisal of the Setting and Implementation of Indoor Exposure Limits in the EU), Commission of the European Union, Joint Research Centre-Institute for Health and Consumer Protection January 2005.

D. Kotzias, O. Geiss, S. Tirendi : Evaluation of total exposure to benzene and formaldehyde in European countries. *Epidemiologia & Prevenzione*, Anno 29 (5-6) Settembre-Dicembre 2005.

Perfluorinated organic compounds in the European environment

Pim de Voogt

Institute for Biodiversity and Ecosystem Dynamics, University of Amsterdam
Nieuwe Achtergracht 166, 1018 WV Amsterdam, Netherlands

E-mail: pdevoogt@science.uva.nl

Perfluorinated chemicals (PFCs) is a general term used to describe chemical substances which are largely comprised of or contain a perfluorinated or polyfluorinated carbon chain moiety such as $F(CF_2)_n-$ or $F(CF_2)_nC_2H_4-$. Several of the PFCs have been shown to increase in levels in environmental compartments, such as sediments and biota, although recently a decline in notably electrochemical fluorination related PFCs seem to become manifest. The PERFORCE project is a research project funded by the European Union Framework programme. The project started in July 2004 and covered a period of two years. Its principal aim was to make an exposure assessment of perfluorinated organic compounds in the European environment. At the start of the project it was realised that Europe was lagging behind North America with respect to the collection of knowledge and data on these compounds. Several tools were considered necessary to fulfil the task indicated above. These included the development of chemical analytical and bioanalytical tools for identification and quantification of the compounds, the validation of these methods, and the collection of relevant physicochemical compound property data that would serve to understand their fate and to model and explain their behaviour in environmental compartments. The tools were then used in a Europe wide monitoring campaign that included sampling of surface waters, air, sediments, biota, and wastewater treatment plants. The campaign was aimed at identifying possible sources of PFCs, and establishing spatial and temporal trends in Europe.

The Perforce project selected some representative PFCs from the many that are manufactured or observed in the environment. The chemical analytical and quality assurance work packages showed that blank contamination is an item of paramount importance in the analysis. Analytical methods for four different matrices were developed and validated; these include water, sediment, air, and biota. For these matrices analytical protocols were developed that are deliverables of the project. The analytical methods developed showed good accuracies on the matrices included in the validation, demonstrating that these methods are fit-for-purpose. A worldwide interlaboratory study was organised using a fish tissue, fish liver extract and a water sample. The results revealed large variations in the between-laboratory results, showing that participating laboratories were not yet able to generate comparable results.

The results of the sampling campaigns show that PFCs are ubiquitously present in the European environment. Levels of PFOS in sediments have increased from 1990 to 2005, whereas for PFOSA an initial increase was followed by a possible decreases after 2000. The annual loading to the European environment of PFHxA, PFHpA, and PFOA from rivers is estimated to be of the order of 10, 2, and 20 tonnes. The Danube and Rhine watersheds are particularly important source regions, whereby the Elbe and Po also make a significant contribution for PFHxA and PFHpA/PFOA, respectively. In European air, PFOA was often the predominant PFC found in the particulate phase, while 6:2 FTOH and 8:2 FTOH were the prevailing analytes found in the gas phase. Many other compounds were also present in air.

Spatial differences were observed particularly in biota. PFOS and PFOSA concentrations were higher in North Sea cod liver than in cod liver from the Kattegat and the Baltic. In marine mammals concentrations of PFOS are higher in species feeding close to the shore or in estuaries than in off shore feeders. A relationship appears to exist between concentrations of PFOS and trophic levels in marine mammals. In these mammals perfluorinated carboxylic acids

are relatively low in all species and tissues analysed. PFOS, PFDA and PFUnA bioaccumulate in a simple estuarine food chain, PFOA accumulates significantly less.

The PERFORCE study has obviously taken away some of the important knowledge gaps that existed several years ago with regard to the occurrence of the PFCs in the European environment. In particular the exposure levels in Europe are much better known as a result of the project. Yet, it is obvious that further work is necessary to identify unknown origins, e.g. of PFHxA, to assess the fluxes to the environment from STPs, and to quantify loading of river water and identify sources. There is also a need to improve our understanding of PFC transfer to as well as removal from the atmosphere, oceanic transport routes, and the mechanisms of bioaccumulation / biomagnification / bioelimination of PFC.

The siloxane case: Screening of new chemicals in Sweden

Eva Brorström-Lundén
IVL, Swedish Environmental Research Institute
Box 5302, 400 14 Göteborg, Sweden

E-mail: Eva.BL@ivl.se

INTRODUCTION

Volatile methylated siloxanes (VMS) form a group of chemicals, which are used in large quantities in a vast number of industrial and household products. Examples of use include fuel, car polish, cleaners, anti foaming agents, car waxes and various personal care products. The widespread use of siloxanes as well as their high volatility has raised concern about these compounds within various disciplines of environmental science.

As a result of their wide use, siloxanes are presumably spread into the environment both via point sources and diffuse sources and may be found everywhere in the environment. Recent studies have suggested that siloxanes may have direct or indirect toxic effects on various biological processes.¹

A screening study on environmental occurrence and distribution of VMS has recently been carried out within Sweden, and in parallel in the Nordic environment including all six Nordic countries (Kaj et al., 2005a,b). The main objectives of the screening were to determine the concentrations of selected siloxanes in a variety of environmental media, to highlight important transport pathways and to assess the possibility of current emissions.

Substances included were: hexamethyl-disiloxane (MM or HMDS), octamethyl-trisiloxane (MDM), decamethyltetrasiloxane (MD2M), dodecamethylpentasiloxane (MD3M) and the cyclic siloxanes octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5) and dodecamethylcyclohexasiloxane (D6). In addition, hexamethylcyclotrisiloxane (D3) was analysed in biota.

Information on consumption within the Nordic countries was compiled, and is displayed in Figure 1 for D4 and D5. Judging from the figure, it seems that the consumption of D4 has gone down since the peak in 2002, mainly as a result of reduced use in Sweden and Denmark.

As VMS are very volatile substances, they are likely to partition mainly to air, but also, because of a relatively high K_{ow} -value, accumulation in surface sediments is possible, especially when the primary receiving medium is water (e.g. via sewage water outflows). A modelling exercise using the EQC model confirmed this. Thus, air and sediment were identified as particularly important sampling matrices.

A sampling strategy was set up, based on identified possible emission sources, use as well as the physical-chemical properties and likely behaviour in the environment. Sampled media types were air, biota, sediment, sludge, soil and water in urban and background areas and close to possible point sources. In the Swedish study, human breast milk was also included. Due to the

¹ The TCNES working group under European Chemicals Bureau has recently suggested octamethylcyclotetrasiloxane (D4) to be excluded from the working list of potential PBT and vPvB substances (ECB, 2006). D4 is still classified as a PBT/vPvB and phase-out substance in the Swedish national priority database PRIO (KemI, 2006)

ubiquity of the VMS, specific care was taken to reduce the risk for contamination of the samples in the experimental part of the study.

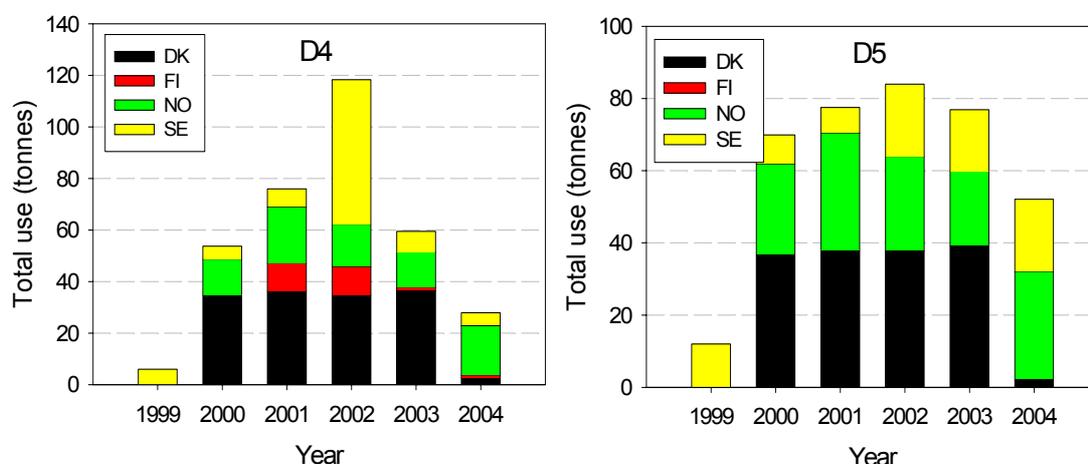


Figure 1. Use of D4 and D5 within four of the Nordic countries between 1999 and 2004 (SPIN, 2006).

Results

The results indicate that there is a general pollution of VMS in the Swedish and the Nordic environment. VMS were found in all the analysed sample types except soil. There was, however, a great variation in concentrations. The cyclic VMS occurred in all media in significantly higher concentrations than the linear VMS. Table 1 shows the observed concentration ranges in different matrices within the Nordic study.

Table 1. Observed concentrations of VMS in various sampling matrices. Environmental data are from the Nordic study, and milk data from the Swedish study.

Substance	Air ($\mu\text{g}/\text{m}^3$)	Water ($\mu\text{g}/\text{L}$)		Sludge ($\text{ng}/\text{g dw}$)	Soil ($\text{ng}/\text{g dw}$)	Sediment ($\text{ng}/\text{g dw}$)	Biota ($\text{ng}/\text{g ww}$)	Human milk ($\mu\text{g}/\text{L}$) ⁴
		Sewage/ industrial ¹	Coastal/ Watercourse					
MM	<0.004	<0.0005-0.14	<0.0005-<0.0006	<0.5 - <3	<0.1	<0.02-<0.7	<0.4	<0.004 – 0.006
MDM	<0.008	<0.0005-0.014	<0.0005-<0.0006	<1-64	<0.1	<0.02-<0.7	<0.3	<0.002 – 0.008
MD2M	<0.006	<0.0005-0.078	<0.0005-<0.0006	1-450	<0.1	<0.02-29	<0.4 – 1.1	<0.005-0.013
MD3M	<0.02	<0.004-0.23	<0.002-<0.004	3-550	<0.1	<0.02-57	<0.5	<0.04
D3	n.a ²	n.a	n.a	n.a	n.a	n.a	<50-90.4 ³	n.a
D4	0.08-4.0	<0.06-3.7	<0.04-<0.09	96-960	<6-<10	<3-84	<5-70	<2 – 10
D5	0.05-19	<0.04-26	<0.02-<0.05	1100-89000	<3-<5	<2-2000	<5-2200	<2 – 4.5
D6	0.02-2.1	<0.04-3.8	<0.02-<0.05	220-11000	<2-<4	<1-170	<5-74	<2 – 4.8

¹ Samples represent influent and effluents to and from sewage treatment plants, landfill leachate and industrial storm water ² n.a = not analysed ³ Detected levels were below limit of quantification ⁴ Human milk was only included in the national Swedish study

D5 was the dominating VMS in all matrices but air, where D4 dominated. At a first glance, this is not in agreement with data on use in the Nordic countries, which indicates that the consumption of D5 and D4 until recently has been fairly equal. New consumption data from 2004, however indicate a significantly decreased use of D4, which may partly explain the observed pattern. The dominance of D4 in air may be a result of its higher vapour pressure combined with a longer atmospheric half-life.

The results of the air measurements indicate a regional variation, with highest concentrations in Norway and lowest in Sweden. This is in agreement with consumption data from 2004, which show that at present, Norway is the largest consumer of both D4 and D5 (Figure 1). Diffuse

sources seem to be most important for the observed concentrations of siloxanes. The concentrations were generally elevated in urban areas and in areas close to sewage treatment plants.

VMS were detected in biota samples. They were mainly found in fish from sites representing urban/diffuse sources whereas only a few background samples showed detectable levels. The concentrations in fish liver were fairly variable.

In the Swedish study, one or more of the targeted substances were found in 15 out of 39 human breast milk samples.

There was a great variation in concentrations of the VMS in the samples from sewage treatment plants both in the effluent water and in the sludge. The concentration levels in sludge are in the same order of magnitude as other widespread organic contaminants found in sludge. Siloxanes therefore add to the list of organic pollutants that may make it problematic to use municipal sewage sludge in a sustainable way, i. e. as a source of nutrients in agriculture.

No Observed Effect Concentrations (NOECs) for D4 and estimated Chronic Values (ChV) for D5 were only exceeded in samples representing incoming sewage water to sewage treatment plants. These levels were, however, significantly reduced in the outgoing water from the same treatment plants. Since only little amounts of toxicity data are available for other siloxanes than D4 and No Observed Effect Levels and Chronic Values are estimated from a limited amount of data, the possibility of effects in the local environment close to emissions should not be excluded.

Conclusions

Siloxanes (VMS) are present as common pollutants in the Nordic environment and in many different matrices. They seem to be emitted through diffuse pathways and they enter the aquatic food chain. They are also present in samples of human breast milk. At present, the observed environmental concentrations are not alarmingly high, and many background sites seem to be non-contaminated. Data from in- and outgoing water in sewage treatment plants (STPs) indicate efficient removal of VMS, yet high levels may be reached locally in densely populated areas and/or close to STPs.

The use of siloxanes is extensive, but at current consumption levels they should not pose any risk to the environment due to quick removal mechanisms as pointed out by CES (2006). An increased use could, however, lead to increased environmental levels. It may therefore be motivated to keep an eye on the emissions and environmental concentrations of these substances, in order to avoid concentrations eventually reaching effect levels.

ACKNOWLEDGEMENTS

The Swedish study was performed by IVL Swedish Environmental Research Institute and funded by the Swedish EPA and the Nordic study was carried out jointly between the Norwegian Institute for Air Research (NILU) and IVL and financed by the Nordic Council of Ministers.

REFERENCES

CES. 2006. Re: Octamethylcyclotetrasiloxane (D4), CAS Nr: 556-67-2 (#75 on the list); Decamethylcyclopentasiloxane (D5), CAS 541-02-6 (#124 on the list);

Comments to the report: "Siloxanes in the Nordic Environment". Letter addressed to Mr.Arto Kultamaa, Finnish Environment Institute, 13 March 2006

ECB. 2006. Status report for the 13th Joint Meeting of the competent Authorities for the Implementation of Council Directive 67/548/EEC (New Substances) and Council Regulation (EEC) 793/93 (Existing Substances). European Chemicals Bureau, Doc: JM/10/2006

Kaj L., Andersson J., Palm Cousins A., Remberger M., Brorström-Lundén E., Cato I. 2005a. Results from the Swedish National Screening Programme 2004. Subreport 4: Siloxanes. IVL B1643

Kaj L., Schlabach M., Andersson J., Palm Cousins A., Schmidbauer N., Brorström-Lundén E. 2005b. Siloxanes in The Nordic Environment. Tema Nord 2005:593

Kemi. 2006. PRIO – A Tool for Risk Reduction of Chemicals. http://www.kemi.se/templates/PRIOEngframes_4144.aspx, October 2006

SPIN. 2006. Substance for Preparation in Nordic Countries. Chemical Substance Database. Available at: <http://www.spin2000.net/spin.html>, Oct, 2006

Benzotriazole anticorrosives in municipal wastewaters and in the aquatic environment

Walter Giger, Christian Schaffner, Dimitra Voutsas
Swiss Federal Institute of Aquatic Science and Technology
Eawag, 8600 Dübendorf, Switzerland

E-mail: giger@eawag.ch

INTRODUCTION

The complexing agents benzotriazole (BT) and tolyltriazole (TT, a mixture of 4- and 5-methyl isomers in the benzene ring of BT) are widely used as anticorrosive agents (e.g. in cooling and hydraulic fluids, in antifreezing fluids, in aircraft de-icing fluids, in dish washing liquids for silver protection, etc.), as chemical intermediates for dyes, pharmaceuticals, fungicides, as antifogging constituents in photographic applications and as ultraviolet stabilizers (Hart et al. 2004). These compounds are characterized by high water solubility (28 and 7 g/L, respectively), low vapour pressure and low octanol water distribution coefficients ($\log K_{ow}$: 1.23 and 1.89, respectively) (Hem et al. 2003; Hart et al. 2004). Moreover, these compounds are quite resistant to biodegradation. Consequently, it must be expected that they occur in wastewaters and eventually in ambient waters.

The objective of the first part of this study was to investigate the occurrence of BT and TT in municipal wastewaters and to evaluate their behaviour in mechanical-biological wastewater treatment. The second part of this project aimed to determine residual concentrations and mass flows of BT, TT, NP, OP and BPA in the Glatt River in Switzerland. The overall objective of this study was to investigate the environmental occurrence of BT and TT in rivers, lakes, bank filtrates, and groundwater. Composite samples were collected in the rivers Glatt, Limmat, Rhine, Aare, Aabach, and Ustermer Aa and detailed vertical profiles in the water columns were studied in the Greifensee, Lake Zurich, and Lake Geneva. Based on the measured concentrations and mass flows, this investigation aimed to recognise different input sources, i.e. municipal wastewaters and discharges from an airport. The obtained results should provide insights into the environmental behaviour of the two complexing agents BT and TT and provide a basis for assessing their environmental risk.

The BT and TT concentrations reported in this article amend and substantially extend the data which were reported in an earlier abstract publication (Schaffner and Giger 2004). The investigation of the phenolic compounds NP, OP and BPA is part of a comprehensive programme dealing with the occurrence and the environmental behaviour of oestrogenic substances in the aquatic environment of Switzerland. Previous studies have described the occurrence and behaviour of various organic micropollutants in the Glatt River, e.g. alkylphenolic compounds (Ahel et al., 1994b, 2000) and antibacterial agents (Golet et al. 2002; Mc Ardell et al. 2003). In this report the data for NP in Glatt River are remeasured almost twenty years after the legal ban on the usage of NPnEO surfactants in laundry detergents was issued in Switzerland. The levels of the examined compounds are compared to the analogous concentrations reported for other rivers in other parts of the world.

Experimental Study Area

The Glatt Valley is a densely populated region of 260 km² with 240,000 inhabitants in the northeastern part of Switzerland. The Glatt River catchment includes a northern part of the city of Zurich. The Glatt River has its origin as the outflow of the Greifensee, has a total length of 36 km and is a tributary to the Rhine River. Water flows ranged from 1.7 to 10.9 m³/sec; the lower values were measured in August 2004. Ten municipal wastewater treatment plants (WWTPs)

based on aerated sludge treatment discharge their final effluents into the Glatt River or its tributaries.

Enrichment

A quantitative analytical method was developed using solid-phase enrichment for extraction of aqueous samples and LC/MS/MS for separation and detection. OASIS HLB cartridges were found to be best suited for enrichment. Underivatized extracts in methanol /water (1:1) were analysed by LC/MS/MS with electrospray ionization. Water samples (25 mL for wastewater, 100 mL for river water) were filtered through glass fibre filters (Whatman, GF/F 47mm), the filtrates were acidified to pH 2.5-3.0 and spiked with 50 ng of 5,6-dimethyl-1H-benzotriazole as surrogate standard. BT and TT were enriched from water by SPE through OASIS HLB cartridges (Waters, 60 mg, 3 mL). Solid-phase extraction was performed using a 12-port vacuum extraction manifold. The cartridges were sequentially conditioned with 2 x 3 mL of methanol and 2 x 3 mL of Milli-Q water by applying a slight vacuum. Water samples were percolated through the cartridges at a flow rate of 5 mL/min. The cartridges were dried under vacuum for 10 min and the analytes were eluted with 1.5 mL of dichloromethane containing 3% methanol. The eluates were evaporated to dryness under a gentle stream of nitrogen. Dry residues were redissolved in 0.5 – 1 mL of the LC mobile phase (methanol : water 7:3 with 0.4% formic acid).

Separation, Detection and Quantitation

Underivatized extracts dissolved in the LC mobile phase were analysed by LC-MS/MS for BT and TT. 5,6-Dimethyl-BT served as surrogate standard. An HP Series 1100 system (Agilent) coupled with a triple quadrupole mass spectrometer (API 4000, Applied Biosystems) equipped with a vacuum solvent degassing unit, a binary high-pressure gradient pump, an automatic sample injector and a column thermostat was used. Separation was accomplished with a 125 x 2.1 mm i.d. endcapped C8 column (Macherey-Nagel, Düren, Germany). Isocratic elution was used with a mixture of methanol/water/formic acid (70:30:0.4) as a mobile phase at a flow rate of 0.2 mL/min. Detection of the analytes was accomplished with electrospray ionisation in positive mode and using multiple reaction monitoring (MRM). The following main ions $[M+H]^+$ and two or three fragment ions for MS determination were chosen: for BT from m/z 120 to 64.85 and 92.05, for TT from m/z 134 to 76.85 and 78.95 and for 5,6-dimethyl-BT from m/z 148 to 77.05, 90.95 and 92.85. Due to the highly specific detection, only a partial chromatographic separation was necessary. Thus, short analysis times of only 5 min could be applied. Currently available LC separation performance did not achieve the separation of the 4- and 5-methyl-1H-benzotriazole isomers. As a consequence, the results are reported as the sum of the two isomers, noted by the common name tolytriazole (TT). Quantification of BT and TT was carried out by calculating the relative response factors based on the area of 5,6-dimethyl-BT. Six calibration standard solutions (10 to 500 ng absolute) were used to produce a calibration curve for each compound relative to the internal standard. Recoveries were $99\pm 8\%$ for BT and $97\pm 10\%$ for TT. Limits of detection calculated as 3 times the standard deviation of low level standard were 8 ng/L for BT and 3 ng/L for TT. Limits of quantitation (10 times the standard deviation) were 30 and 10 ng/L for BT and TT, respectively.

Results and Discussion

BT and TT were found in the $\mu\text{g/L}$ range in all samples of primary and secondary effluents from 24 municipal WWTPs in Switzerland. The BT concentrations were always higher than the corresponding TT values, by a factor of 10 to 100. The median values for BT concentrations in primary and secondary effluents are 18 and 10 respectively. BT and TT concentrations in primary and secondary effluents of municipal wastewater treatment plants ranged from below 10 to 100 $\mu\text{g/L}$.

It is evident that both concentration sets contain several outliers with two remarkably high BT concentrations of 100 and 83 µg/L in the secondary effluents. It can be inferred that the occurrence of BT in municipal wastewaters is caused by its application as an anticorrosive additive in dishwasher products. This conclusion could be corroborated by analyses of dishwasher detergent products and of raw municipal wastewaters in the town of Duebendorf [Ort, 2006; Ort et al. 2006]. It is currently not clear how TT gets into municipal wastewaters, because most of its applications are not directly connected to municipal wastewaters.

The elimination of BT and TT in WWTPs are relatively low, as illustrated by the results from 10 WWTPs in the Glatt Valley catchment shown in Table 1.

Table 1 : Benzotriazole and tolyltriazole concentrations in municipal wastewater and elimination rates in WWTPs in Switzerland.

Wastewater treatment plant		Concentrations (µg/L)					
		Benzotriazole			Tolyltriazole		
		effluent type			effluent type		
		primary	secondary	elimination %	primary	secondary	elimination %
A	Fällanden	22	12	45	4.0	1.8	55
B	Bassersdorf	60	58	3	1.1	0.9	18
		75	30	60	1.1	0.8	27
		73	50	32	1.6	0.7	44
C	Dübendorf	17	11	35	2.3	0.7	70
D	Kloten -Opfikon	14	11	23	2.7	1.8	33
E	Niederglatt	64	82	-28	3.2	2.3	28
		68	100	-47	3.1	2.4	23
F	Bülach	39	15	62	2.9	1.2	58
		27	13	52	2.5	1.2	52
G	Glattfelden	15	13	13	0.2	0.1	50
H	Stadel	14	11	21	2.3	0.6	74
I	Mönchaltorf	13	11	15	5.6	3.8	25
K	Uster	16	11	31	5.4	1.9	65

The BT levels in primary effluents ranged from 13 to 39 µg/L, whereas in the two WWTPs B and E substantially higher BT concentrations were observed (60–75 µg/L). The effluents of the WWTPs B and E caused the outlier values in Fig. 1. The higher BT inputs to these two WWTPs can currently not be explained. It is, however suspected that there could be some special inputs from small industries. Currently, no conclusive information is available on the input sources of the TT found in municipal wastewaters. The latter showed in the relatively narrow ranges at the WWTPs of the Glatt Valley: 1.1–5.6 and 0.1–3.8 µg/L in primary and secondary wastewater

effluents, respectively. In WWTP E the BT concentrations even increased from the primary to the secondary effluent. It is assumed that this effect can either be caused by an input variation or a formation during the treatment. For the latter, there would be a need for a precursor chemical. WWTP B showed drastically different elimination rates for BT (3, 32 and 60%). Again an input variation could be invoked to explain this result. If the special WWTPs B and E are not taken into account, the elimination of TT was generally higher (23 – 74%) compared to the corresponding values for BT (13 – 62%). This difference could be caused by the slightly better biodegradability of the methylated benzotriazole (TT). WWTP B again gave an exceptional result: TT was only eliminated by 18% in the same sampling campaign, in which the elimination rate for BT was only 3%.

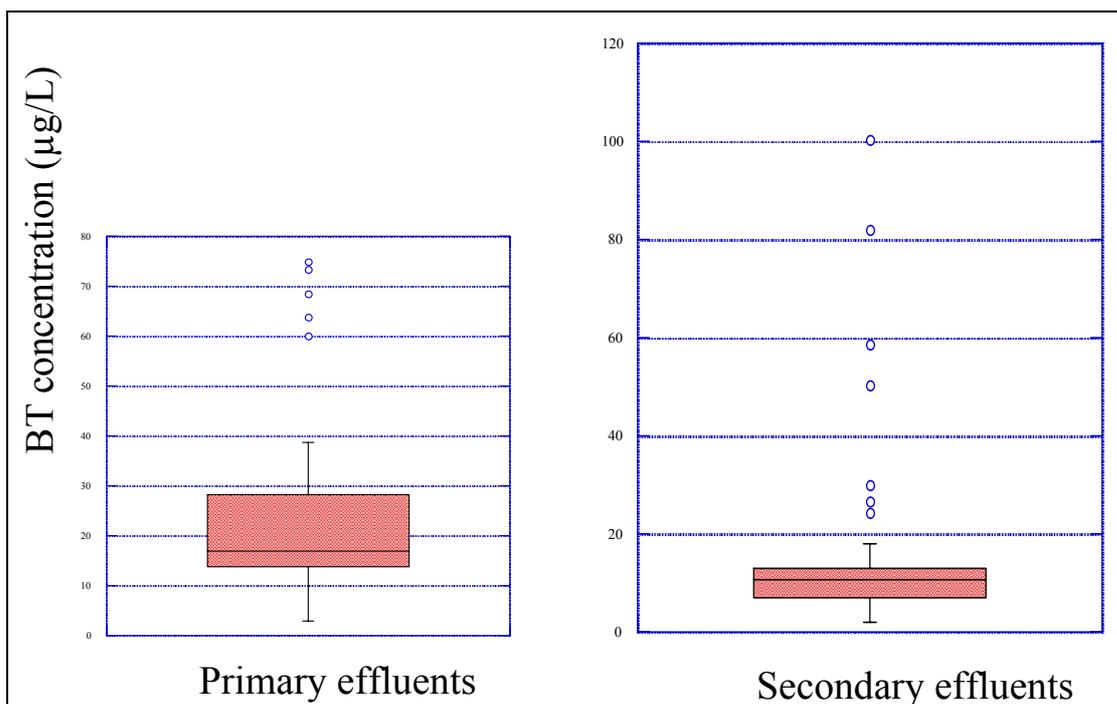


Fig. 1: Benzotriazole concentrations in primary and secondary effluents of Swiss wastewater treatment plants. The box plots indicate 25th, 75th percentiles, median and outlier concentrations.

A wastewater investigation in Berlin yielded results within the concentration ranges reported here. The concentrations were 11.9 and 9.6 µg/L for BT in the influent and in the effluent of one WWTP (Weiss and Reemtsma 2005). The corresponding concentrations for the separated TT isomers in the influent were 2.5 and 2.2 µg/L for 5-TT and 4-TT, respectively. The analogous values for the effluent were 2.0 and 2.1 µg/L.

The results of weekly profiles measured at the two WWTPs Kloten-Opfikon and Thun showed that no decreases could be observed over the weekends, indicating an industrial input, which would be higher on weekdays. The BT levels decreased in the biological treatment of the WWTP Kloten-Opfikon from 2 to 30%. The sand filter had very little impact. In the Thun WWTP BT and TT show higher concentrations and higher eliminations. The higher input levels are attributed to the large number of vehicle repair shops in the city of Thun. Despite the relatively high elimination in the Thun WWTP, the residual concentrations are still in the range of the input levels in the other WWTPs.

The BT concentrations in the Glatt River ranged from 636 to 3690 ng/L. The TT concentrations were 3-6 times lower than for BT, ranging from 122 to 628 ng/L. The highest BT concentrations were found at sites 8 and 9 (3600 and 3350 ng/L). An increasing trend along the longitudinal profile of the river was observed for BT and TT. The sharpest increase was in the June sample

from sampling station 7 to 8. This could possibly be explained by the contribution of the Niederglatt WWTP, which discharges its effluent after sampling site 7 and shows high residual BT concentrations. The concentrations of BT and TT found in this study are similar to the concentrations previously published for the Glatt River (1000-5500 ng/L for BT and 200-1000 ng/L for TT), whereas lower concentrations were reported for the larger Rhine River below Basel (200-500 ng/L for BT and 50-200 ng/L for TT) (Schaffner and Giger 2004).

Concentration ranges in grab samples from the Glatt River in ng/L were 640 – 3700 for BT and 120 – 630 for TT. The corresponding mass flows in kg/d were 0.093–1.9 for BT and 0.018 – 0.36 for TT with clearly increasing trends along the longitudinal river profile. During winter 2003/4, BT loads in weekly composite samples from a station in the lowest stretch of the Glatt clearly indicated the effect of the nearby Zurich airport, where de-icing fluids were used, that contained BT as an anticorrosive additive. In weekly composite samples of water from the Rhine River at Weil am Rhine, below Basel, 0.05 to 0.5 µg BT/L were found approximately corresponding to weekly mass flows of 220 kg BT. The waters of Lake Zurich contained BT and TT concentrations of 93 – 170 and 30 – 53 ng/L, respectively

There are very few data available in the literature on the presence of these compounds in ambient waters. Most of the published data emphasize the presence of these compounds in run-off from airports after anti-icing and de-icing activities and on water bodies, which are directly affected by these fluids. Cancilla et al. (1998) published estimated concentrations in mg/L in subsurface water close to an airport: 126 for BT and 17 for 4-TT and 198 for total TT. High levels of BT have also been determined in a secondary airport run-off outfall (1.67 and 2.16 mg/L for 4- and 5-TT), whereas the concentrations in receiving streams were less than 0.08 mg/L (Cancilla et al. 2003). A small number of results of surface water and bank filtrate analyses from the Berlin area were recently published (Weiss and Reemtsma 2005). In Lake Tegel 0.9 µg/L BT and 0.2 µg/L TT were detected and in the corresponding bank filtrate 0.2 and 0.05 µg/L were measured for BT and 4-TT. In 2 samples from the Landwehr Canal the average concentrations in µg/L were 0.9 for BT, 0.2 for 4-TT and 0.1 for 5-TT.

The investigated contaminants occur at quantitatively measurable but varying concentrations in municipal wastewaters and in the Glatt River, reflecting their ubiquitous input into wastewaters and their different behaviour during biological wastewater treatment.

The anticorrosive agents BT and TT occur in all municipal wastewater effluents and are only partly removed in mechanical-biological wastewater treatment because of their high polarity, i.e. high solubility in water, and their resistance to biodegradation. Thus, residual amounts of BT and TT are widely distributed in the receiving ambient waters. In particular, BT is - after EDTA - the second most abundant individual contaminant in many natural waters. BT can be tracked back to its use as an anticorrosive agent in dishwasher detergents. However, the question of how TT enters municipal wastewaters remains unanswered. Regarding BT and TT it will be interesting to investigate whether discharges in the winter season from the international airport of Zurich have an impact on the concentrations and loads in the Glatt River. The airport is located close to the Glatt River. At the airport, antifreezing and de-icing liquids are applied which contain BT as an additive for the inhibition of corrosion. Additional questions of concern are how BT and TT behave during bank filtration and how they are affected by the various procedures of drinking water treatment plants using lake water as a water resource.

REFERENCES

Cancilla D.A., Martinez J., van Aggelen G.C. (1998): Detection of aircraft de-icing/ anti-icing fluid additives in perched water monitoring well at an international airport. *Environ Sci Technol* 32, 3834-3835.

Cancilla D.A., Baird J.C., Geis S.W., Corsi S.R. (2003): Studies of the environmental fate and effect of aircraft de-icing fluids: detection of 5-methyl-1H-benzotriazole in the fathead minnow (*Pimephales promelas*). *Environ Toxicol Chem* 22 (1), 134-140.

Hart D.S., Davis L.C., Erickson L.E., Callender T.M. (2004): Sorption and partitioning parameters of benzotriazole compounds. *Microchem J* 77, 9-17.

Hem L.J., Hartnik T., Roseth R., Breedveld G.D. (2003): Photochemical degradation of benzotriazole. *J Environ Sci Health. Part A* 38, 471-481.

Ort C., Giger W., Schaffner C., Gujer W. (2006): Modeling stochastic load variations in sewer systems. *Wat Sci Technol* 52(5), 113–122.

Schaffner C., Giger W. (2004): Anticorrosive benzotriazoles as contaminants in wastewaters and rivers. Fall Meeting 2004 of Swiss Chemical Society, *Chimia* 58 (7/8), 453.

Weiss S., Reemtsma T. (2005): Determination of benzotriazole corrosion inhibitors from aqueous environmental samples by liquid chromatography-electrospray-tandem mass spectrometry. *Analyt Chem* 77 , 7415–7420.

Voutsas, D., Hartmann, P., Schaffner, C., Giger, W (2006): Benzotriazoles, Alkylphenols and Bisphenol A in Municipal Wastewaters and in the Glatt River, Switzerland. *Environ Sci Pollut Res* 13 (5), 333–341.

Engineered Nanoparticles

Richard Owen

Principal Scientist, Environment and Human Health
Environment Agency of England and Wales (UK)

E-mail: richard.owen@environment-agency.gov.uk

What is Nanotechnology? [Slide 2] Nanotechnology involves the production and application of substances and structures at the nanoscale, typically with several dimensions below 100nm (0.1microns). Size really matters - substances manufactured in this size range can have very different properties when compared to their larger counterparts, reflecting surface properties and quantum effects that become important at the nanoscale [Slide 3]. Engineered nanoparticles are an important sector of nanotechnologies, representing a diverse range of substances currently on the market, from metal and metal oxide based nanoparticles to carbon – based nanotubes and fullerenes. In fact nanoparticles are far from new, occurring widely, from volcanic dust to atmospheric pollution. What is new is the scale of manufacture of novel nanoparticles and other nanomaterials, exploiting the enhanced properties of materials when produced at this very small size range [Slide 4]. The enhanced properties of nanomaterials offer huge potential socio – economic, health and environmental benefits, which has in turn fuelled a rapid increase in current nanomaterials manufacture. The range of current consumer products alone that incorporate nanotechnology is large: for more information a useful inventory has been established by the Woodrow Wilson Institute (www.nanotechproject.org), (see Inventories) [Slide 5]. This illustrates both the diversity of products and the fact that nanotechnologies represent a wide range of substances which share two or more dimensions in the nano range: some are ‘fixed’, where the nanoscale feature is within a larger object (e.g. computer chips) and others are ‘free’ e.g. nanoparticles or nanotubes.

While engineered nanoparticles offer significant potential benefits, there are also considerable uncertainties with regards to potential risks to environment and human health. If nanoparticles have enhanced properties, are they also more toxic or more persistent? [Slide 6]. Are they more mobile within organisms, do they have novel effects? Do they affect the behaviour and toxicity of other substances they interact with in the environment? Are they emerging pollutants? Are risk assessments for substances in their bulk form sufficient for the same materials as nanoparticles? Are they new or existing substances?

Building public confidence in this important and exciting technology area requires responsible innovation, with appropriate and proportionate controls, based on robust evidence of risks and benefits that are communicated in a meaningful and inclusive way [Slide 7]. So what is the evidence of risks to environment and human health?

In 2003 the UK Government commissioned two leading UK scientific bodies (the Royal Society and Royal Academy of Engineers) to independently assess the evidence: their report, published in July 2004 (www.nanotec.org.uk/finalReport.htm) identified large uncertainties with characterising risks to environment and human health. [Slide 8]. They concluded that most nanotechnologies probably posed few risks, notably nanomaterials that were ‘fixed’. But there were considerable uncertainties with regard to engineered or manufactured nanoparticles. Notable was the lack of data on exposure and hazard of manufactured nanoparticles in the context of environmental exposure.

This was largely based on pulmonary toxicology studies with incidentally – produced, so – called ‘ultrafine’ nanoparticles such as coal dust, which highlighted the potential for health risks from engineered nanoparticles. However the fate, behaviour and toxicity of these materials in the environment is largely unknown, and while there are likely to be current releases the ability

to measure their presence is also currently limited. This presents important challenges to Industry, scientists and regulators whose aim is to promote the responsible development of the technology through a comprehensive understanding of benefits and risks.

Addressing the data gaps for risk assessment of engineered nanoparticles requires both fundamental research and more applied work, the latter looking for example at the appropriateness of current test methods for assessing hazard, development of reference materials and technologies for detection and measurement of engineered nanoparticles in the environment. In the UK research is being co-ordinated through a body established by the UK Government (the Nanotechnologies Research Co-ordination Group) [Slide 9]. In November 2005 it published its research strategy that outlined 19 key research objectives for risk assessment and risk communication (www.defra.gov.uk/environment/nanotech/nrcg). These covered issues of nomenclature and standardisation, metrology and characterisation, exposure, human health hazard and risk, environmental hazard and risk and stakeholder dialogue / public engagement. This report is freely available on the web, or by contacting the email address below. At the same time the EU Commission has developed an action plan that also considers societal, health and environmental issues.

A number of research publications and research programmes are now beginning to address the environmental risks of manufactured nanoparticles [Slides 10 and 11]. Included in this is the UK Environmental Nanosciences Initiative (ENI), which has been established specifically to address this issue, acting as a hub for environmental nanosciences research in the UK.

For more information on the UK Research programme, ENI or general enquiries follow the contact details on [Slide 12].

The presentation is available on the Norman webpage: www.norman-network.net.

Water Framework Directive and Emerging substances: Implications for policy development, research and monitoring

Nick Cartwright
Environment Agency for England and Wales
E-mail: nick.cartwright@environment-agency.gov.uk

The Water Framework Directive (WFD) achieves its objectives of good ecological & chemical status for surface waters and good chemical & quantity status for groundwater through a prescriptive river basin planning process. Under these you establish river basin districts and identify the water bodies within them. You then characterise these water bodies by evaluating their risks from a range of pressures and draw up risk maps that are submitted to the European Commission. You then monitor to clarify whether the risks are real and establish objectives for the water bodies. Programmes of Measures to achieve these objectives are then captured in River Basin Management Plans. Progress toward the objectives are then evaluated at the end of the cycle and the process starts again.

Member States have to establish environmental quality standards for specific pollutants belonging to groups of chemicals identified in Annex V of the WFD that are discharged in significant quantities. So the risk maps are helpful in prioritising which substances will need EQSs. In the UK EQSs for part of classification for good ecological status so if these standards are failed in a water body it must be classified as less than good status. In parallel to this, EQSs set for 33 priority substances by the EC are used to determine the chemical status. If any of these EQSs are failed then not only is the chemical status failed but the overall classification must be less than good, even if the biological status is good. Chemical standards are therefore very important when classifying water bodies.

The UK submitted its risk maps for the first planning cycle in 2004, so at this stage the pressures identified are for known pollutants such as metals, pesticides and other dangerous substances not emerging pollutants. Risk maps are drawn up in different ways depending on the pressures but for example for point sources of metals we estimated loads entering rivers from discharge consents, allowed for river flow and compared the predicted environmental concentrations (PECs) against existing EQSs or predicted no effect concentrations (PNECs).

There are 3 planning cycles 2009-2015, 2015-2021 and 2021-2027. So the UK will publish its river basin management plans in 2009 and programmes of measures will be implemented by 2011 to achieve the objectives in the plans by 2015. In 2015 we have to issue the next set of river basin management plans, this means that from 2009 we will be refining our risk maps so that we can publish these in 2013 to allow for the extensive public consultation necessary before the plans can be put in place in 2015. The EC revises the list of priority substances on Annex X every 4 years- so you can see that there should be 2 revisions in 2008 and 2012 during the next planning cycle. However, 2012 is very late in this cycle to establish monitoring to clarify risks so the key revision for the next cycle is likely to be in 2008 for any emerging pollutants, together with consideration of any additional national EQSs.

So how can we identify emerging pollutants. In 2000, the Environment Agency for England and Wales developed a Chemical Strategy to help us prioritise our activities on chemicals. We have 3 main approaches to priority setting: screening individual substances; reviewing groups of substances and looking for signals in the environment. You can identify groups of substances based on what they are designed to do and potential for environmental exposure. This not only applies to pesticides and pharmaceuticals but also to groups of industrial chemicals that need certain properties that can make them more problematic for the environment if they are to meet their function. Examples are flame retardants and high temperature lubricants. Here you also need to consider substitutes for substances that are already being restricted because of their risks. For example, following concerns about nonylphenol we reviewed all alkylphenols used in the UK and subsequently prioritised a number of substances for investigation. We did a similar exercise for flame retardants and have considered not only brominated flame retardants but also some phosphate substitutes.

Examples of environmental signals include our work on steroids following the identification of feminised fish in our rivers. This has been linked to sewage discharges and to the contraceptive pill (ethinylloestradiol) and natural steroids (oestrone and oestradiol). Another example is cypermethin, a sheep dip chemical whose use has been temporarily suspended while we investigate ecological impacts close to sheep dipping facilities.

Our chemicals screening activities feed into a range of national and international programmes and work on persistent, bioaccumulative and toxic substances or their substitutes is now taken forward under a UK co-ordinated chemical risk management programme. It is important that as well as identifying high hazard substances we screen and possibly evaluate potential substitutes. Our screening approach provides a hazard rating based on combinations of persistence, bioaccumulation and toxicity which is combined with an exposure ranking to give an overall risk rating. It does not address metals. For the purposes of the Water Framework Directive we have adapted this approach to prioritise exposure via the water column as we are only currently setting water column EQSs for specific pollutants.

Determining environmental significance is important as this helps prioritise which specific pollutants need EQSs. We seek to make best use of information emerging from other chemical activities but significant gaps remain on hazard information. We have sometimes used QSARs to help fill these but in due course REACH will provide a firmer basis for hazard information. Member States consider environmental hazards when setting EQSs for specific pollutants but the EC also consider human health. The WFD requires that the EC technical guidance for risk assessment is adopted when deriving EQSs. Where there are data gaps this process uses uncertainty factors of up to 1000 when deriving PNECs. This is appropriate in risk assessment where the uncertainties and uncertainty factors can subsequently be reduced by requiring further information from industry. However, there is no mechanism to obtain additional data from industry when deriving EQSs under the WFD so very precautionary EQSs can result. This represents a very significant analytical challenge for some substances as their limit of quantification has to be about 30% of the EQS to enable monitoring. There is also likely to be pressure against setting EQSs for substances with significant data uncertainties, so we have to consider how these can be filled for emerging substances. We also need to consider how field data can be better used in the derivation process.

Estimating exposure is often even more difficult. We are unlikely to have monitoring or emission information for emerging pollutants and there is no mechanism to estimate chemical usage at member state level. REACH will still not address these issues.

To obtain better information on exposure we have added a number of these substances on to our Pollution Inventory. This will provide information on emissions from sites we regulate under Integrated Pollution Prevention and Control but will not address diffuse inputs. Eventually, emission inventories such as the European Pollutant Emissions Register and the emerging Pollutant Release and Transfer Registers will provide more information. However, broader emission inventories will also be required under the WFD to help report progress on the progressive reduction of concentrations of priority substances. We have also used targeted risk based monitoring programmes to undertake short campaigns on a number of substances. These have to be carefully selected because monitoring is expensive and the time and effort required to develop suitable new analytical techniques has to be balanced against statutory monitoring required by EC directives. The WFD has extensive monitoring requirements for substances with EQSs so we must be careful that substances are not added unless there is a real environmental benefit if we are to retain any capacity for investigatory monitoring.

Priorities will in future emerge from chemical regimes and it is important that chemicals legislation complements the WFD. We are also part of the current UK Competent Authority on chemicals with specific responsibility for undertaking environmental risk assessments. We have an active programme including both national risk assessments undertaken under the UK Chemicals Coordinated Risk Management Programme and ones undertaken for the Existing Substances Regulations (ESR).

Where risks to water are identified for a substance under the ESR it is often suggested that it should be considered for prioritisation under the WFD. However, the sources leading to a risk are often Member State specific and we will need to be sure that the risks are sufficiently widespread to justify the development of EC EQSs. Where they are justified, diffuse inputs are often significant and information collated under the Water Framework Directive needs to be fed back to inform decisions on whether the EC need to restrict the uses of these chemicals, as this cannot easily be done by Member States. In such cases it may be more cost effective to restrict the use of a substance than to upgrade sewage treatment facilities to reduce emissions from household sewage. Examples are the restrictions on the use of nonylphenol that used to be widely used in cleaning products and possibly in the future DEHP a phthalate that is present in plastics.

The new EU Chemicals Strategy REACH may enter into force as early as April 2007 and the registration of industrial chemicals would start a year later. Chemical safety reports will have to be developed as part of the registration process and these must propose risk management measures to address any risks that are identified. These must be communicated down the supply chain and it is the users responsibility to ensure that these are adopted. Some very hazardous substances such as Carcinogens, Mutagens or Reproductive toxicants (CMRs) or substances that are Persistent, Bioaccumulative and Toxic (PBT) or Very Persistent and Very Bioaccumulative (vPvB) will require authorisation by a new European Chemicals Agency for their continued use.

There have been previous initiatives on PBT and vPvB substances under OSPAR where they have been targeted for progressive reduction and phase out because they are likely to accumulate in the marine environment. Under REACH these substances cannot be authorised on the basis of adequate control and continued use can only be justified on the basis of a socio-economic appraisal. Initial estimates suggested that about 200 PBT substances might be identified under REACH.

However, recent work we have done to identify PBTs suggests that many potential PBTs drop out with further testing so we now think this may be an overestimate. Such substances would also be potential candidates for Priority Hazardous Substances under the Water Framework Directive with the aim to phase out and eliminate emissions, losses and discharges.

However, the value of this is questionable because decisions on controls will be made at EC level. While the monitoring required under the Water Framework Directive would provide information on the effectiveness of these decisions, this will reduce the resources available for Member States to identify and address local risks.

In conclusion, we can see that the first river basin management plans are likely to concentrate on traditional pollutants and any views on emerging priority pollutants will be needed soon if they are to feed into the second cycle. It will be important that EU Chemicals legislation complements the WFD. REACH is likely to be important in controlling chemicals at source to tackle diffuse inputs if we are to achieve the Water Framework Directive's objectives for chemical quality, particularly for priority hazardous substances.

Management of emerging pollutants in the marine environment from the perspective of a National Monitoring Authority

Norbert Theobald
Federal Maritime and Hydrographic Agency
Hamburg, Germany

E-mail: theobald@bsh.d400.de

INTRODUCTION

The Federal Maritime and Hydrographic Agency (BSH) is responsible for monitoring water and sediment matrices of the marine environment in the German EEZ of the North and Baltic Seas. Because of the very low concentrations observed in the open sea (water: pg/L, sediment: ng/kg), there are special sampling and analytical techniques requirements for the monitoring of organic contaminants in the marine environment. Administrative, logistic and financial parameters also have to be considered and optimised for monitoring strategies.



Fig. 1 Glass bowl sampler for 100 litres (left) and SPE system for 1 to 30 litres (right)

Analytical challenges

On the one hand, the investigation of time trends requires the application, over many years, of constant procedures and a good quality control system. On the other hand, the implementation of surveys for newly emerging contaminants requires that methods should be continuously updated and developed.

As concentrations in the open sea are generally 2 or 3 orders of magnitude lower than on land, for nearly all new compounds the development of new methods (or at least an improvement of existing procedures) is necessary. Method development and analysis therefore take more time and are quite expensive. Down to concentrations of about 50 pg/L, analysis is challenging but with some practice, skill, and experience it can be managed with a reasonable amount of effort. But below 10 pg/L, the problems increase considerably, as blank problems increase and selectivity of normal GC-MS reaches a critical limit. To overcome these limits the following principles are used:

- Larger sample sizes
- Additional clean-up steps
- More selective detection systems.

By using more selective MS techniques, such as MS-MS or NCI, it is often possible to avoid additional clean-up steps. On the other hand, it is often necessary to develop new sampling systems for sampling large water volumes of 10 to 100 litres. (Fig. 1 shows examples for a 100 litre sampler for LLE and a SPE-extraction system for 1 to 30 litres.)

Table 1 summarises the procedures currently used in the BSH for the investigation of the WFD priority pollutants. As can be seen, it is not possible to use only 1 or 2 procedures, but altogether more than 8 different GC-MS and HPLC-MS procedures are used, combined either with LLE (for non-polar substances) or SPE (for polar compounds) extraction procedures.

With all these techniques, a very good repertoire of methods is available, which means that they can be applied to new contaminants relatively quickly.

Table 2 Analytical methods for the analysis of WFD substances

Substance	Method	LOQ [ng/L]	Remarks
Brom. Diphenylether	GC-NCI-MS (UBA-Project)		Sed. / Biota
C10-30-Chloroalkanes	GC-MS-MS (UBA-Project)		Sed. / Biota
Anthracene	LLE GC-MS	0.003	
Hexachlorbenzene	LLE GC-MS-MS	0.001	
Hexachlorbutadiene	LLE GC-MS	0.01	
Hexachlorcyclohexane	LLE GC-MS	0.01	
Naphthalene	LLE GC-MS	0.05	
PAH (6 to 16 comp.)	LLE GC-MS	0.003	
Pentachlorobenzene	LLE GC-MS	0.005	
Trichlorobenzenes	LLE GC-MS	0.005	
Di(2ethylhexyl)phthalate	LLE GC-MS special	5.0	
Organotin Compounds	LLE/Derivat. GC-AED	0.5	
Nonylphenols	LLE/Derivat. GC-MS	2	
Octylphenols	LLE/Derivat. GC-MS	0.5	
Atrazine	SPE HPLC-MS-MS	0.3	
Diuron	SPE HPLC-MS-MS	0.1	
Isoproturon	SPE HPLC-MS-MS	0.1	
Simazine	SPE HPLC-MS-MS	0.4	
Alachlor	SPE HPLC-MS-MS	0.1	
Pentachlorophenol	SPE HPLC-MS neg.	0.2	
Chlorfenvinphos	SPE GC-NCI-MS	0.02	
Chlorpyrifos	SPE GC-NCI-MS	0.01	
Endosulfan	SPE GC-NCI-MS	0.03	
Trifluralin	SPE GC-NCI-MS	0.005	

LODs vary, ranging from 1 pg/L to 5 ng/L (low LOD are generally restricted by blank problems) but are generally sufficient to determine most pollutants in marine waters.

Selection processes for emerging pollutants

Three different approaches can be identified for selecting new pollutants for monitoring: A scientific, a rational economic, and an administrative approach. All three have their pros and cons, therefore a combination of all three will give the best results; especially as they are partially interconnected.

The scientific approach starts from scientific investigations and results which are specifically looking for possible new pollutants. These can start, for example, from structural considerations, looking for analogues or homologues of known pollutants (brominated flame retardants, fluorinated compounds such as PFOS). Other approaches use results of toxicological investigations, non-target screening surveys or the combination of both – toxicity directed analysis. All these are innovative but expensive, as experimental studies are necessary.

The rational economic approach starts from products which are suspected of posing possible environmental problems. This would apply, for example, for substances which are likely to show biological effects – such as pesticides or pharmaceuticals. A second aspect concentrates on large volume compounds that show a possible threat just by the great amounts used and released to the environment. A prominent, classic example for this is mineral oil. More recent examples are tensides (nonylphenol ethoxylates), additives to polymers (phthalates) or personal care products. Although this approach is in principle straightforward, it is in reality often very difficult to get information such as production volumes from companies, as they often consider this information as confidential.

The administrative approach uses agreed lists of compounds of possible concern or lists for priority action. Generally these are based on tools using elements of the two other approaches. It is therefore a sound approach but, because of the harmonising process, it is slow and presents the smallest common denominator.

Nevertheless, for a monitoring authority like the BSH, the lists of Priority Pollutants of various international organisations, such as the EU (EU-Water Framework Directive: EU-WFD), OSPAR Commission (for the protection of the Marine Environment of the North-East Atlantic) and HELCOM Commission (Baltic Marine Environment Protection Commission) are the most important starting points for the investigation of novel contaminants. Prioritisation procedures within the commissions help to rank the numerous compounds. For the evaluation, and before establishing a monitoring programme on a routine basis, limited initial surveys are needed to investigate the occurrence and distribution of new pollutants in the marine environment. Generally, these studies are first performed on a national basis.

The way OSPAR (and similarly HELCOM) deals with new hazardous substances is shown in the scheme in Fig. 2. The Hazardous Substance Committee (HSC) uses an evaluation process called DYNAMEC to identify and evaluate hazardous substances. In a stepped process it reduces a larger list of “Substances of possible concern” to a small list for “priority action”. Criteria used for the evaluation are shown in the red circle on the left. At the national level the German Environmental Agency (UBA) and the BSH are involved. The BSH mainly contributes by gathering information on concentrations of the hazardous substances in the marine environment, which are essential for the “background paper”. If no information is available, “one-off surveys” will become necessary. This procedure illustrates that the process of implementing new pollutants would profit if the monitoring agency (BSH) could identify and analyse emerging pollutants in advance of the official prioritisation processes (s.a.)



Fig. 2 Prioritisation processes within OSPAR

As there are too many substances of possible interest, a strategy has to be found for ranking emerging pollutants. In addition to the described criteria which are used for the prioritisation processes on the administrative level, a monitoring agency has to consider additional, more practical parameters for setting priorities.

New investigations

As ca. 90 % of the resources are taken up by routine work, only 10 % at most are available for including additional, emerging pollutants in the survey programme. It is therefore important to optimise the efficiency of all processes and to find ways to get free resources.

Good quality is a prerequisite for all environmental investigations, but quality is not a rigid parameter. As time (labour, cost) and quality are directly proportional it is worth considering and checking the quality of a survey which is necessary to reach the monitoring objectives.

As is schematically shown in Fig. 3, quality and effort can change during the monitoring life cycle. Generally, investigations start in Phase I with a limited screening (what is the concentration range, where are the compounds detectable?). Then, a quite intensive Phase II concentrates on spatial distributions and temporal trends and possibly processes. It might be possible to reduce the effort as early as Phase III, when processes are known or when changes are constant. It is often difficult to confess to Phase IV, when the pollutants have decreased to nearly zero. (Experts are 'in love with' their methods and field of interest).

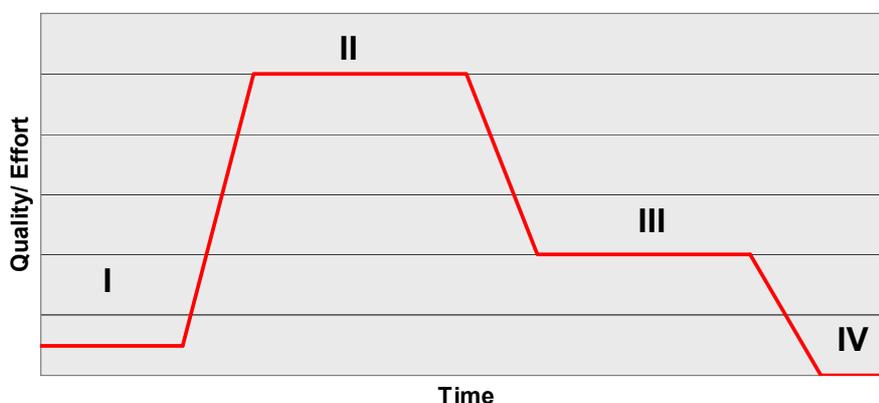


Fig. 3 Quality requirements during monitoring life cycles

This shows that it is not always necessary to analyse all compounds with the highest precision. By checking the quality needs for old pollutants it might be possible to free some resources.

This is valid not only for the number of compounds (analysis of indicator compounds instead of a great number of isomers or homologues) and the precision and sensitivity of the analysis, but can be applied for the sampling strategy as well, where a compromise has to be found for temporal and spatial resolution. Here again, the monitoring objectives define the necessary precision.

As sampling in the marine environment is highly expensive and time-consuming, optimisation of this field is of special importance. As the optimal sampling strategy with high temporal and spatial resolution is too expensive for routine monitoring, the following compromises were developed for the BSH monitoring strategy:

Compromise 1 is applied mainly for the classical pollutants: one survey per year is analysed to a high quality (high spatial resolution and many compounds (70)), the other 2 or 3 surveys are analysed for a few major compounds only (economy analysis, for better time resolution of selected (indicator) compounds).

Compromises 2 is used for 35 new polar pesticides: All surveys are treated equally, but only a reduced set of stations has been selected, thus only a reduced spatial resolution is obtained.

Although, after optimisation of all processes, some free valences could be generated, these were insufficient, by far, to survey the great number of new substances of interest. Therefore, co-operation with other institutions and participation in research projects were considered as necessary additional tools for the investigation of emerging pollutants and these became of vital importance for obtaining fast results.

Examples for these projects together with the core (routine) parameters are shown in Fig. 4. While the centre core contains the classical pollutants, the extended outer shell contains some 30-40 new polar pesticides.

Projects are grouped in the periphery. Some projects were funded, some were loose co-operations. From this periphery of projects, some new pollutants meanwhile moved into the outer routine shell after being considered as important for monitoring.

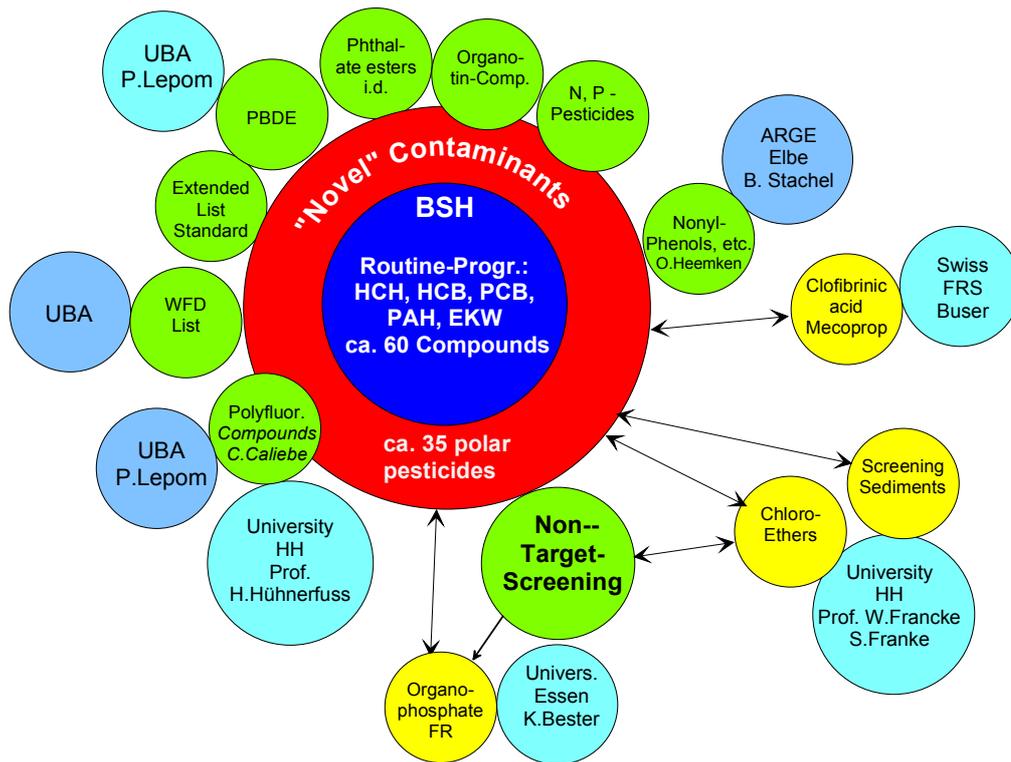


Fig. 4 Network of co-cooperations and projects of the BSH surveys

Examples of the investigation of emerging pollutants

In contrast to 'classical' pollutants, most of the emerging hazardous substances are more polar and/or need special analytical procedures. In particular, HPLC-MS-MS enabled the investigation of a great range of new compounds. This showed that many new pesticides and other xenobiotics are spread into the marine environment and are observed in part at much higher concentrations than classical non-polar pollutants. Examples are presented for different herbicide classes (triazine, phenylurea and phenoxyacetic acid) and perfluorinated compounds (PFOA, PFOS) in the North and Baltic Seas.

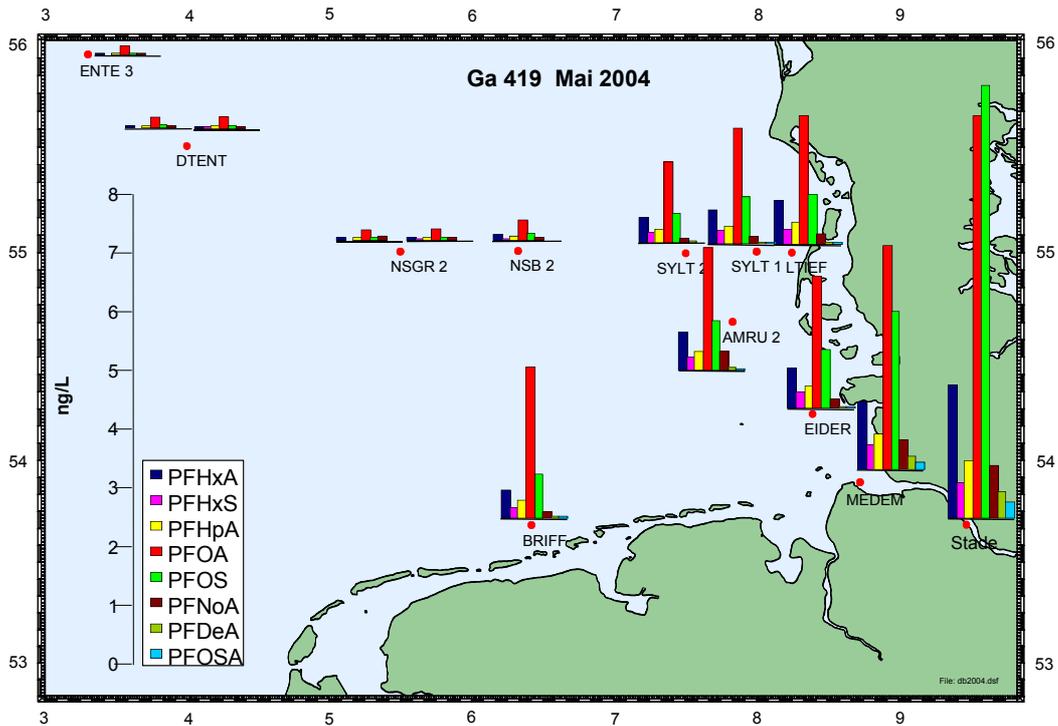


Fig. 5 Concentrations of perfluorinated compounds (PFC) in surface water of the German Bight in May 2004

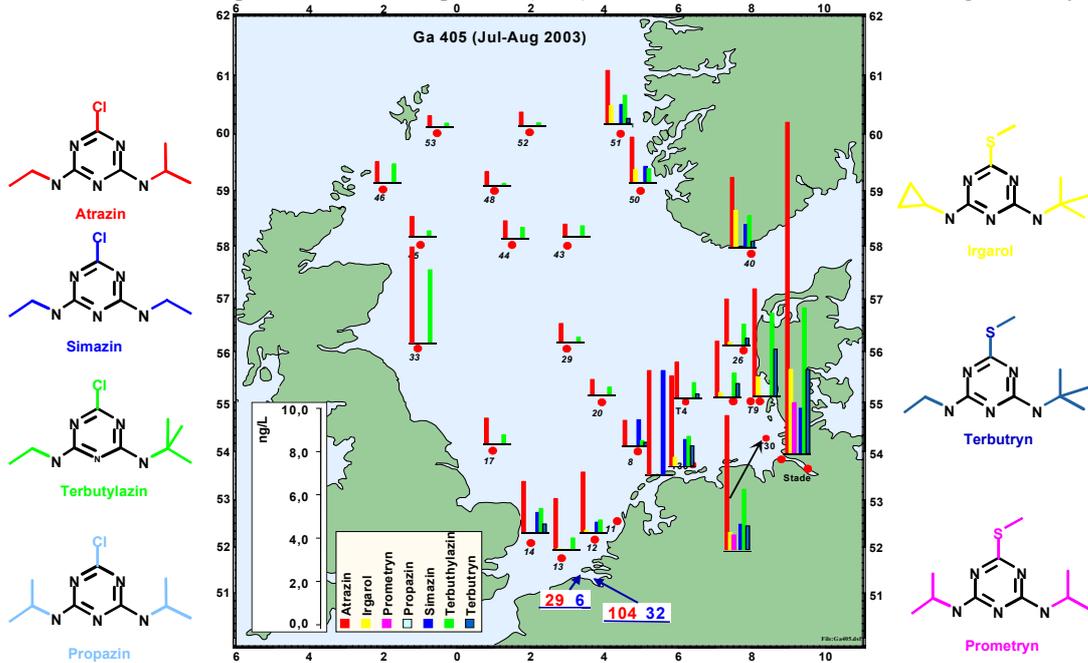


Fig. 6 Concentrations of triazine herbicides in surface water of the North Sea in Jul/Aug 2003

These examples underline the necessity of investigating emerging pollutants in the marine environment. In addition to activities within the monitoring bodies it is essential to use any scientific information available to identify new possible pollutants and to obtain a most comprehensive picture of the contamination burden. In this respect it is considered necessary to perform non-target screening investigations by different MS techniques in order to identify as yet unknown contaminants.

Large knowledge gaps still exist in the field of effects and evaluation, especially for chronic effects of low concentrations and multi-component mixtures. As the integration of chemical and

biological monitoring is still very problematic, the precautionary principle becomes of special significance for the marine environment.

SUMMARY

- Monitoring of organic pollutants is a permanent challenge, as the list of analysing compounds has to be updated constantly.
- Investigation of emerging pollutants is a very demanding analytical and logistic challenge - especially in the Marine Environment.
- OSPAR, HELCOM and EU have set up valuable tools for identification and ranking of emerging pollutants.
- Rapid information exchange is necessary.
- Co-operation with other institutions is of vital importance.

How the drinking water industry deals with emerging pollutants – three decades of experience in the Netherlands

Jurgen Volz and Margreet Mons
Kiwa Water Research, Nieuwegein, Netherlands

E-mail: j.volz@planet.nl

Summary

Since the early 1970s the Dutch drinking water industry has been forced to deal with the (potential or proven) occurrence of an ever increasing number of emerging environmental pollutants (EEPs) in ground water, surface water and drinking water. Historically, the focus of concern has shifted from toxic heavy metals (e.g. mercury and cadmium) and disinfection by-products (e.g. trihalomethanes) to pesticides, endocrine disruptors, pharmaceuticals and a host of other organic EEPs. The EU Drinking Water Directive and the Dutch Drinking Water Ordinance require drinking water suppliers to guarantee a) compliance with drinking water standards (MAC= Maximum Admissible Concentration) for several dozens of substances, b) that drinking water does not contain any unregulated substances (e.g. EEPs) in concentrations which may be harmful to human health. The second requirement demands adequate monitoring and risk assessment strategies. The development of these strategies, which will be illustrated with some examples, is one of the main tasks of Kiwa Water Research, the joint R&D institute of the Dutch drinking water industry. One of the most serious problems with EEPs is that regulators tend to develop purely ecotoxicological EQS (Environmental Quality Standards) for these substances without taking drinking water aspects into account.

INTRODUCTION

The concept of emerging environmental pollutants (EEPs) encompasses an implicit time dimension: an EEP is 'born' whenever someone for some reason labels a previously unknown or seemingly innocuous substance as EEP. Some EEPs have a relatively short 'life span', say about ten years, in which scientific research proves that they pose no threat to the environment (anymore). In that case the EEP is allowed to 'die' and resume its life as an 'ordinary' substance. But in most cases EEPs are pretty 'stubborn' and hard to eradicate, as is illustrated by EEPs which were 'discovered' in the 1970s but are still causing us trouble today. The Dutch drinking water industry has more than three decades of experience in dealing with EEPs and the problems they cause. Kiwa Water Research, the joint R&D institute of this industry, has been involved in all stages of the ongoing process of coming to terms with EEPs. This process started around 1970 when newly developed analytical methods revealed elevated concentrations of toxic heavy metals (e.g. mercury, cadmium and chromium) in the river Rhine, an important source of drinking water in the Netherlands and Germany. In 2006 these substances are no longer regarded as a threat to drinking water supply, mainly because successful emission control programmes have ensured that compliance with the strict drinking water standards for these substances is now easily achieved in all parts of the Rhine basin.

Emerging pollutants and drinking water

Why are drinking water companies in the Netherlands and elsewhere concerned about EEPs? The provision of safe drinking water to all citizens is a cornerstone of public health policy in the European Union. According to the EU Drinking Water Directive¹ drinking water is wholesome and clean if it

¹ Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption; Official Journal of the European Communities, L 330, 5 December 1998

- a) meets the minimum requirements set out in Annex I, Parts A and B, and
- b) is free from any substances which constitute a potential danger to human health.¹

Annex 1 enumerates mandatory Drinking Water Standards (DWS) for about 35 regulated chemical substances (e.g. arsenic, benzene, cadmium and mercury) and several microbiological parameters (e.g. *E. coli*). Compliance with these standards is not only monitored by the water utilities themselves, but also regularly checked by the national health authorities, who are obliged to submit annual reports to the EU Commission.

There are no mandatory procedures to check (non)compliance with regard to the second requirement (b), however. This is one reason why monitoring for unregulated and potentially dangerous substances such as EEPs in drinking water is such a tremendous and increasingly difficult task for water utilities. Another problem is sheer numbers.

At present, there are hundreds, if not thousands of EEPs whose presence or absence in drinking water warrants to be checked. For technical and financial reasons this is practically impossible. So, how can water utilities convince their regulators and customers that the drinking water they supply is 'free' of these unwanted substances? A pragmatic case to case approach to deal with this problem has gradually evolved over the past three decades in the Netherlands. The basic elements of this approach, which has proved particularly useful for unregulated EEPs, are:

1. Assess likelihood that a 'new' EEP is present in your source (surface or ground) water
2. If presence can't be ruled out with certainty, conduct limited monitoring survey of representative source waters
3. If source waters contain the substance, check the drinking water produced from these sources
4. If present in drinking water, inform regulatory authorities and assess toxicological risks
5. If risks cannot be ruled out, investigate and implement treatment and source protection options.

Historically, two groups of emerging pollutants have created many problems for the drinking water industry in the Netherlands and elsewhere: disinfection by-products (DBPs) and pesticides. DBPs are a special EEP category because of their unusual origin. In 1974 a Dutch scientist employed by Rotterdam Waterworks discovered that the worldwide treatment practice of chlorine disinfection resulted in the formation of trihalomethanes and other halogenated compounds², some of which were known carcinogens. In due time regulators all over the world (e.g. the World Health Organisation, the U.S. Environmental Protection Agency and the EU Commission) reacted with strict DBP DWSs (= Maximum Admissible Concentrations) and treatment guidelines for drinking water utilities. The drinking water industry responded by trying to optimize the treatment process (e.g. enhanced removal of organic precursors to minimize DBP formation) or by replacing chlorine with another disinfectant such as ozone.

It took quite a number of years to discover that ozone disinfection of source waters that contain bromide may also lead to the formation of an undesirable toxic DBP (bromate, a known carcinogen), which immediately raised bromide to EEP status. Thus, the dilemma of maintaining the necessary disinfection (microbiological safety) of drinking water while minimizing the risks of DBPs was not easily overcome. Eventually, it took more than 30 years to phase out drinking water chlorination in the Netherlands and replace it with less problematic technologies such as membrane filtration, advanced oxidation and UV irradiation.

¹ Our emphasis

² Rook JJ, (1974) Formation of haloforms during chlorination of natural waters *Wat. Treatm. Exam.* 23, 234-243.

The emergence of pesticides as a new EEP category in the 1980's was a special case, too, because it was provoked by an administrative action, the first EU Drinking Water Directive¹. This directive introduced a DWS of 0.1 µg/L for individual pesticides (0.5 µg/L for the sum concentration of all pesticides), which was upheld in the revised directive of 1998. A DWS at the 0.1 µg/L level inevitably makes each new pesticide on the market a guaranteed EEP for the drinking water industry.

Both EEP groups discussed so far share the characteristic trait that they were regulated at a relatively early stage of their emergence. Regulated substances are easier to deal with for water utilities because there is a mandatory DWS to be complied with. Of course, failure to comply means trouble. The utility is obliged to notify its regulatory health authority, which may or may not allow a temporary derogation.

Eventually the regulator will demand better treatment such as pesticide removal by activated carbon filtration in order to solve the problem. A less expensive option for groundwater resources may be to decommission contaminated wells, if possible. Whatever the remedy – the additional costs of EEP monitoring and enhanced treatment will appear on consumers' bills in the end. This is why the water industry strongly advocates source protection such as use restrictions or total bans of problematic pesticides and Environmental Quality Standards (EQS) and emission standards for other EEPs.

There seems to come no end to an incessant stream of EEPs that may exert a negative impact on drinking water quality. The 'discovery place' of a new EEP seems increasingly irrelevant in a globalized world. Experience with EEPs such as MTBE suggests that if the occurrence of substance X in Californian aquifers is publicized by American journals, alarm bells should start ringing in the ears of European water utility managers. Conversely, if new and extremely sensitive analytical methods reveal the presence of substance Y in the river Rhine, it would come as no surprise to find the same substance in American or Japanese rivers, if the same methods were applied there.

Lesson no. 1 is thus: Be on the alert at all times and try to keep in touch with what is going on in the world around you. The mere fact that a 'new' EEP has surfaced somewhere ought to trigger an automatic response – an urge to assess whether this EEP is likely to have a bearing on your own situation. But there are other, technology-driven triggers for action as well. Water quality monitoring systems are improving at an incredible pace.

The micrograms of yesteryears are nanograms now and may turn into picograms in a few years time. In addition, new analytical methods are bound to disclose unidentified (meaning presently unidentifiable) substances in our rivers or environment at large. And finally, there is the fact that we are increasingly encountering biological (e.g. endocrine) effects, which can not or not entirely be attributed to known chemical compounds.

EEP monitoring in the Netherlands

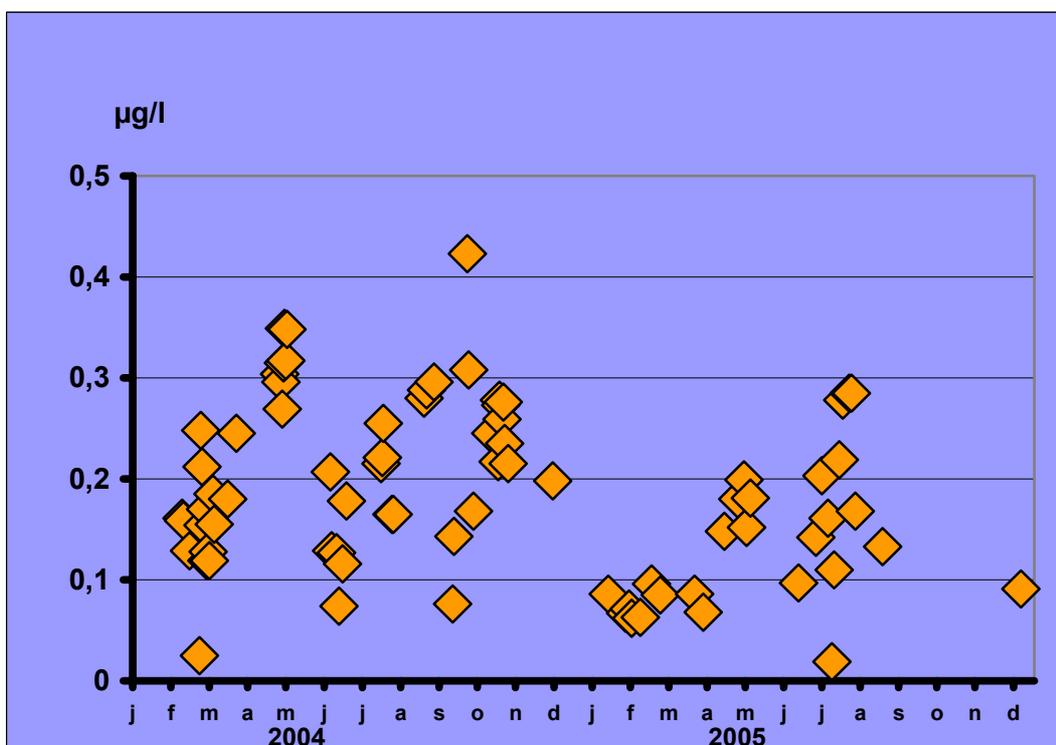
The Dutch drinking water industry has a long tradition of devoting lots of energy and effort towards monitoring of source water quality, in particular the quality of the rivers Rhine and Meuse which satisfy over 40% of the national drinking water demand. As an example, take the

¹ Council Directive 80/778/EEC of 15 July 1980 relating to the quality of water intended for human consumption; Official Journal of the European Communities, L 229, 30 August 1980

partly automated water quality monitoring station Keizersveer on the river Meuse, which is jointly operated by Rijkswaterstaat (National Water Management Board) and Evides, the regional drinking water company. The station is adjacent to the water intake for 2.5 million drinking water customers in Rotterdam and the South West Netherlands. In 2004, no less than 330 organic compounds were monitored at this site, with analytical frequencies ranging between 13 and 365 times per year. 180 (55%) of these were pesticides (or their metabolites) and another 60 were other regulated EEPs (e.g. polycyclic aromatic hydrocarbons [PAH], polychlorinated biphenyls [PCB] and aromatic anilines).

Total monitoring costs amounted to about € 150,000 per year, or an additional 0.1 €cents per cubic meter of drinking water. Water quality monitoring at Keizersveer has yielded interesting results, especially since HPLC-DAD equipment was deployed in the spring of 2004. Some of these results, kindly provided by Evides, are presented here.

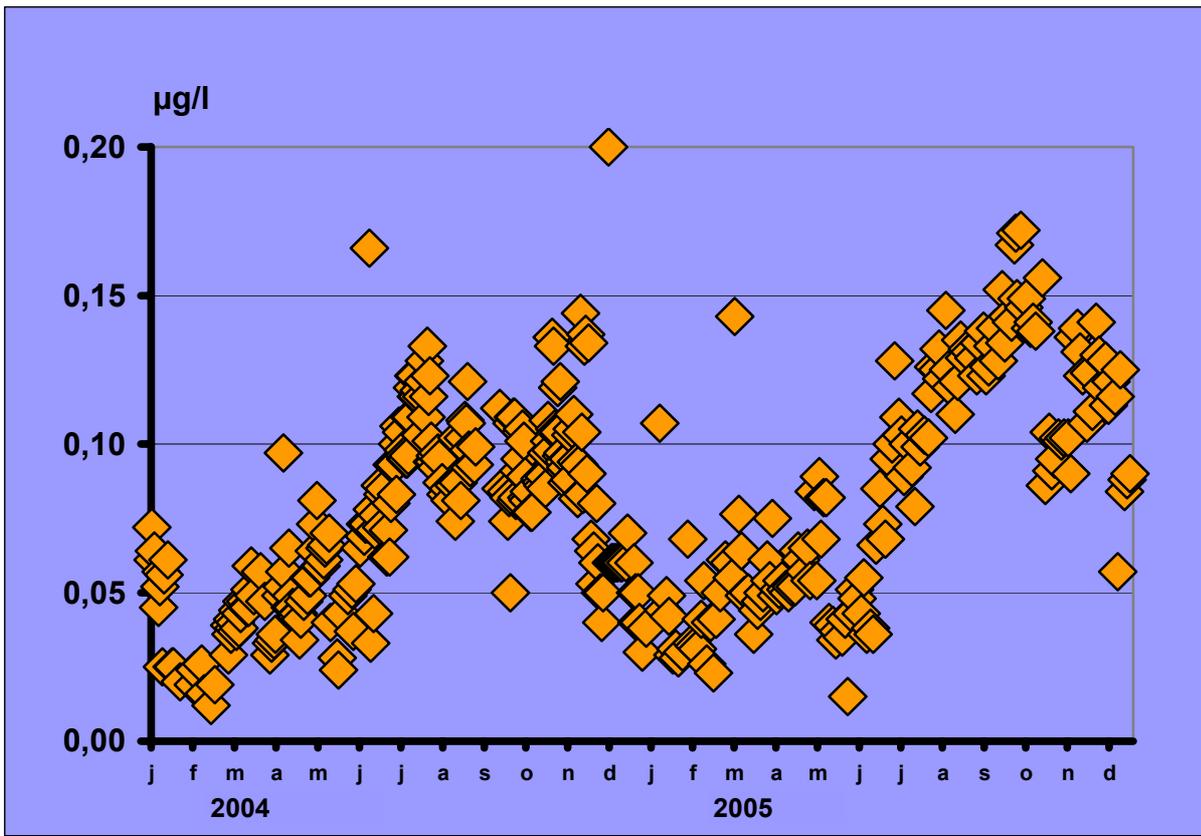
Figure 1: Carbendazim in Meuse water (Keizersveer 2004-2005)



Carbendazim is a benzimidazole fungicide whose presence in Meuse water was hitherto unknown. The figure shows that the pesticide DWS of 0.1 µg/L is exceeded frequently. Carbendazim is mainly used in agriculture, in particular by potato farmers.

A second example refers to a different group of EEPs, pharmaceuticals.

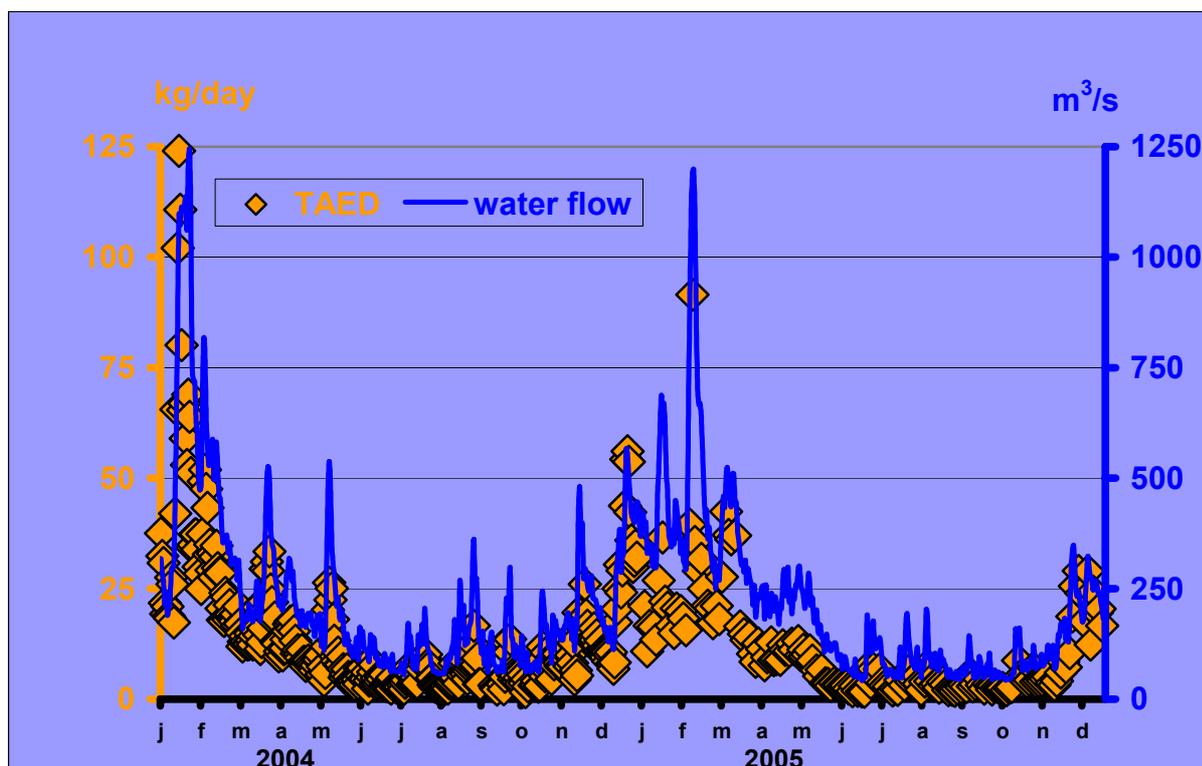
Figure 2: Carbamazepine in Meuse water (Keizersveer 2004-2005)



The presence of nanogram/L levels of carbamazepine and other pharmaceuticals (e.g. clofibrinic acid) in the water of the rivers Meuse and Rhine was no new fact, but all previous investigations were confined to a very limited number of water samples. The high-frequency HPLC-DAD monitoring at Keizersveer revealed the rather disturbing fact that traces (20-200 ng/L) of carbamazepine can be detected in practically every Meuse water sample. It is likely that the same situation exists in the river Rhine and other European rivers.

Another EEP, TAED (Tetra Acetyl Ethylene Diamine), a common bleaching agent in detergents, was likewise present in almost every Meuse water sample with concentrations ranging from 0.25 to 1.5 µg/L. Remarkably, there exists an almost perfect correlation between the TAED load and the water flow in the river Meuse. A logical explanation for this phenomenon has not been found yet.

Figure 3: TAED load and water flow in the river Meuse (Keizersveer 2004-2005)



From monitoring to risk assessment

The demonstrated presence of EEPs like carbendazim, carbamazepine and TAED in its source water forces a water utility like Evides to investigate, whether these substances are (likely to be) present in its drinking water as well, and, if this turns out to be the case, to carry out a human health risk assessment.

Since carbendazim is a regulated substance with a DWS of 0.1 µg/L, Evides checked drinking water samples from relevant treatment stations, but did not detect any traces of carbendazim. Obviously, the multi-barrier approach, which is typical for all Dutch water utilities with surface water sources, is sufficiently robust to completely remove a substance like carbendazim during treatment. The other two EEPs are unregulated substances without a DWS, so a toxicological risk assessment was needed in their case. According to EU experts TAED is practically not toxic at all¹ and easily biodegradable in sewage (and water) treatment works. Therefore, the present concentrations of this substance in Meuse water pose no threat whatsoever from a drinking water perspective. In a survey commissioned by the Dutch Drinking Water Inspectorate and carried out by RIVM² in 2002 trace levels of carbamazepine were only detected once in a single, relatively old treatment station. The concentration found was 23 ng/L, equivalent to a lifetime exposure³ of 1.2 milligrammes, whereas the average therapeutic dose of this pharmaceutical drug is 400 milligrammes per day! Based on a toxicological assessment RIVM recommended a tentative DWS of 50 µg/L, which was more than 2,000 times higher than the concentration found in drinking water. Hence the conclusion was drawn that trace levels of carbamazepine in drinking water had no health significance at all. The treatment station where

¹ <http://www.heraproject.com/ExecutiveSummary.cfm?ID=203>

² Rijksinstituut voor Volksgezondheid en Milieu (National Institute for Public Health and the Environment)

³ Assumption: drinking water consumption of 2 L/day during 70 years

carbamazepine had been detected has nevertheless been retrofitted and modernized (activated carbon filtration and UV disinfection) since 2002 and no traces of carbamazepine have been detected ever since.

Terra incognita

Some EEPs which concern drinking water utilities do not even have a name yet. Broad screening methods such as those employed in Dutch rivers like the Rhine and Meuse (e.g. HPLC-DAD, HPLC-UV and GC/MS) frequently yield unknown peaks. How to deal with these substances X, Y or Z? If a peak X appears more or less regularly in source water, it is necessary to check the drinking water produced from this source. If X is detected there as well (regularly and in quantities which cause concern), efforts may be made to identify and quantify this compound. Successful identification and quantification are necessary prerequisites for the last steps: toxicity assessment and, if necessary, routine monitoring and additional treatment. However, this perfectly logical strategy may encounter practical difficulties such as lack of toxicological data, even if the toughest nut – identification – is cracked. In May 2006 Kiwa Water Research commissioned a state-of-the-art LTQ Orbitrap MS-MS system, which is capable to analyze more than 100 target compounds in one run. It is expected that this system will have a much higher identification success rate. The Dutch water industry is nevertheless convinced that even the most sophisticated chemical analysis is not capable to cover the whole ground. The remaining parts of 'terra incognita' (the EEPs we don't know yet because we lack the means to detect them) must be covered with biomonitoring systems, which target the combined toxicity of all compounds of the extremely complex surface water matrix.

Early Warning Stations

Biomonitoring systems have been installed at seven early warning stations along Rhine and Meuse river branches in the Netherlands.

Figure 4: Early Warning Stations in the Netherlands



Two of these stations (Lobith and Eijsden) are located at the entry point of the Rhine and the Meuse into the Netherlands and are managed by Rijkswaterstaat, the National Water Management Board. The other stations are located near abstraction points and are managed by the regional drinking water utilities. Common biomonitoring systems in the Netherlands include *Daphnia*, algae and mussel monitors, which are primarily designed to detect any unreported toxic spills that may have occurred upstream. Alarm signals from these biomonitors usually trigger a river water intake stop. Only on very rare occasions has it been possible to isolate and identify a single compound which triggered a biomonitor alarm: in 2004 repeated *Daphnia* monitor alarms at Keizersveer early warning station were caused by a hitherto unknown compound, later identified by Kiwa Water Research as 3-Cyclohexyl-1,1-Dimethylurea.

Historical lessons and recommendations for the future

National water quality monitoring programmes in the Netherlands and elsewhere have tended to neglect EEPs with drinking water relevance, in particular pesticides, which has forced drinking water utilities to take much of the monitoring into their own hands. The main focus of these programmes is on EEPs which pose a threat to the aquatic ecosystem. Worse still, if mandatory Environmental Quality Standards (EQS) for critical EEPs are discussed, national and EU authorities often fail to consider that the DWS is much lower than the EQS for most pesticides.

In the Netherlands, for example, the current EQS for the herbicide glyphosate is 70 µg/L, while the DWS is 0.1 µg/L as for all pesticides!¹ In the worst case this means that a water utility using 'ecologically safe' river water would have to achieve 99.9% treatment efficiency, which is practically impossible. Whether the wrongs of the past will be righted in the future is largely depending on how the EU Water Framework Directive (WFD)² will be implemented in the years ahead. Article 7, paragraph 3 of the WFD states:

“Member states shall ensure the necessary protection for the bodies of water identified with the aim of avoiding deterioration in their quality in order to reduce the level of purification treatment required in the production of drinking water.”³

Taken seriously this provision means that the EQS for pesticides in surface waters (at the point of abstraction) must be the same as the EQS which the EU has already adopted for the protection of ground water, namely 0.1 µg/L. Secondly, it is essential that the water quality monitoring programmes the WFD requires from the member states are suited to protect not just the aquatic environment but also our drinking water. Against the background of the strict DWS of 0.1 µg/L this means in particular, that all pesticides must be monitored with sufficient frequency and accuracy (detection levels below DWS).

¹ The European DWS is based on the precautionary principle. The United States DWS are based on toxicological assessments instead, resulting in a DWS of 700 µg/L for glyphosate.

² Directive 2000/60/EC of the European Parliament and of the Council establishing a framework for the Community action in the field of water policy, 23 October 2000, http://ec.europa.eu/environment/water/water-framework/index_en.html

³ Official Journal of the European Communities, L327, 22 December 2000 (our emphasis)

Management of emerging pollutants in soil

Claudio Carlon

European Commission – DG Joint Research Centre, Institute for Environment and Sustainability, Rural, Water and Ecosystem Resources Unit

E-Mail: claudio.carlon@jrc.it

Risk management of contaminated land in Europe

The management of contaminated land is commonly based on risk assessment methodologies. In Europe, the Risk Based Land Management (RBLM) concept has inspired several national regulatory systems, and more recently the preparation of the European Soil Thematic Strategy.

According to the RBLM approach, the management of contaminated land differs, but is closely related to the management of the air and water compartments, as follows:

- the term “land” indicates the need for an integrated approach to contaminated soil, surface water nearby and groundwater beneath.
- the definition of sustainable solutions requires the proper consideration of the temporal and spatial dimensions.
- as for the temporal dimension, long term care objectives should be defined in consideration of the mobility (low mobility for some contaminants in soil) and degradability of contaminants.
- a distinction is usually made between the historic contamination (inherited from the past) and the prevention of future contamination.
- as for the spatial dimension, the remediation of contaminated land is closely linked to spatial planning and is usually driven by the “fitness for use” concept.
- a distinction is usually made between local and diffuse contamination, being the former a problem to be solved by the landowners, and the latter a problem related to multiple stakeholders and environmental protection strategies at larger scale.

In support of the management of contaminated land, the risk assessment is usually applied at three different levels:

- the relative risk assessment, aimed at the identification and ranking of contaminated sites at regional scale,
- the screening risk assessment, which provides screening concentration thresholds of contaminants in soil and water based on standard scenarios,
- the site specific risk assessment, which estimates the risk at a specific site based on local conditions in support to remediation actions.

Due to wide differences in the application and outcomes of risk assessment for contaminated land across Europe, in the last few years both regulators and the scientific community invoked a certain degree of harmonisation.

For this purpose the JRC, in collaboration with several other European research institutes, launched a long term research framework, named HERACLES, **H**uman and **E**cological **R**isk **A**ssessment for **C**ontaminated **L**and in **E**uropean **M**ember **S**tates, (Carlon, 2005).

HERACLES is an open research framework that addresses three levels of risk assessment, *Relative Risk Assessment*, *Screening Risk Assessment*, *Site Specific Risk Assessment*, and encompasses both human health and ecological risk assessment. It combines research and pilot projects and workgroups discussion (<http://eusoils.jrc.it:8081/index.cfm?ID=203>).

With regard to emerging pollutants

With reference to the risk management of contaminated land, the assessment and management of emerging pollutants raises several open questions about major sources, their occurrence and effects. Moreover, regulatory systems might be not prepared to address emerging pollutants in soil.

A distinction between local contamination and diffuse contamination can be convenient.

Local contamination can be associated to e.g. landfills or industrial facilities. With this regard, some years ago regulators focused the attention on gasoline additives such as Methyl-tert-butyl ether (MTBE), (EFOA, 2002). The suspect of carcinogenic effects of MTBE was a high concern due to the frequent occurrence of spillages at gasoline stations and the high solubility and mobility of MTBE in groundwater. The EC Risk Assessment Report published in 2002 concluded that MTBE is not carcinogenic according to the criteria set forth in the EU Directive on Dangerous Substances. Notwithstanding, there is still wide uncertainty about the proper regulation of MTBE in soil and groundwater, as it is evident from the large variation of environmental quality criteria proposed by different European countries: (serious risk) threshold values of MTBE in soil varies between 9 (Belgium Flanders and Walloon Regions) and 100 mg/kg (Lithuania) for most sensitive land uses, and between 70 (Finland) and 250 (Italy) mg/kg for less sensitive land uses. Negligible risk values thresholds are set as low as 0.7 mg/kg (Finland). The widest variation is for MTBE thresholds in groundwater: from 10 µg/L (Italy) to 300 µg/L (Belgium) and 9,200 µg/L (The Netherlands).

A concern exists that the disposal of electronic equipment (e-waste) may leach toxic chemicals into the leachate of lined landfills or contaminate groundwater near unlined landfills. Out of these chemicals, lead is a major potential contaminant. The leaching of brominated flame retardants (BFR) like Polybrominated diphenylethers can be also relevant, since electrical and electronics account for a very high consume of BFR (US-EPA, 2003).

In the case of local contamination, the regulatory system addresses the contaminated media (the soil) and the remediation burden is loaded on the polluter. However, emerging pollutants are not usually analyzed, or the responsibility of the polluter is difficult to be proved. Concentration thresholds (based on screening risk assessment) are not provided, and a site-specific risk assessment might be necessary. At site-specific level, the cause-effect relation can be hard to be proved. The site-specific ecological risk assessment (SS-ERA) usually relies on the TRIAD approach, where chemical, eco-toxicological and ecological evidences are jointly considered (Long and Chapman, 1985; Jensen and Mesman, 2006). Based on bioassays, the TRIAD approach might outline eco-toxicological and/or ecological effects that can be hardly related to the occurrence of specific substances in a mixture. In any case, the SS-ERA methodology applied to contaminated soil is far from being a standardised approach and is still in the domain of the scientific research.

For example, Figure 1 shows potential sources of soil contamination by emerging pollutants. Beside the direct exposure to contaminated soil, the most critical pathway of exposure for human health and ecological receptors is likely to be the leaching to groundwater.

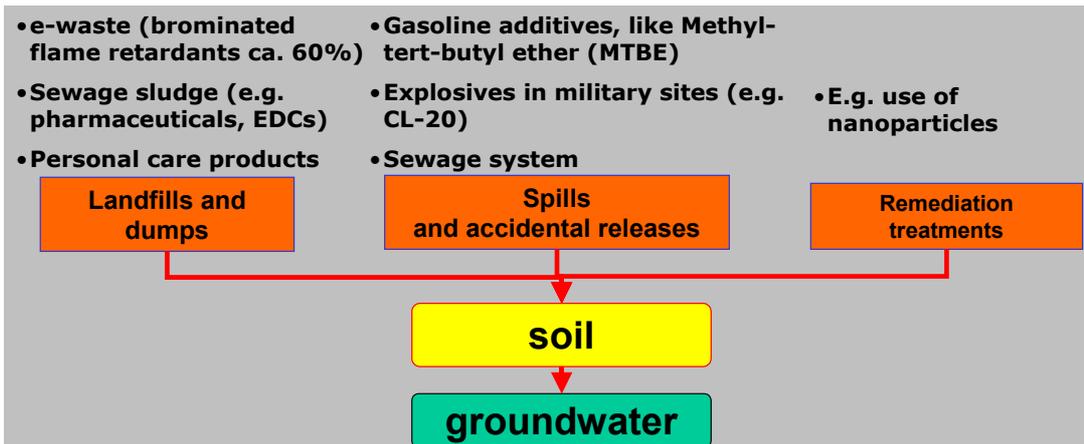


Figure1 Examples of potential sources of local soil contamination by emerging pollutants.

As to the *diffuse soil and groundwater contamination*, one example is the contamination by endocrine disruptors and pharmaceuticals caused by amendments of soil by sewage sludge and manure produced by animal excreta (Petrovic et al., 2004; Kong et al., 2006; Harrison et al, 2006). In general, atmospheric deposition of incineration emissions account for one of the most relevant sources of diffuse contamination. The application of polar pesticides in agriculture is also a concern for diffuse contamination of soil and water.

In the case of diffuse contamination, the regulatory system might lead to preventive measures or land use restrictions.

Figure 2 shows potential sources of diffuse soil contamination by emerging pollutants. Beside the direct exposure to contaminated soil, the main concern is still associated to the contaminants leaching to groundwater.

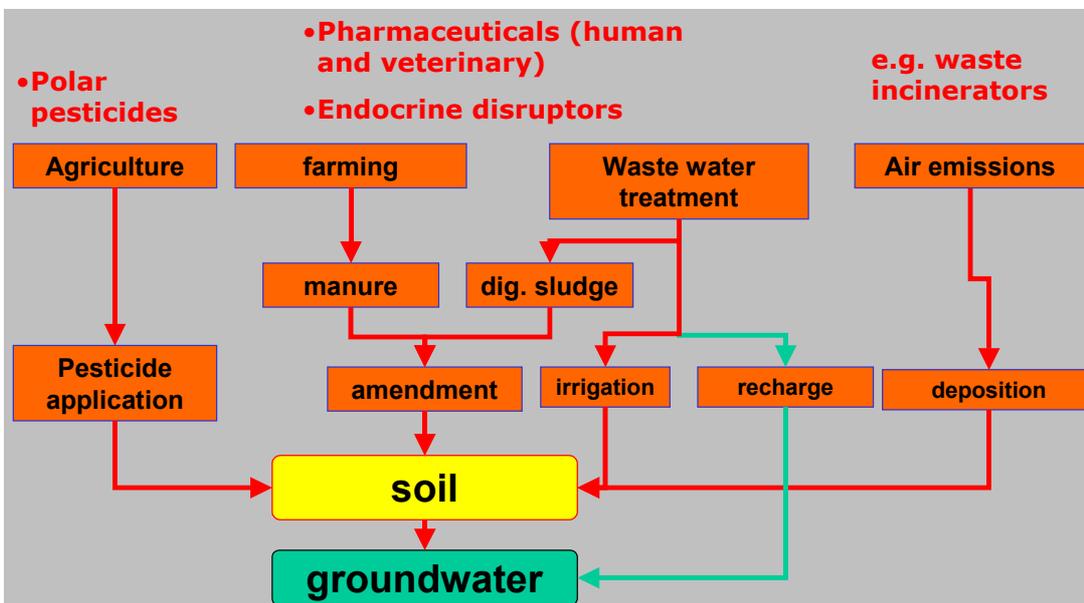


Figure 2 Examples of potential sources of diffuse soil contamination by emerging pollutants.

Emerging pollutants might have effects on humans at population level and on the ecosystem at larger scale. However, few data are available on the occurrence and bioavailability of emerging pollutants in soil (Petrovic et al., 2004).

In conclusion, most of the research work on emerging pollutants has been focused on water contamination so far, and little is known about the most relevant sources and potential effects associated to soil contamination. As regards the risk assessment for soil contaminants, large uncertainties and needs for harmonization of methods still exist for most common chemicals. In this context, the problem of emerging pollutants in soil has been mainly considered in relation to the potential leaching to groundwater and human exposure by drinking uses (Oppel et al., 2004). It is not without saying that direct exposure of human beings and the ecosystems to emerging pollutants in soil is potentially relevant. Besides the consumption of groundwater, other pathways of exposure are likely to be relevant for human beings, like soil ingestion, indoor inhalation of soil derived vapors and bioaccumulation/magnification of contaminants through the food chain. Analogously, direct contact, ingestion and the food chain are likely to be relevant pathways for ecological receptors. Potential large scale effects on to soil ecosystem biodiversity, safe agricultural practices and groundwater drinking reservoirs should be better defined.

As a final remark it can be said that, due to the difficulty of proving cause effects relations between chemical concentrations and ecosystem impairments, in particular when mixture of contaminants in complex media are considered, the combination of chemical, ecotoxicological and ecological evidences in a TRIAD scheme (Figure 3) appears to be the best approach to outpoint effects of emerging pollutants.

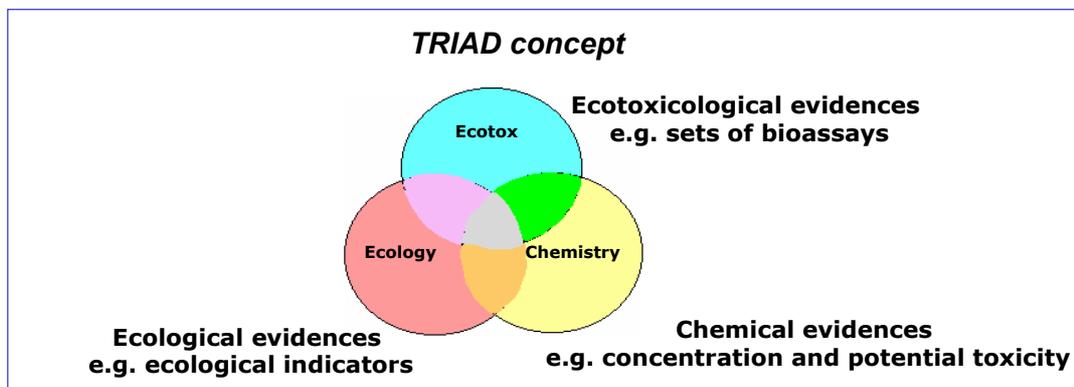


Figure 3. The TRIAD concept for the site specific ecological risk assessment.

REFERENCES

Carlson, C. (2005) The HERACLES research framework to promote the development of common references of site specific ecological risk assessment for contaminated land in Europe. Proceedings of Consoil 2005. Bordeaux, 3-7 October, 2005.

Carlson, C. D'Alessandro, M. The HERACLES research framework towards the development of common references for human health and ecological risk assessment of contaminated land in Europe. SETAC Europe, 7 - 11 May 2006. Den Hague. The Netherlands

EFOA (2002). MTBE Resource Guide. Revised version n.2 The European Fuel Oxygenates Association. (downloaded from www.efoa.org, visited 6th June 2006)

Harrison, E.Z., Oakes, S. R., Hysell, M., Hay, A. (2006). Organic chemicals in sewage sludge. Science of the Total Environment. 367(2-3):481-497

Jensen, J., Mesman M. (2006). Ecological Risk Assessment of Contaminated Land. Decision support for site specific investigations. RIVM report 711701047. ISBN90-6960-138-9, pp.136

Kong, W.D., Zhu, Y.G., Fu, B.J., Marschner, P., He, J.Z. (2006). The veterinary antibiotic oxytetracycline and Cu influence functional diversity of the soil microbial community. *Environmental Pollution* 143: 129-137

Long, E.R., Chapman, P.M. (1985) A sediment quality triad: measures of sediment contamination, toxicity, and infaunal community composition in Puget Sound. *Marine Pollution Bulletin*. 16:405-415

Oppel, J., Broll, G., Löffler, D., Meller, M., Römbke, J., Ternes, Th. (2004). *Science of the Total Environment*, 328:265-273

Petrovic, M., Eljarrat, E., Lopez de Alda, M.J., Barceló, D. (2004). Endocrine disrupting compounds and other emerging contaminants in the environment: a survey on new monitoring strategies and occurrence data. *Anal Bioanal Chem* 378:549-562

US-EPA (2003). Region/ORD workshop on emerging pollutants. Summary Report. Chicago (IL), August 11-14, 2003 (downloaded from <http://www.epa.gov/osp/regions/emerpoll.htm>, visited 6th June 2006).

Integrated assessment of health risks from environmental stressors in Europe - the INTARESE project

David Briggs
Department of Epidemiology and Public Health, Imperial College London

E-mail: d.briggs@imperial.ac.uk

The INTARESE project is designed to support implementation of the European Environment and Health Action Plan, by providing the methods and tools that are essential to enable integrated assessment of health risks from environmental stressors.

Integrated assessment in this context is more than the simple summation of traditional assessment methods. It demands the ability to analyse and compare different aspects of the environment, human populations and health, at different spatial and temporal scales, and to produce coherent information on the combined and cumulative risks and impacts of environmental stressors in ways that can improve decision-making and enhance policy.

Integration thus involves:

- tracking risks through the full chain from source to impact (both on health and related monetary and social costs)
- assessing the combined and cumulative effects of different sources and stressors in relation to each specific health outcome
- assessing the different health effects arising from each source or stressor
- linking different policy areas and issues within a consistent and comparable assessment framework
- providing tools for risk assessment that meet the needs of the different stakeholders and users involved in any issue.

As such, integrated risk assessment requires linkage and use of a wide range of data, scientific knowledge and methodologies, including:

- monitoring technologies (including ground- and space-based environmental monitoring, biomonitoring and health surveillance);
- risk and impact assessment methodologies;
- methods and tools for risk characterisation and risk communication.

In recent years, major scientific advances have been made in each of these areas. The need now is to bring these advances together, identify and fill key gaps in the existing knowledge and methodologies, and develop the tools needed to make the knowledge and technologies operational.

The aim of the INTARESE project is to achieve this integration. Drawing upon the large range of studies carried out in Europe over recent years, and in close collaboration with users, it will develop a methodological framework and a set of tools and indicators for integrated assessment that can be applied across different environmental stressors (including pollutants and physical hazards), exposure pathways (air, water, soil, food) and policy areas.

To this end, the project will:

1. develop a conceptual framework for, and systematic approach to, integrated risk assessment that spans the entire source-impact chain;
2. review, assess the adequacy, link and enhance the monitoring systems needed to support such assessments;

3. test and apply the approach through a series of integrated assessments of exposures and health risks in a number of specific policy areas, including transport, housing, agriculture, water, wastes, household chemicals and climate;
4. develop and bench-test a computer-based system and decision support tool for
5. applying this approach on a routine basis.

Throughout, particular attention will be given to issues of uncertainty, sensitive or susceptible groups, and possible interactive and cumulative effects of different stressors. Throughout the project, also, close liaison and contact will be maintained with users (including those in the policy, industrial and research arenas) in order both to ensure that the work addresses their needs, and to provide testing and evaluation of the project results.

This paper outlines the conceptual basis for the INTARESE project, and discusses how the methods used might be used to help identify, assess risks from, and communicate risk information about emerging health issues.

EU FP6 project: NoMiracle, Novel methods for integrated risk assessment of cumulative stressors in Europe

Hans Løkke
National Environmental Research Institute (NERI), Denmark

E-mail: hlo@dmu.dk

The NoMiracle Consortium consists of 38 partners from 17 European countries. The aim of the project is to develop methods. The project supports

- The European Environmental and Health Action Plan (Action No 7)
- Thematic Strategy on the Sustainable Use of Pesticides
- Plant Protection Directive 91/414/EEC
- Biocide Directive 98/8/EEC
- Pharmaceutical directive
- Strategy for Soil Protection
- Strategy for Waste Reduction and Recycling
- REACH

The projects have 7 main scientific objectives:

1. To develop new methods for assessing the cumulative risks from combined exposures to several stressors including mixtures of chemical and physical/biological agents
2. To achieve more effective integration of the risk analysis of environmental and human health effects
3. To improve our understanding of complex exposure situations and develop adequate tools for sound exposure assessment
4. To develop a research framework for the description and interpretation of cumulative exposure and effect
5. To quantify, characterise and reduce uncertainty in current risk assessment methodologies, e.g. by improvement of the scientific basis for setting safety factors
6. To develop assessment methods, which take into account geographical, ecological, social and cultural differences in risk concepts and risk perceptions across Europe?
7. To improve the provisions for the application of the precautionary principle and to promote its operational integration with evidence-based assessment methodologies

The project deals with molecules designed for provoking significant interactions with biological structures, such as:

- Pesticides
- Biocides
- Pharmaceuticals,

but also includes some:

- VOCs and semi-VOCs
- selected chemicals with baseline or reactive mode of action
- metals, in particular Ni

The project is not specifically dealing with emerging pollutants; however the array of methods from the project may be useful in the assessment and evaluation of the risks posed from emerging pollutants.

The project is organised in four research pillars on “scenario selection”, “exposure assessment”, “effect assessment”, and “risk assessment”, respectively.

The Research Pillar 1 on scenario selection has two work packages:

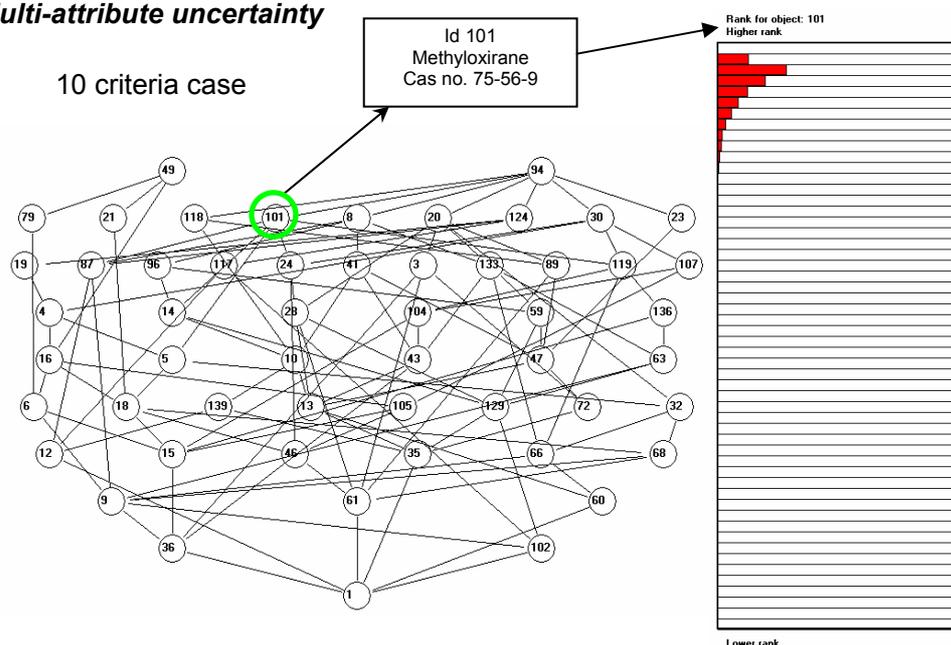
- WP 1.1 Establishment of data background for scenario selection (Leader: Alberto Pistocchi)
- WP 1.2 Scenario selection and ranking (Leader: Peter B. Sørensen)

In particular, the multi criteria ranking methods allowing for assessment of the uncertainty could be very useful in the identification and prioritisation of emerging chemicals from complex databases. The principle is illustrated below. The technique uses a so-called Hasse diagram, and allows for estimation of the uncertainty of ranking of scenario selection.



WP 1.2: Application of multi criteria methods in scenario selection

Multi-attribute uncertainty



In the Research Pillar 2 on Exposure Assessment, new methods and approaches are developed to improve the fate assessment of chemicals. The area is covered by four work packages:

- WP 2.1: Matrix-compound interaction (Leader: Gerrit Schüürmann)
- WP 2.2: Available exposure (Leader: Philipp Mayer)
- WP 2.3: Metabolic fate (Leader Ovanes Mekenyan)
- WP 2.4: Region-specific environmental fate (Leader: Mark Huijbregts)

New experimental and theoretical methods for estimating degradation have been developed, among these a new water-sediment test system designed to provide realistic degradation rates for polar compounds

The Research Pillar 3 on Effects Assessment is organised in four work packages:

- WP 3.1 Interactive toxicological effects in diverse biological systems (Leader: Almut Gerhardt)
- WP 3.2 Combined effects of natural stressors and chemicals (Leader: Martin Holmstrup)
- WP 3.3 Toxicokinetic modelling (Leader: Kees van Gestel)
- WP 3.4 Molecular mechanisms of mixture toxicity (Leader: Aldo Viarengo)

In work package 3.2 some of the key questions of NoMiracle are addressed: How do natural stressors and chemicals play together, can the combined effect of natural stressors and chemicals be quantified along the same principles as chemicals, and by comparing, which is the most deleterious?

The work package 3.4 is of special interest in the case of emerging pollutants. For some emerging compounds, relevant data may be scarce, and reliable computational methods might help. Such methods from NoMiracle are developed under headlines like “Molecular mechanisms of mixture toxicity”, “Unveiling modes of action of prioritised chemicals and mixtures by means of high throughput analyses” and “Investigation on single critical toxicity parameters”.

The NoMiracle Research Pillar 4 on Risk Assessment is organised in the following four work packages which all will produce useful tools for analyses and forecasting of risks from chemicals in a complex world:

- WP 4.1 New concepts and techniques for probabilistic risk assessment (Leader: Ad Ragas)
- WP 4.2 Explicit modelling of exposure and risk in space and time (Leader: Uwe Schlink)
- WP 4.3 Dealing with multiple and complex risks in a management context (Leader: Mikael Hilden)
- WP 4.4 Risk presentation and visualisation (Leader: Joost Lahr)

All in all, NoMiracle will provide new concepts and methods to deal with existing and new chemicals in a real world of cumulative stressors such as:

Exposure assessment tools

- methods for matrix-compound interactions
- methods to measure available exposure, based on chemical activity and other novel approaches
- methods for metabolic fate
- models for exposure assessment, incl. modelling of exposure and risk in space and time

Integration of human health and environmental methods

- Risk scenarios to identify most likely combinations of chemical and other stressors, and methods to make risk mapping
- Exposure assessment (bioavailability) based on chemical activity
- Mechanistic approach in effects assessment, including uptake mechanisms
- Methods for toxicokinetics - single chemical uptake and interactive effects
- Demand for less use of mammalian test animals; in vitro methods and invertebrate testing in focus
- General biomarkers for human and environment
- New concepts and techniques for probabilistic risk assessment

Development of methods for assessing uncertainty

- separation of true uncertainty and individual variability in predicted risks of human populations from exposure to pesticides through all relevant environmental pathways
- describing the metabolism and preliminary pharmacodynamic data in human subgroups. Derivation of uncertainty factors for subgroups and test species (single chemicals and mixtures)

Models and risk maps:

- Risk presentation techniques
- Spatial aggregation of risks to man and environment
- Multimedia fate and exposure model with varying spatial resolution
- Up-scaling methods based on small scale modelling
- Model for health risks in cities
- Ecological vulnerability analysis
- Development of methods to present and visualise risks

How is industry contributing to the development of science based approaches to the environmental risk assessments of pollutants

Martin Holt
ECETOC

E-mail: martin.holt@ecetoc.org

The chemical industry philosophy is that the management of chemicals should be based on a risk assessment that considers both hazard and exposure. It would be impossible to try to describe all the work that is being carried out within the many sectors of the chemical industry in such a short presentation. This talk will focus on the work being done within ECETOC to improve the understanding of the fundamental science that environmental risk assessment (ERA) is built upon. ECETOC activities, include the commissioning of Task Forces and workshops to review current scientific knowledge, identify significant data gaps, define and prioritise research needs which are then often funded by the CEFIC Long range Research Initiative. The major part of the presentation will address two projects related to monitoring and modelling which I hope will be of major interest to the participants at this workshop. The first project will be used to describe the learnings of the “investigative” monitoring exercises that were carried out to support the development of a higher tiered model to predict the concentration of down the drain chemicals in European rivers. The second project relates to the needs for greater cooperation and harmonisation in the conduct of monitoring programmes and the problems associated with the reporting and accessibility of monitoring data.

ERA is a science-based process combining hazard and exposure and forms an essential element in chemical legislation and management worldwide. They are usually tiered to ensure cost-effective generation of data proportional to the risks that exist. The assessment of whether a substance presents a risk to organisms in the environment is based on a comparison of the predicted environmental concentration (PEC) with the predicted no effect concentration (PNEC) to organisms in ecosystems. This assessment can be performed for different compartments (e.g. air, water and soil) and on different spatial scales (local, regional). This is further captured in a number of EU Commission documents (Technical Guidance Documents supporting the Commission Directive on Risk Assessment of New Chemicals (93/67/EEC) and Commission Regulation on Risk Assessment of Existing Substances (1488/94/EEC) in support of Existing Substances Regulation(793/93/EEC)) and computerized calculation model EUSES (European Uniform System for Evaluating Existing Substances, [1,2,3]).

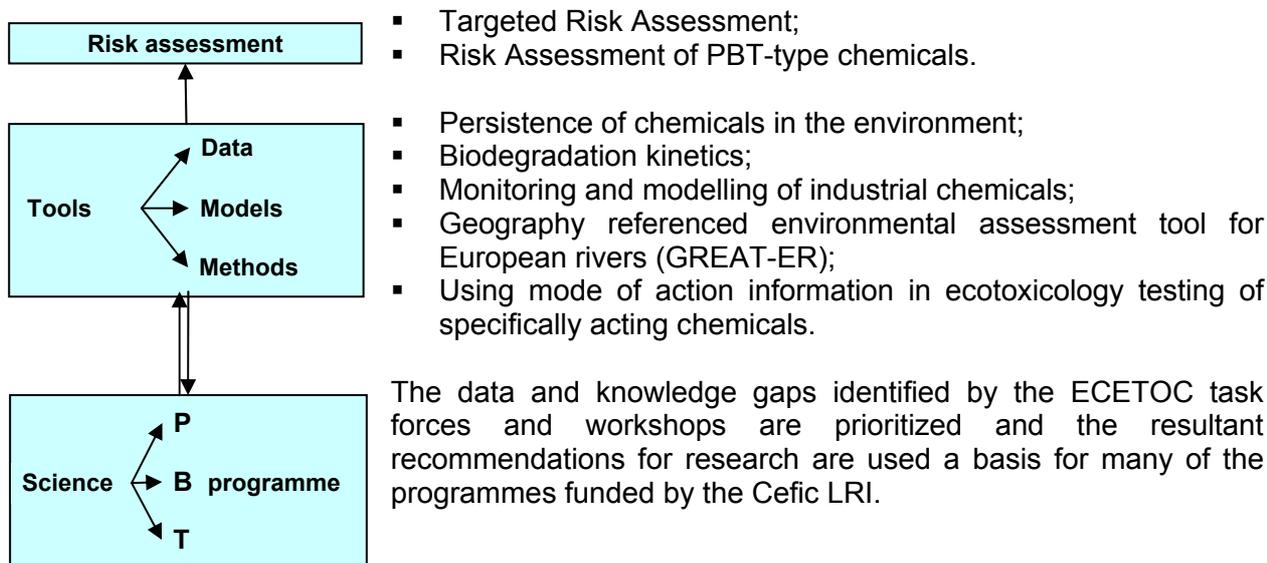
Sources of uncertainty exist in ERA:

- due to true variability - inherent properties of the environment, for example rates of biodegradation;
- extrapolation, for example, from laboratory to field, short- to long-term effects within species, from test species to other species and from structure to process.

Uncertainties can be reduced through generation of more detailed information (higher tier), through the use of more sophisticated models and by developing greater scientific understanding of the scientific aspects of exposure and effects assessments.

The lack of publicly available data on the hazardous properties of chemicals and the slow progress of risk assessment and management of industrial chemicals were the driving forces behind the development of a new chemicals policy in the European Union (EU) and as a consequence the Commission proposed Registration, Evaluation, Authorisation and Restrictions of Chemicals (REACH). One of the key challenges of REACH is that it requires the registration and evaluation of approximately 30,000 chemicals by producers, and importers over the next few years. To make REACH workable, a scientific and practical approach to prioritise

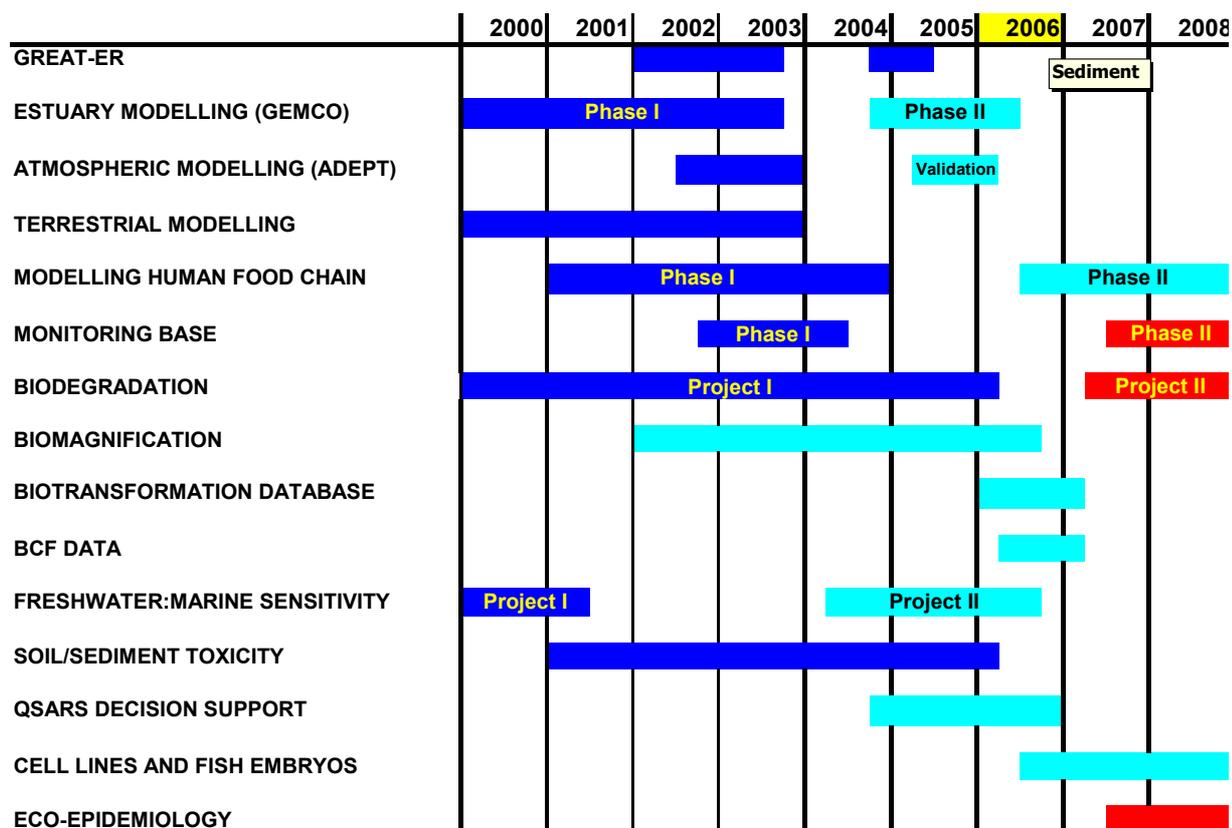
substances for assessment will be required. An ECETOC task force has developed 'targeted' risk assessment methodology which involves a tiered iterative approach to risk assessment. Using this approach the level of refinement and detail of information required for a risk evaluation is proportional to the potential risks of a chemical based on consideration of both hazards and exposures together rather than in isolation. The concepts of the approach have been programmed into a web tool that integrates the core concepts into an easy to use format (<http://www.ecetoc-tra.org>). There are a number of initiative within the EU aimed at the regulation of persistent, bioaccumulating and toxic (PBT) substances. A second task force has recently published an approach for the risk assessment of 'PBT-type chemicals' which reviews the criteria used to identify PBT substances, the uncertainty associated with the associated methodologies and proposes a scientifically sound risk based approach based on the mode of action of the chemical. The recent topics for ECETOC task forces and workshops are shown in Figure XX. They have continued to develop the tools, data, and methods needed to improve how exposure and effects are assessed.



ECETOC have had a memorandum of agreement to manage the strategic research programme on human health and the environment funded under the Cefic Long Range Research Initiative (LRI) since its inception in 1997. The LRI environment programme has two themes:

1. Exposure - Development and validation of fate and distribution models to improve predictions of exposure, develop databases and tiered model system.
2. PBT and long-term risk to ecosystems:
 - a) Development of an understanding of the significance of the factors that affect bioavailability, and ecotoxicity in various compartments;
 - b) Development of methods to measure degradation and, improvements in the extrapolation from laboratory studies to the prediction of environmental half-lives;
 - c) Tools for modelling bioaccumulation, understanding of biotransformation in food chains;
 - d) Improvement of the understanding of 'mode of action' and critical body burden.

The following projects have been funded since 2000 - Details on the specific project can be found at www.cefic-lri.org.



Investigative monitoring to support model development

The interplay between integrate monitoring and modelling programmes and the resulting benefits will be illustrated by discussion on two specific industry projects.

GREAT-ER

The first is the development of GREAT-ER. The goal was to develop and validate a powerful and accurate chemical exposure prediction tool for use within the EU environmental risk assessment schemes. Current techniques to estimate regional predicted environmental concentrations (PECs) use a generic multi-media 'unit world' approach and do not account for spatial or temporal variability in landscape characteristics, river flows and/or chemical emissions. The results are therefore merely applicable at a generic screening level because these models do not offer a realistic prediction of the actual steady-state background concentrations. Furthermore, the default EU generic regional environment assumes only 70% of the wastewater mass loading is treated in a sewage treated plant, leaving the other 30% to be released into the receiving environment untreated.

A new database, model and software system have been developed to calculate the distribution of PECs, both in space and time, of down the drain chemicals in European surface waters on a river and catchment level. The system uses Geographical Information Systems (GIS) for data storage and visualisation, combined with simple mathematical models for prediction of chemical fate. Hydrological databases and models are used to determine flow and dilution data.

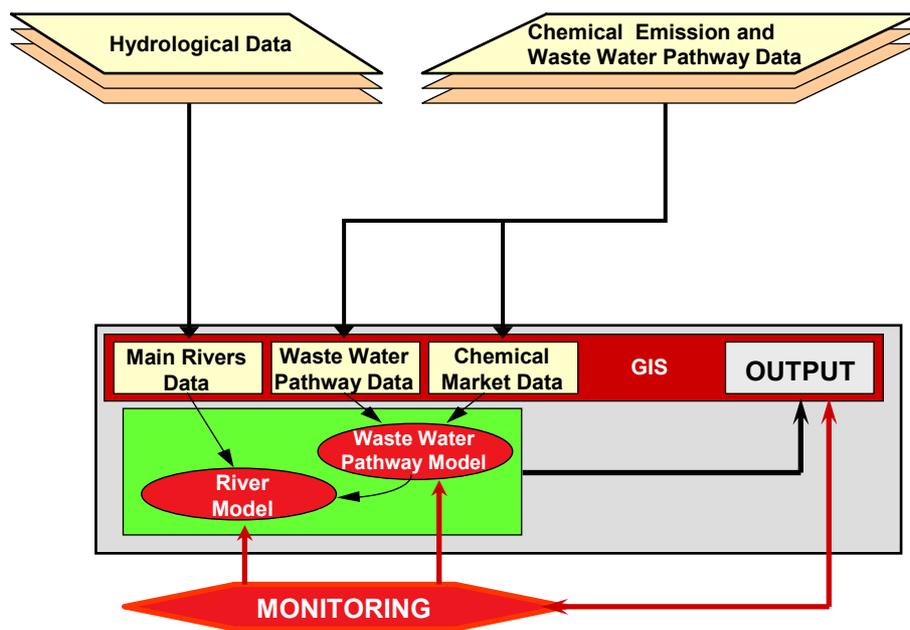
A monitoring programme was undertaken in both the Yorkshire region of the U.K and in the Lambro catchment in Italy to validate GREAT-ER. Linear alkylbenzene sulphonate (LAS) which

undergoes both adsorption and biodegradation in rivers and boron, a conservative compound, were chosen for model validation. Data on dissolved oxygen, biochemical oxygen demand and ammonia were used to assess water quality and to provide data for calibration.

The refined exposure assessment tool should greatly enhance the accuracy of current local and regional exposure estimation methods, ultimately on a pan-European scale. The first phase started in 1997 and the GREAT-ER 1.0 CD was released in 1999: The model development was carried out on behalf of ECETOC at a cost of 1,200,000 EUR. The partners were UK-Environment Agency, Universities of Osnabruck, Gent, Milan, The Institute of Hydrology (UK), Yorkshire Water Plc and other basin agencies. Funding came from the Environmental Risk Assessment Steering Committee (ERASM) of the Association Internationale de la Savonnerie, de la Détergence et des Produits d'Entretien (AISE) and the Comité Européen de Agents de Surface et Intermédiaires Organiques (CESIO) in co-operation with the UK Environment Agency and Yorkshire Water Plc. The second phase to develop GREAT-ER 2.0: Desktop and web version (<http://www.great-er.org>) was started in 2003, cost 400,000 EUR and was funded by Cefic LRI. The third phase to incorporate a sediment module (available soon): 100,000 EUR was also funded by Cefic LRI.

A modular approach was used to develop the model (see Figure 1).

Figure 1: Modular approach to development of GREAT-ER



Modules

a) GIS Data Manipulation

In the data manipulation module, input data sourced from several data bases and from the hydrology module was transformed into appropriate GIS formats

b) Hydrology

The hydrology module combined several hydrological databases with a hydrological model. It provides the GREAT-ER system with the required flow distributions and river characteristics.

c) Waste Pathway and River Modelling

This module is used for the prediction of chemical emission, of chemical transformation during conveyance and treatment, and of chemical fate in rivers. Data on type, flow, capacity and populations served was collected for all sewage treatment plants (STP) in the catchments

d) Monitoring

A series of monitoring programmes were set up to address the exposure requirements of the wastewater, river and fate models necessary to support the prediction of environmental concentrations of specific consumer chemicals with reference to their spatial location and seasonality. Sampling sites were chosen based specifically on the study objectives

UK monitoring

Two specific monitoring programmes were carried out in the UK. The first addressed the river catchments. The four catchments monitored were the Aire, Calder, Don (all highly industrialised) and Went (predominantly rural). The river water and effluents sampling programme started in August 1996 and continued for 24 months. River water samples were collected monthly and sewage treatment effluents every 2 weeks (minimum 26 samples per plant) at the regular Environment Agency monitoring sites. All samples were grab samples (>1000 effluent samples and >2500 river waters)

The second programme addressed fate of chemicals in trickling filter type plants. Six such plants were chosen in the Aire and Calder catchments having a range of industrial inputs from 0-33%. The works treated population equivalents of between 2000 and 120,000 and were considered by the authorities to be representative of both the Yorkshire region and the UK in general. Automatic samplers were used to collect samples of de-gritted raw sewage, primary settled and final effluent for 7 consecutive days. Daily flow proportional composite samples were prepared from 12 x 2 hour (4 x 30 min) grab samples for water quality measurements. Separate samplers were used to prepare 24 hour flow proportional composite samples for LAS analysis. The daily flow proportional samples were prepared from discrete 2 hourly samples (4 shots at 30 minute intervals), with proportions based on the measured flow into the plant. The discrete 2 hourly samples were used to measure diurnal variations in both the influents and effluents at each site. Preservative was added at 3% prior to sampling and 'in field' standard additions were made at the environmentally relevant concentration. Consumer use was estimated from boron measurements which were used as a conservative tracer. Using this information it was shown that removal of >50% LAS occurred 'in sewer'.

LAMBRO monitoring

The monitoring programme in the Lambro had to be redesigned to address a rather different situation to that found in the UK. There were three activated sludge type sewage treatment plants in the monitoring zone and although the initial programme was based on a similar plan to the UK, unexpected concentrations were found along the river stretch. Following further discussions with the plant operators we were advised that one of the plants only had the capacity to treat approximately 60% of the daytime flow. The remaining 40% flowed untreated into the Lambro. At night the flow into the plant fell to just below the treatment capacity and hence only treated effluent is discharged. This imposes a very strong diurnal variation in load upon the receiving water. The influence of the two other treatment plants discharging further down the catchment were practically negligible in comparison. Sampling was carried out, at fortnightly intervals, at 4 sites along the river. Duplicate samples were collected every 20 minutes over 24 hours. Daily time proportional samples were prepared routinely and some discrete samples had to be analysed to establish the diurnal variations.

Conclusions

The following conclusions were drawn based on the experiences gained:

- Establish a balanced steering group, with involvement of all interested parties from the earliest stages and set clearly defined objectives;
- pilot studies should be carried out to adequately characterise the sites, confirm their 'representativeness' (i.e. sufficient information concerning the chemical and the environment, the release history of the chemical with respect to the monitoring site, including distance from and strength of release sources, and the environmental characteristics which will determine the residence time of the chemical in that site), and establish the analytical feasibility;
- the choice of the site(s) should be associated with a particular scenario in order to be of use in establishing the realistic risk scenario, the 'reasonable worst case' or 'representative or realistic case';
- choose sites which have good historical databases available;
- availability of 'on line' flow measurements at the sewage treatment plants are important for chemicals which exhibit wide diurnal variation in use (e.g. detergents);
- ensure analytical and QA procedure in place, use validated sample collection and preservation techniques; include standard additions at the appropriate concentration in the field;
- a thorough understanding of the catchment is important for data interpretation and model validation;
- the sampling regimes may need to be very different and should be specific to both the aims of the programmes and the characteristics of the catchments; select the monitoring period to be compatible with the scenario in respect of season, weather conditions etc.;
- the data should include how many analyses a concentration represents and how the numbers were composited.

Examples of how GREAT-ER is being used

1. What if scenarios. For example what happens to the concentrations in the effluent and river if
 - Sales of chemical are increased
 - STP operating conditions are modified
2. To predict the concentration of down the drain chemicals such as pharmaceuticals and personal care products.

A pilot study in rural catchments in the UK to monitor and model the fate and concentration of pharmaceuticals and personal care products (PCP) was carried out in 2005. Compounds measured included: Atenolol, Cimetidine, Diclofenac, Felodipine, Fluoxetine, Metformin, Triclosan, Metoprolol, Naproxen, Norfluoxetine, Paroxetine, Propranolol, Ranitidine.

Pharmaceuticals Pilot Study - Conclusions

The conclusions of the study were that measured influent and effluent concentrations were consistently lower than predicted (typically within an order of magnitude). There were larger differences for effluent concentrations which suggest better removal in the sewage treatment plant than was predicted. Further understanding of model parameters including regional use patterns, human metabolism, in-sewer removal, STP removal (e.g. adsorption versus degradation) and in-stream removal.

MONITORINGBASE

The second project to be described is MonitoringBase which was carried out by RIVO in the Netherlands.

The goals of the project were:

- To identify on-going and planned European institutional field monitoring programmes, including the Arctic, that can be joined into to maximise the amount of data and limit the number of samples;
- To review and catalogue available measured environmental concentration data of organic chemicals in water, sediment and biota from the freshwater and marine environments, in particular:
 - ✓ Which contaminants, in which compartments, have and/or are being monitored?
 - ✓ Who is monitoring contaminants, when and where?
 - ✓ Where can information be found on environmental measured concentrations? (e.g. useful for trends analysis, spatial distribution)
 - ✓ What concentrations have been measured in the field for a selected set of contaminants?
 - ✓ Where can databases containing information on environmental measured concentrations be found on internet?
- To support and accelerate the harmonisation of (a) Europe-wide monitoring database and to improve accessibility to data http://www.rivo.dlo.nl/ftp_dir/Environment_FoodSafety/Cefic

The database consists of 2 parts:

The *programmes section* gives details on 160 planned, ongoing and completed monitoring programmes in Europe and Arctic, It covers > 90% of programmes in Europe and Arctic and gives details of who is measuring what, where, how often, etc.

The *measured concentrations section* contains data on WFD priority substances, (excluding metals and pesticides) and 71 other substances some of which can serve as input or validation data for environmental models (e.g. exposure models, food chain models, identification of time trends). Links are provided to extractable measured data, e.g. databases available on internet. Substances with large datasets which could flood the database have been excluded (PCB, PAH, etc.).

Integrated monitoring and modelling

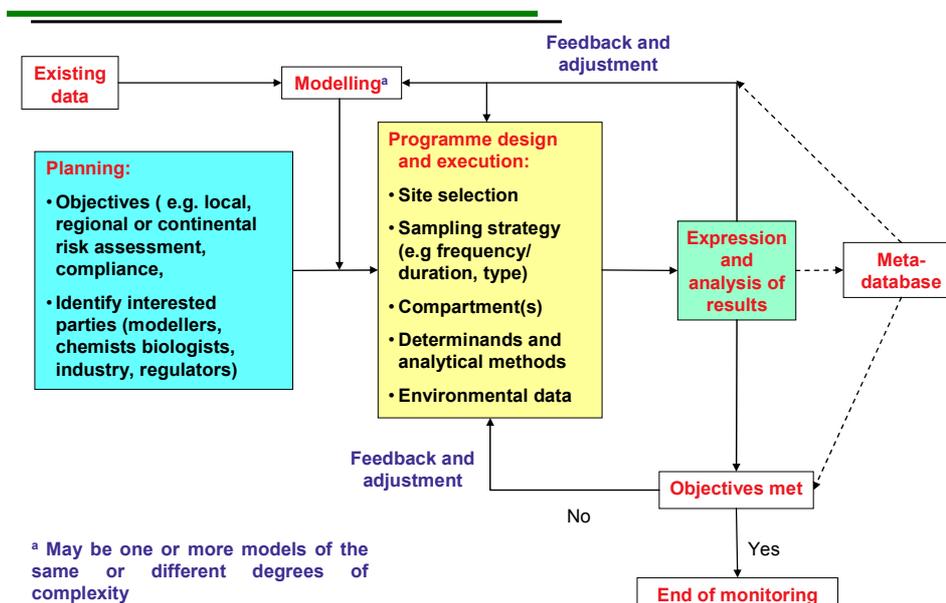
Monitoring and modelling are integral parts of risk assessment. In practice, laboratory and field data are used to provide parameters for the models, while monitoring data are used to validate models' predictions. Discrepancies between the results of models and monitoring should be investigated in terms of both the representativeness of the models and the monitoring data. Thus, comprehensive risk assessments require the integration of laboratory and monitoring data with the model predictions.

To be successful, a monitoring study must be well planned. The goals and objectives of the study need to be well defined and the planning of monitoring programmes should think 'multimedia' (i.e. include water, air sediment and biota). Adequate planning and definition of study objectives will allow an evaluation of the availability of sufficient resources for the programme. To ensure these resources are effectively used it is important that the relevant parties, whose knowledge and practical experience can be used and whose endorsements are necessary for the acceptance of the study, are identified and involved at all stages. Attention should be given to identifying and involving regulatory authorities, local officials, trade organisations, laboratories, industry and academia. Monitoring programmes should integrate

knowledge generated in the past and become more fit for purpose. There is a need to ensure that future programmes are ‘information rich’ and not ‘data rich’. Following initial discussions with interested parties, which should establish a commitment to the study, a management team should be set up. Their role is to agree to a project protocol which clearly states the aims and objectives, identifies individual responsibilities and allocates resources.

The planning and objectives will determine the site selection, the extent of sampling (times, duration frequency and numbers of samples), the types of samples, the data requirements, the analytical methods, etc. There should be greater interplay between analytical chemists, biologists and modellers. Team composition should reflect the needs and considerations of the different disciplines. Execution of the plan requires co-operation of those on site, adequate training of personnel, and numerous other technical details. The figure below illustrates some of the key stages in design and execution of an integrated monitoring programme.

Integrated Monitoring



It will be impossible to monitor everywhere for everything (indeed any such philosophy should be opposed) and greater use of models to guide and inform monitoring programmes should be encouraged. There is however a real need to improve the applicability of the existing models which will require access to more measured data. As data is generated it should be used to refine and develop existing models. To help increase accessibility to data, an effort should be made to harmonize monitoring programmes across Europe and ensure appropriate data logging and data access. Ideas of how to harmonise monitoring and incorporate the wealth of data that exists into a database should be investigated. In addition, guidelines should be developed and agreed to ensure ready availability and transparent access of data via standardised procedures. A dedicated data centre whose role is to co-ordinate data acquisition and dissemination may be a cost-effective way of achieving this goal.

SUMMARY

Whilst measured data (chemical and biological) have a major role in the assessment of emerging pollutants, many aspects relating to the design and the coordination of monitoring programmes and the interpretation of the data need to be much more fully and widely debated.

Project teams should comprise individuals from different scientific disciplines together with other relevant expertise from all interested parties – integrated modelling programmes.

Monitoring and modelling play a major role in exposure assessment but there is still much to do to:

- improve the quality and applicability domain of higher tiered models, and
- optimise the use of resources.

Validation of models is complex issue; need to continue to develop and link to new databases. Accessibility to data is a major problem.

Industry has ongoing programmes committed to improving the way that risk assessments are performed by addressing knowledge gaps essential for the improvement and reduction in uncertainty within the process.

Neither hazard potential nor measured concentration should be used in isolation to manage chemicals. Exposure and hazard must be considered jointly and all decisions should be based on risk.

PARTING THOUGHTS - CHEMICALS IN THE ENVIRONMENT

- What does detection of a chemical in a given compartment indicate?
- What does its presence mean in terms of environmental effects?
- What do the results of individual species effects studies mean in terms of environmental relevance?

VII. List of participants

Borco **ALEKSOV**

Central Environmental Laboratory, Ministry of
Environment and Physical Laboratory
Drezdenska str. 52
1000 Skopje
MCE - 1000 Skopje
Macedonia

Laurence **AMALRIC**

BRGM
BRGM MMA/APO
3 avenue Claude Guillemin BP 6009

F - 45060 ORLEANS

Jeanette **ANDERSSON**

IVL Swedish Environmental Research Institute
Box 210 60
S - 10031 Stockholm

Damià **BARCELÓ**

CSIC
Jordi GIRONA 18-26
E - 08034 Barcelona

Denis **BARD**

Ecole Nationale de la Santé Publique
Av Pr Léon Bernard
F - 35043 Rennes

Rachel **BENSTEAD**

Environment Agency (UK)
4 The Meadows, Waterberry Drive,
Waterlooville, Ha
UK - PO7 7XX Waterlooville

Philippe **BERSUDER**

Cefas Burnham Laboratory

Remembrance Avenue
UK - CM0 8HA Burnham-on-Crouch

Giovanni **BIDOGLIO**

IES – Soil, Water & Ecosystem Resources
Unit
JRC – Via E. Fermi
I – 21020 - Ispra

Maria **BIHARI**

VITUKI Kht
Budapest, Kvassay Jenő; street 1
H-1095 Budapest

Tetyana **BODNARCHUK**

Laboratory of the State Department of
Environment and Natural Res.
Stryyska St.
UA - 79026 Lviv

Stephanie **BOPP**

European Commission - DG Joint Research
Centre
IES Institute for Environment and Sustainability
JRC
I - 21020 Ispra

Ulrich **BORCHERS**
IWW Institute for Water Research
Am Lohbach
D-45470 Muelheim an der Ruhr

David **BRIGGS**
Imperial College London
Department of Epidemiology and Public Health
Norf
UK - W2 1PG London

Eva **BROSTROEM-LUNDEN**
Swedish Env. Research Inst. Ltd - IVL
Unit
P.O. Box 47086
S - 402 58 GOETEBORG

Claudio **CARLON**
I.E.S. - Soil, Water & Ecosystem Resources
JRC - via Enrico Fermi
I - 21020 ISPRA

Nick **CARTWRIGHT**
Environment Agency
Environment Agency, Block 1, Government
Buildings,
UK - BS10 6BF Bristol

Laure **CHANCERELLE**
INERIS
PARC ALATA
F - 60550 VERNEUIL EN HALATTE

Miriam **COLLOMBON**
RIVM
PO Box 1
NL - 3720BA Bilthoven

Marina **COQUERY**
CEMAGREF
3 bis quai Chauveau, CP 220
F - 69336 LYON Cedex 09

Helena **CRNOJEVIC**
Croatia Waters, Central Water Management
Laboratori
Ulica Grada Vukovara 220
HR - 10 000 ZAGREB

Nicole **DE BRUCKER**
VITO
Boeretang 200
B - 2400 MOL

Pim **DE VOOGT**
Inst. for Biodiversity and Ecosystem
Dynamics IBED-ESPM
Nieuwe Achtergracht 166
NL – 1018 WV Amsterdam

Geneviève **DEVILLER**
JRC - Via Fermi
I - 21020 Ispra (Italy)

Anja **DUFFEK**
UBA (Federal Environmental Agency)
Bismarckplatz 1
D-14193 Berlin

Valeria **DULIO**
INERIS
Parc Technologique ALATA - B.P. N°2
F - 60550 Verneuil-en-Halatte

Daniela **DURKOVICOVA**
Slovak Hydrometeorological Institute
Jeseniova 17, 83315 Bratislava, The Slovak
Republic
SK - 83315 Bratislava

Steven **EISENREICH**
Joint Research Centre
Via E. Fermi 1, IES TP 290
I - 21020 Ispra

Ulla **ERIKSSON**
ITM, Stockholm University
Frescativägen
S - 10691 Stockholm

Marinella **FARRE**
IIQAB-CSIC
C/Jordi Girona
E - 08034 Barcelona

Anne-Marie **FOUILLAC**
BRGM
3 AVENUE CLAUDE GUILLEMIN
BP 6009
F - 45060 ORLEANS CEDEX

James **FRANKLIN**
CLF-Chem Consulting
28 Rue Edouard Olivier
B - 1170 Brussels

Thomas **GARETH**
Lancaster University
Environmental Science Department, Lancaster
UK - LA1 4YQ Lancaster

John **GARROD**
Defra
Asdown House, 123 Victoria Street
UK - SW1E 6DE London

Reinhard **GERHARDS**
Degussa
Goldschmidtstr. 100
D - 45127 Essen

Walter **GIGER**
Giger Research Consulting
Im oberen Boden

CH - 8049 Zurich

Antonietta **GLEDHILL**
Waters Corporation
Atlas Park, Simonsway, Wythenshawe
UK - M22 5PP Manchester

Anders **GOKSØYR**
University of Bergen
Department of Molecular Biology
PO Box 7800
N-5020 Bergen

Jadwiga **GZYL**
Institute for Ecology of Industrial Areas
6 Kossutha St, 40-844 Katowice, POLAND
PL - 40-844 Katowice

Georg **HANKE**
EC JRC IES
Via Enrico Fermi
I - 21020 Ispra (VA)

Benoit **HAZEBROUCK**
INERIS
Parc Technologique Alata BP 2
F - 60550 Verneuil en Halatte

Ester **HEATH**
IJS
Jamova
SLO - 1000 Ljubljana

Louise **HEATHWAITE**
Lancaster University
Centre for Sustainable Water Management
Lancaster
UK - LA1 4YQ Lancaster

Juliane **HOLLENDER**

eawag
Überlandstrasse
CH - 8600 Dübendorf

Martin **HOLT**

Ecetoc
Av.E.van Nieuwenhuysse
Bte 6
B - 1160 Brussels

Tania **HUBER**

I.E.S. - Inland & Marine Waters Unit
JRC – via Enrico Fermi
I – 21020 ISPRA

Cristina **JAFFRES**

L'Oréal
River Plaza
29 Quai Aulagnier
F - 92600 Asnières

Anders **JOHNSON**

Swedish Environmental Protection Agency
Blekhölmsterrassen 36
S - SE-106 48 Stockholm

Rakesh **KANDA**

STL
STL Reading
Unit 27 Robert Cort Estate
Britten R
UK - RG2 OAU Reading

Dimitrios **KOTZIAS**

IHCP
JRC - Via Enrico Fermi
I - 21020 ISPRA

Špela **KOZAK LEGISA**

Environmental Agency of the Republic of
Slovenia
Vojkova 1b
SLO - SI-1000 Ljubljana

Zoltan **KRASCENITS**

Water Research Institute
Nabr.L.Svobodu 5
SK - 812 49 Bratislava

Frank **LAME**

TNO Built Environment and Geosciences
P.O. Box 80015
NL - 3508 TA Utrecht

Katherine **LANGFORD**

NIVA
Brekkeveien 19,
PO Box 173,
Kjelsås
N - NO-0411 Oslo

Peter **LEPOM**

Federal Environment Agency
Bismarckplatz 1
D - 14193 Berlin

Heather **LESLIE**

IVM
De Boelelaan 1087
NL - 1081 HV Amsterdam

Dean **LEVERETT**
UK Environment Agency
Biological Effects Laboratory, 4 The Meadows,

Wate
UK - PO7 7XX Waterlooville

Igor **LISKA**
ICPDR
Vienna International Center, D0443,
P.O.Box 500

A - 1400 Vienna

Hans **LOEKKE**
Dir. of Research Department, Nat. Env. Research
Inst. (NERI)
Vejloseove 25, P.O. Xox 314
DK - 8600 SILKEBORG

Robert **LOOS**
EC JRC IES
TP 290
I - 21020 Ispra

Daniela **LUD**
Ecoappraisal-Tauw Group
Piazza Leonardo da Vinci

I - 20133 Milano

Andrea **LUPTAKOVA**
Slovak Hydrometeorological Institute
Jeséniova
SK - 833 15 Bratislava

Emira **MALJEVIC**
Environmental Control Lab. Republic
Hydrometeorological Service of Serbia
Kneza Visislava 66
Y - 1100 BELGRADE

Corinne **MANDIN**
INERIS
Parc Technologique ALATA BP2

F - 60550 Verneuil en Halatte

Jaakko **MANNIO**
Finnish Environment Institute SYKE
P.O. Box 140
Mechelininkatu 34a
FIN - 00251 Helsinki

Antonio **MARCOMINI**
University of Venice
Calle Larga S. Marta
I - 30123 Venice

Michael **McLACHLAN**
Stockholm University
Krossbacken 35
S--18770 Täaby
tel. :+46 8 674 7228 - fax:

Tomáš **MICANIK**
Water Research Institute T.G.M.
Macharova (street)
Ostrava (city)
CZ - 70030 Ostrava

Zaharie **MOLDOVAN**
National Institute of Research and Development
for Isotopic and
Street Donath
RO - 400293 Cluj-Napoca

Margreet **MONS**
Kiwa Water Research
PO Box 1072
NL - 3430 BB Nieuwegein

Anne **MORIN**
INERIS
PARC TECHNOLOGIQUE ALATA
RUE JACQUES TAFANEL
BP
F - 60550 VERNEUIL EN HALATTE

Lea **MRAFKOVA**
SHMU
Jeseniova 17, 83315 Bratislava
SK - 83315 Bratislava

Richard **OWEN**
UK Environment Agency
Block 1, Government Buildings
Burghill Rd
Westbu
UK - BS10 6BF Bristol

Milan **PAULOVIC**
VÚV Praha
Podbabská 30
160 62 Prague
CZ-160 62 Prague

Willie **PEIJNENBURG**
RIVM - Laboratory for Ecological Risk
Assessment
PO Box 1
NL - 3720 BA Bilthoven

Mira **PETROVIC**
CSIC
Jordi Girona 18-26
E - 08034 Barcelona

Stefano **POLESELLO**
CNR-IRSA
via della Mornera
I - 20047 Brugherio

Véronique **POULSEN**
BERPC
60-62 rue d'Hauteville
F - 75010 Paris

Alfred **RAUCHBUECHL**
Federal Agency for Water Management
Marxergasse
A - 1030 Wien

Marina **RICCI**
EC-JRC-IRMM
Retieseweg
B - 2440 Geel

Rod **ROBINSON**
NPL
Queens Road
UK - TW11 0LW Teddington

Heinz **RUEDEL**
Fraunhofer IME
Institute for Molecular Biology and Applied
Ecolog
D - 57392 Schmallenberg

Christen **SACHSE-VASQUEZ**
RIFM
50 Tice Blvd
3rd Floor
USA - 07677 Woodcliff Lake

Martin **SCHLABACH**
NILU
POBox 100
N-2027 Kjeller

Gabriele **SCHOENING**
European Environment Agency
Kongens Nytorv

DK - 1050 Copenhagen K

Marca **SCHRAP**
RWS RIZA
P.O. Box 17
NL - 8200 AA Lelystad

David **SCHWESIG**
IWW
Rhenish-Westfalian Institute for Water
Moritzstra
D - 45476 Muelheim an der Ruhr

Katarina **SILHAROVA**
Water Research Institute
Nabr.L.Svobodu 5

SK - 812 49 Bratislava

Jaroslav **SLOBODNIK**
Environmental Institute
Okruzna
SK - 97241 Kos

Joan **STAEB**
Min of transport and water management RWS-
RIZA
P.O. Box 17
NL-8200 AA Lelystad

Anne **STRUGEON**
BRGM
3 AVENUE CLAUDE GUILLEMIN
BP 36009

F - 45060 ORLEANS CEDEX 2

Andy **SWEETMAN**
Lancaster University
Environmental Science Department
Lancaster Univer
UK - LA1 4YQ Lancaster

Reet **TALKOP**
Ministry of the Environment of Estonia
Narva mnt 7A, 15172 Tallinn Estonia
EST - 15172 Tallinn

Thomas **TERNES**
Bundesanstalt für Gewässerkunde
Am Mainzer Tor
D - 56068 Koblenz

Norbert **THEOBALD**
Bundesamt für Seeschifffahrt und
Hydrographie
Bernhard-Nocht-Str. 78
Hamburg
D - 20359 Hamburg

Kevin **THOMAS**
NIVA
Brekkeveien 19, Kjelsås

N - 0411 Oslo

K. Clive **THOMPSON**
ALcontrol Laboratories
Templeborough House, Mill Close, Rotherham,
South

UK - S60 1BZ Rotherham

Céline **TIXIER**
IFREMER
Dpt Biogeochemistry - Ecotoxicology
Lab. Biogeochem
F - 44311 NANTES Cedex 3

Peter **TOLGYESSY**
VUVH
Nabr. arm. gen. L. Svobodu 5, Bratislava,
SK - 81249 Bratislava

Renaud **TUTUNDJIAN**
Cemagref
Cemagref - Groupement de Lyon
3 bis quai Chauveau
F - 69336 Lyon

Sofie **VAN VOLSEM**
flemish environmental agency
a. van de maelestraat
B - 9320 Erembodegem

Dolf **VAN WIJK**
Euro Chlor
Av. E. van Nieuwenhuysse
B-1160 Brussels

Jurgen **VOLZ**
Kiwa Water Research
P.O.Box 1072
NL - 3430 BB Nieuwegein

Michael **WALDOCK**
Cefas
Barrack Rd
The Nothe
Weymouth
UK - dt4 9pp Dorset

David **WESTWOOD**
Environment Agency
56 Town Green Street
Rothley
Leicestershire
LE7
UK - LE7 7NW Leicester

Leah **WOLLENBERGER**
Federal Environment Agency
Wörlitzer Platz
D - 06813 Dessau

Roberto **ZUBIAGA**
LABEIN-TECNALIA
C/Geldo-Parque Tecnológico de Bizkaia.
Edificio 7
E - 48160 DERIO (Bizkaia)

European Commission

EUR 22806 EN – Joint Research Centre

Title: *Emerging Environmental Pollutants. Key Issues and Challenges*

Editor: Valeria Dulio

Luxembourg: Office for Official Publications of the European Communities

2007 – 120 pp. – 21 x 29,7 cm

EUR – Scientific and Technical Research series – ISSN 1018-5593

ISBN 978-92-79-06227-8

Abstract

This report presents the outcome of the workshop on *Emerging Environmental Pollutants - Key Issues and Challenges* organised by the NORMAN project, the Network of Reference Laboratories for the Monitoring of Emerging Environmental Pollutants, on 19-20.6.06 in Stresa, Italy. It contains a summary of the workshop, the extended abstracts from all keynote presentations and summaries of the results from 4 parallel discussion sessions dedicated to data sources, prioritisation criteria for emerging pollutants and the monitoring, modelling of emerging pollutants.

The mission of the Joint Research Centre is to provide customer-driven scientific and technical support for the conception, development, implementation and monitoring of European Union policies. As a service of the European Commission, the Joint Research Centre functions as a reference centre of science and technology for the Union. Close to the policy-making process, it serves the common interest of the Member States, while being independent of special interests, whether private or national.



The NORMAN project is funded by the European Commission under the 6th Framework Programme - Priority 1.1.6.3: Global Change and Ecosystems.

To know more about NORMAN, visit our website at the page <http://www.norman-network.net>

