Network of reference laboratories
for monitoring of emerging substances

BULLETIN

http://www.norman-network.net

WELCOME TO ISSUE N°3
OF THE NORMAN NETWORK BULLETIN

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

Editorial

Emerging substances of toxicological concern in a world full of chemicals - the NORMAN way to find the needles in the haystack

Werner BRACK
Helmholtz-Centre for Environmental Research – UFZ, Leipzig, Germany
werner.brack@ufz.de

Having a look on the website of the Chemical Abstract Service (CAS) is always quite instructive if we want to get an idea of the challenge of emerging pollutants. When I checked this website, 65,452,041 organic and inorganic substances were registered; and the number is increasing every minute. The number of intentionally produced chemicals is probably two orders of magnitude lower, but still an impressive number and continuously increasing. One group of specific concern is the biocides, as highlighted by Heinz Ruedel in this issue. Other identified groups of chemicals range from pharmaceuticals, personal care products, pesticides, dyes and other industrial chemicals to engineered nanomaterials. Many of these compounds are metabolised by bacteria, plants, animals and humans or are transformed by non-biotic processes such as environmental photochemistry or water disinfection processes. Thus, every intentionally produced chemical may end up in a large number of transformation products. They are often less hydrophobic than the parent compounds and thus may more easily pass through wastewater treatment plants and end up in aquatic ecosystems and drinking water. While we assume that most transformation products are less toxic than the parent compounds, the opposite has been shown for quite a number of them. Our chemosphere is very complex and it is a great challenge to identify and prioritise those chemicals which are of (eco)toxicological concern. NORMAN is the network to address this challenge.

Under the Water Framework Directive (WFD) the European Commission and the EU member states make great efforts to monitor compounds that have been shown to have adverse effects on the aquatic environment and that have been prioritised on a European or river basin scale. There is, however, increasing concern about risks due to unregulated and unmonitored compounds, which are often referred to as emerging substances. The NORMAN network compiles information on these compounds, attempts to prioritise them and to trigger monitoring activities focusing on emerging substances. However, an approach based on individual target compounds has well known limitations as it cannot take into account the complexity of environmental contamination and its effects. NORMAN therefore also attempts to trigger screening and effect-based approaches for identification of the toxicants responsible for adverse effects in the environment even if they do not appear as targets on priority monitoring lists. Site-specific effect-directed analysis (EDA) and multivariate approaches to correlate chemical screening data with effect patterns are promising tools to address these challenges. To advance and promote these tools was the reason for supplementing existing working groups on prioritisation (WG1) and bioassays (WG2) with a new working group on EDA in NORMAN (WG3). This working group has made some significant achievements within its, so far, short existence. Some of them are highlighted in this bulletin, including a new book on EDA, a common Initial Training Network called EDA-EMERGE funded by the European Commission and the MassBank database for collection of mass spectrometric data for environmental contaminants.

The majority of emerging pollutants are polar compounds that are better analysed with LC-MS/MS techniques than with GC-MS, but the lack of spectra libraries and of efficient common strategies for the identification of new compounds still hamper progress in the identification and monitoring of emerging pollutants. And so, following the motto "let's share the knowns and focus on the unknowns", NORMAN has established a web-based mass spectra database for environmental contaminants, adapting the MassBank database that has been developed in the field of metabolomics. As highlighted by Tobias Schulze et al. in this issue, we feel that the benefit of this database for users from NORMAN and beyond will be enormous, since NORMAN MassBank will open new perspectives for unravelling the environmental chemosphere and for supporting European policy makers in prioritising compounds for monitoring and management. All NORMAN members are invited to make NORMAN MassBank as strong as possible with their contributions.

But a better assessment of emerging substances for risks to ecosystems and human health needs not only proper identification and monitoring tools, but also clever combinations of monitoring and exposure models. This is shown by Matthew MacLeod and Martin Scheringer with an example on human biomonitoring. They propose to link biomonitoring with estimates of population-level intake from exposure pathway analysis to build up a complete picture of the uptake and clearance of pollutants by human populations.

Although we can look back with satisfaction on some good achievements, a lot remains to be done by NORMAN and its members to provide the knowledge and the tools to help decision-makers to optimise, despite their limited resources, the early recognition, assessment, monitoring and management of emerging contaminants in the environment. Effect-based and screening tools will play an increasing role in addressing this challenge, and the NORMAN working group on bioassays and biomarkers will support the development of concepts and guidelines required for effect-based monitoring on a European scale. Effect-based monitoring is the missing link that may help us to understand the connections between contamination and ecological status and may even trigger a paradigm shift in chemical monitoring. While many tools are readily available for application, substantial research is required to cover a broader range of potential effects, to better address mixture effects and interactions with non-chemical stressors and to advance the tools to link effects to causative toxicants in complexly contaminated environments. The development of systems biological approaches and high throughput cell reporter array systems may help to unravel cause-effect relationships. Combined EDA and pattern recognition approaches integrating high resolution analytical and advanced computer and modelling tools, together with new databases as developed in NORMAN and elsewhere, are required to enhance the throughput and analytical power of emerging toxicant identification. EDA-EMERGE and other successful initiatives have shown that NORMAN is an excellent platform for developing this kind of research, bringing together highly innovative science with the expertise of NORMAN to act as a science-policy interface.

Issue N°2 - April 2011

NORMAN Association (N° W604002510) - Network of reference laboratories, research centres and related organisations for monitoring of emerging environmental substances.
This Bulletin is produced with the generous support of INERIS.

Environmental monitoring of biocides: an emerging issue?

Heinz Ruedel
Fraunhofer Institute for Molecular Biology and Applied Ecology (Fraunhofer IME), Department Environmental Specimen Bank and Elemental Analysis, Auf dem Aberg 1, D-57392 Schmallenberg, Germany
heinz.ruedel@ime.fraunhofer.de

IMPLEMENTATION OF THE BIOCIDAL PRODUCT DIRECTIVE

The European Biocidal Product Directive 98/8/EC (BPD, EC 1998) on placing biocidal products on the market was adopted in 1998. In the following years it was transposed into national law by the EU member states. The directive 91/414/EEC on plant protection products (PPP) served as a model for the BPD. As for PPP, it is the aim of the BPD to harmonise the market for biocidal products and their active substances in Europe. At the same time it aims to provide a high level of protection for humans, animals and the environment. While the assessment of biocidal substances is performed at EU level, biocidal products are authorised by the member states. Manufacturers or importers can apply in any member state for an authorisation of a biocidal product. By a request for mutual approval, biocide products can then also become authorised in other member states.

The BPD defines biocidal products as active substances and preparations containing one or more active substances, put up in the form in which they are supplied to the user, intended to destroy, deter, render harmless, prevent the action of, or otherwise exert a controlling effect on any harmful organism by chemical or biological means.

It defines 23 different product types (PTs) for biocidal products. These include disinfectants, substances used for the preservation of products and materials (e.g. leather or masonry), non-agricultural pesticides and anti-fouling coatings used on the hulls of ships – but not substances used in products already covered by other EC legislation (e.g., PPP, pharmaceuticals or cosmetics).

Under the BPD, the only biocides finally allowed on the market are those included in a positive list (BPD Annex I; http://ec.europa.eu/environment/biocides/annexi_and_ia.htm), and all potential biocidal compounds must therefore be assessed for their suitability. As a first step, all existing biocides were identified and catalogued (about 960 entries; EC 2007), but only about 350 biocides were assessed under the review programme (EC 2007) by 1 September 2006, the date by which biocides not covered had to be removed from the market. Moreover, additional non-inclusion decisions by the European Commission caused the removal of about a further 100 biocides from the review programme either completely or in respect of certain PTs. Currently only about 50 compounds are listed in Annex I for uses in certain PTs, but the assessment is still ongoing.

It is assumed that these developments will cause a change in the use of biocidal active substances in EU member states. A number of substances have already been withdrawn from the market, or will be withdrawn soon as a consequence of non-inclusion decisions. Additionally, the use of certain biocides will be restricted by risk mitigation schemes (e.g., for substances of very high concern for which no less harmful alternatives are available).

The expected result of these measures should be a decrease in discharges into the environment of affected biocides. On the other hand, replacement of unauthorised biocides by others may cause increasing environmental levels of other existing or new biocides. These hypotheses may be tested by targeted environmental monitoring in appropriate compartments. On the other hand, monitoring may serve as a success control for the risk assessment process and could confirm that the observed environmental concentrations are below the predicted effect levels.

ENVIRONMENTAL RELEVANCE OF BIOCIDES

A study by COWI A/S (Kongens Lyngby, Denmark; COWI 2009) investigated the significance of environmental exposure routes regarding the use phase of biocides. According to this assessment direct environmental exposure (e.g. of surface waters, soil or air) is most important for wood preservatives, molluscicides, piscicides and insecticides (Table 1). For disinfectants (private areas and public health; food and feed) indirect exposure of the environment by sewage treatment plants (surface waters by effluents, soil by land application of sludge) was assessed as most relevant. The PT-based exposure assessment may be used within a prioritisation concept for biocides for environmental monitoring.

Product type (according to BPD)	Estimated tonnage (annual)	Environmental exposure, direct	Environmental exposure via STPs
1: Human hygiene biocidal products	XXX	-/X	XX
2: Private area and public health area biocidal products	XXX	X	XXX
3: Veterinary and hygiene biocidal products	XXX	X	XX
4: Food and feed area disinfectants	XXX	-	XXX
5: Drinking water disinfectants	XXX	X	X
6: In-can preservatives	XX	X	X
7: Film preservatives	XX	XX	X
8: Wood preservatives	XXX	XX/XXX	-
9: Fibre, leather, rubber, and polymerised materials preservatives	XX	-	X
10: Masonry preservatives	XXX	XX	-
11: Preservatives for liquid cooling and processing systems	XXX	XX	XX
12: Slimicides	XX	XX	XX
13: Metalworking fluid preservatives	XX	-	X
14: Rodenticides	-	XX	X
15: Avicides	-	XX	-
16: Molluscicides	-	XXX	-
17: Piscicides	-	XXX	-
18: Insecticides and products to control other arthropods	XX	XXX	-
19: Repellents and attractants	XX	XX	-
20: Preservatives for food and feedstock	X	-	-
21: Antifouling products	X	XXX	-/X
22: Embalming and taxidermist fluids	-	-	-
23: Control of other vertebrates	-	XX	-

Table 1: Overview of the significance of environmental exposure regarding the use phase of biocides (taken from COWI 2009). The specific exposure assessments do not include consideration of the overall tonnages. XXX=major/high; XX=significant; X = moderate; - = minor/low; STP - sewage treatment plant

CHALLENGES FOR AN ENVIRONMENTAL BIOCIDE MONITORING

The study by COWI (2009) confirmed that biocidal active compounds are entering the environment via different pathways and probably at significant levels. Monitoring in different environmental compartments has therefore to be considered (waters, soil, atmosphere).

Many active biocidal ingredients are used in several application areas, for example as a biocide and PPP, or as a biocide and veterinary or human pharmaceutical. It is therefore often difficult to allocate environmental findings of these active ingredients to certain usages (e.g. PPP vs. biocidal usage). For example, the rodenticides difenacoum, bromadiolone and brodifacoum fall under the scope of the PPP directive and the BPD. Other examples are carbendazim and diuron, which are applied as PPP, e.g. in vegetable cultures, but are also used in facade coatings to prevent the growth of algae.

Moreover, a recent study from Switzerland (Wittmer et al. 2011) revealed that, despite substantially lower amounts being used, emissions to surface waters of biocides used in urban areas were in the same range as those of the most widely-used PPP from agricultural regions. The lower usage in urban regions was compensated by urban loss rates of up to 15% that were significantly higher than agricultural ones (below 1%).

NORMAN Association (N° W604002510) - Network of reference laboratories, research centres and related organisations for monitoring of emerging environmental substances.
This Bulletin is produced with the generous support of INERIS.

BIOCIDES ON THE NORMAN LIST OF EMERGING SUBSTANCES

About 70 compounds identified under the BPD as existing biocides (which are partly also PPP or pharmaceuticals) are currently covered by the NORMAN list of emerging substances (e.g., chlorotoluron, cypermethrin, diazinon, methyl salicylate, terbuthylazine, terbutryne, triclocarban, zinc pyrithione). From the compounds in the BPD review programme about 30 are on the NORMAN list (e.g., carbendazim, chlorophene, chlorothalonil, dichlorvos, hydrogen cyanide, Irgarol (cybutryne), permethrin, prometryne, triclosan). Compounds already listed in BPD Annex I which are identified by NORMAN as emerging substances are dichlofluanid, imidaclopride, N,N-diethyltoluamide (DEET), propiconazole, thiabendazole, tolylfluanid.

But several biocides which may be of concern are currently not covered by the NORMAN list. Examples are coagulant rodenticides which are partly assessed as PBT compounds (persistent, bioaccumulative, and toxic) or vPvB (very persistent, very bioaccumulative). An example is difethialone, which is considered to be a potential PBT and a potential vPvB substance (Anonymous 2007). Other coagulants used as biocides and/or PPP not covered are difenacoum, bromadiolone, and brodifacoum. A recent monitoring study revealed that these compounds were detected in about 20% of tawny owls sampled in the UK between 1990 and 2005 (Walker et al. 2008).

EXAMPLES FROM BIOCIDE MONITORING

Applying a new prioritisation methodology developed within the NORMAN network, von der Ohe et al. (2012) assessed the potential risk of triclosan. This compound is used professionally as a biocide, but also in household products and cosmetics such as toothpastes, or in textiles. The authors applied a refined hazard assessment and evaluated triclosan data from about 800 monitoring sites in the Elbe river basin. They found that triclosan concentrations were above a suggested acute-based predicted no effect concentration (PNEC) of 4.7 ng/L at 75% of the sites. The 95th percentile of the maximum environmental concentrations exceeded the PNEC by a factor of 12, indicating potential hazards for algae, which are most affected by triclosan. The authors suggest including triclosan in routine monitoring programmes and even considering it as a candidate for prioritisation at the European level.

Beside triclosan itself its transformation product methyltriclosan is also relevant. Methyltriclosan is more persistent and more lipophilic than triclosan and thus has a higher bioaccumulation potential. A study by the German ESB revealed that methyltriclosan was detected at clearly higher concentrations than the parent in freshwater fish from Germany. Increasing levels were observed until about 2003-2005 (Böhmer et al. 2004). However, results of a follow-up study (data not yet published) show that the increase in methyltriclosan concentrations has not continued: rather, levels stayed constant or even declined. This shift is apparently a result of the voluntary renunciation of triclosan use in cleansing products announced by a German manufacturers' association (IKW) in 2001.

TOWARDS A BIOCIDE MONITORING STRATEGY

Biocides should be covered more thoroughly by NORMAN. The list of emerging substances should be updated with the relevant compounds covered under the BPD. In addition to the active biocidal substances, their stable transformation products (TP) should also be covered. For several biocides it is known that their TP are more persistent than the parent (e.g., methyltriclosan as TP of triclosan, methylisothiocyanate as TP and active form of the biocides metam sodium and dazomet, or N,N-dimethylsulfamide as TP of tolylfluanid).

An important aspect for the evaluation of biocide monitoring results is how to deal with the overlapping use of compounds under different regulations (BPD, PPP directive, medicinal products directives, REACH directive). To allow an assessment of the influence of BPD implementation the monitoring has to focus currently on those compounds which are solely used as biocides so that possible changes can be correlated clearly with biocide use.

Monitoring can help in assessing whether the implementation of the BPD had positive effects on the environmental quality (are lower concentrations detected in recent years?), whether there is a risk (are the measured environmental concentrations below the derived PNEC?), and whether the use of biocidal products is sustainable in general (are the possible impacts on human health and the environment acceptable under consideration of economic and social aspects?). An improved measuring data basis for relevant biocidal substances supports the preparation of realistic exposure estimations. A check should also be made on whether the derived aquatic PNEC values in the BPD assessment reports ensure a protection level comparable to that ensured by the environmental quality standards for surface waters under the Water Framework Directive.

The forthcoming workshop organised by NORMAN and the German Environment Agency (Umweltbundesamt) in Berlin in November 2012 on "Strategies for monitoring biocides in the environment" could be a first step in exchanging experiences from practical monitoring and in gathering information from EU member states on biocide monitoring data.

REFERENCES

- Anonymous (2007): Difethialone Assessment Report for Product-type 14 (Rodenticides). 21 June 2007. Rapporteur: Norway. http://circa.europa.eu/Public/irc/env/bio_reports/library?l=/assessement_directive/difethialone_210607pdf/_EN_1.0_&a=d
- Böhmer W, Rüdel H, Wenzel A, Schröter-Kermani C. 2004. Retrospective Monitoring of Triclosan and Methyl-triclosan in Fish: Results from the German Environmental Specimen Bank. Organohalogen Comp 66:1489-1494. www.dioxin20xx.org/pdfs/2004/04-645.pdf
- COWI (2009): Assessment of different options to address risks from the use phase of biocides. Final report on behalf of the European Commission Environment Directorate-General, March 2009. COWI A/S, Kongens Lyngby, Denmark. http://ec.europa.eu/environment/biocides/pdf/report_use.pdf
- EC (1998): Directive 98/8/EC of the European Parliament and of the Council of 16 February 1998 concerning the placing of biocidal products on the market. Official Journal of the European Communities L 123/1-63, 24.4.98. http://ec.europa.eu/environment/biocides/pdf/dir_98_8_biocides.pdf
- EC (2007): Commission regulation (EC) No. 1451/2007 of 4 December 2007 on the second phase of the 10-year work programme referred to in Article 16(2) of Directive 98/8/EC of the European Parliament and of the Council concerning the placing of biocidal products on the market. Official Journal of the European Communities L 325/3-65, 11.12.2007. http://eur-lex.europa.eu/LexUriServ/site/en/oj/2007/l_325/l_32520071211en00030065.pdf
- von der Ohe P C, Schmitt-Jansen M, Slobodnik J , Brack W (2012): Triclosan-the forgotten priority substance? Environ. Sci. Pollut. Res. Int. 19, 585-591
- Walker L A, Turk A, Long S M, Wienburg C L, Best J, Shore R F (2008): Second generation anticoagulant rodenticides in tawny owls (Strix aluco) from Great Britain. Sci. Total Environ. 392, 93-98
- Wittmer I K, Scheidegger R, Bader H P, Singer H, Stamm C (2011): Loss rates of urban biocides can exceed those of agricultural pesticides. Sci. Total Environ. 409, 920-932

NORMAN Association (N° W604002510) - Network of reference laboratories, research centres and related organisations for monitoring of emerging environmental substances.
This Bulletin is produced with the generous support of INERIS.

Use of environmental specimen banks for investigations of emerging substances: examples for freshwater fish monitoring studies

Heinz Ruedel
Fraunhofer Institute for Molecular Biology and Applied Ecology (Fraunhofer IME), Department Environmental Specimen Bank and Elemental Analysis, Auf dem Aberg 1, D-57392 Schmallenberg, Germany
heinz.ruedel@ime.fraunhofer.de

The report on the EU NORMAN workshop on environmental specimen banks (ESBs) in Europe was launched recently (Koschorreck 2011). During the meeting in Berlin in 2010, scientists from European ESBs presented evaluations of the current approaches and exchanged their views on possible co-operations.

OVERVIEW OF EUROPEAN ESBS STORING SAMPLES FROM FRESHWATERS

One contribution to the EU NORMAN workshop assessed the use of ESB for monitoring of freshwater ecosystems. In Europe, nine current banking activities dealing with freshwater aspects could be identified (Table 1). The preferred specimen collected and investigated is fish. In some cases sediment and suspended particulate matter (SPM) as well as mussels are sampled and stored in ESBs. Sampling strategies vary widely between the ESBs – which reflects the wide range of purposes of the archived material. In the Netherlands, for example, banking of eels developed from a food monitoring programme, while in Sweden banking is an essential part of the country's contaminant- and effect-monitoring programme. In Germany specimens are archived mainly to follow the efficacy of environmental policy (e.g., decline of environmental concentrations after the ban of chemicals) and to identify chemicals of concern (e.g., chemicals with increasing environmental concentrations).

Also, the programmes differ in their practical performance. Freshwater specimens are sampled from either rivers or lakes, and from pristine or polluted sites; and, in the case of fish, either whole organisms or specific tissues are stored. Most ESBs investigate individual samples, but the German ESB focuses mainly on pooled samples. In this case, subsamples of the pooled material are used for the different investigations.

Table 1: Overview of current banking activities in Europe with limnetic aspects

	Denmark (Greenland)	France (Aquitaine)	France (northeast region)	Germany §	Nether-lands	Norway	Spain (Galicia)	Sweden #	United Kingdom *
Leading organisation	National Environment Research Institute	ORQUE, Pau	ANDRA (Agency radioact. waste manag.)	Federal Environment Agency	IMARES Wage-ningen	Climate and Pollution Agency	Universidade de Santiago de Compo-stela	Swedish Museum of Natural History	Centre for Ecology and Hydrology (CEH)
Limnetic samples	fish (arctic char)	sediments, SPM	fish	fish (bream), mussels, SPM - pooled -	fish (eel)	fish (birds intended)	moss	fish	fish
Type of limnetic sites	not specified	rivers, estuaries	rivers	large rivers, one lake	rivers, lakes	not specified	rivers	lakes	rivers
Background or polluted sites	background	both	both	both	not specified	both	both	background	both
Start of operation (limnetic sites)	2000	2007	2010	early 1990s	1978	about 1990	2001	1967	2007
Measurement of real time data	yes	yes	intended	yes	yes	yes	not known	not routinely	not yet
Recently published monitoring data	-	-	-	Theobald et al. 2011; Sawal et al. 2011 Rüdel et al. 2006	Kwadijk et al. 2010	-	-	Kierkegaard et al. 2004	-

Internet addresses:
http://www.nrm.se/frontpage/researchandcollections/contaminantresearch/environmentalspecimenbank.937_en.html
§ http://www.umweltprobenbank.de/en
* www.ceh.ac.uk/sci_programmes/water/NationalFishTissueArchive.html

In recent years, data on emerging substances investigations of limnetic ESB samples have also been published. A paper by Kwadijk et al. (2010) on trends of perfluorooctane sulfonic acid (PFOS) in historical eel samples was discussed in the previous issue of the NORMAN bulletin. From the German ESB, new data for freshwater fish levels of several perfluorinated compounds (PFCs), hexabromocyclododecane (HBCD) and other brominated flame retardants (BFRs) are available.

HBCD IN BREAM (SAWAL ET AL. 2011)

HBCD is a brominated flame retardant used mainly in polystyrene foam and textile applications. In recent years, measures have been taken to reduce HBCD emissions during its production and use. Sawal et al. (2011) investigated the levels of three HBCD-diastereomers as well as several other BFRs in bream (*Abramis brama*). This species is one of the most common freshwater fish in European waters. ESB samples from the period 1995 to 2009 from 14 locations along six German rivers (the Saar, Rhine, Elbe, Saale, Mulde and Danube) and at the reference site, Lake Belau, were retrieved from the ESB archive. HBCD diastereomers in fish muscle extracts were quantified by LC-MS/MS analysis with a triple-quadrupole API 4000 QTRAP mass spectrometer. Calibrations were performed with 13C-labelled standards of the α-, β-, and γ-diastereomers of HBCD as internal standards. Median concentrations of the sum of HBCD diastereomers in bream muscle at the investigated sites ranged from 11 to 361 ng/g lipid weight (lw). The dominant diastereomer was α-HBCD, which was determined in 98% of the samples. This observation is in line with previous reports on HBCD diastereomer patterns in fish. Samples from the river Saale in Eastern Germany had the highest HBCD levels and the authors report a steep rise in HBCD concentrations until 2007. The Saale catchment is characterised by a high population density and chemical and other industries, although no specific emission source could be linked to the high HBCD levels reported. In fish from the reference site (Lake Belau in Northern Germany, no known anthropogenic influences) only low levels of HBCD were detected (about 11 ng/g lw, mean from two annual samples).

The HBCD levels reported by Sawal et al. (2011) can be compared to a recently published real-time investigation of HBCD. Rüdel et al. (2012) investigated bream muscle tissue sampled at several European freshwater sites annually since 2007. In these samples, too, α-HBCD was mostly predominant, although at one site γ-HBCD concentrations were

NORMAN Association (N° W604002510) - Network of reference laboratories, research centres and related organisations for monitoring of emerging environmental substances.
This Bulletin is produced with the generous support of INERIS.

highest. The lowest HBCD levels (11 ng/g lw) were detected in bream sampled in 2009 from Lake Belau which served as the reference site for this study, too. During the study period from 2007 to 2010 statistically significant decreases in HBCD concentrations were detected in bream from the rivers Rhone (France; -85%, down to 205 ng/g lw in 2010) and Western Scheldt (The Netherlands; -60%, down to 36 ng/g lw in 2010). The downward trend of HBCD levels at these sites may be correlated with the emission reduction measures taken by HBCD manufacturers and users in recent years. High HBCD concentrations (9,500–14,500 ng/g lw) without a clear time trend were observed in bream from the river Tees (UK) which is strongly influenced by a former production site upstream of the sampling site. The investigations are on-going (10-year programme). In the recent EU Commission proposal, an environmental quality standard (EQS) of 167 ng/g wet weight (ww) is proposed for HBCD in fish (EC 2012). This value is only exceeded at the Tees site where levels of 200–400 ng/g ww were detected (Rüdel et al. 2012).

PFC IN BREAM (THEOBALD ET AL. 2011)

The aim of the study by Theobald et al. (2011) was an improvement in information about the spatial distribution and time trends of concentrations of PFCs in fish from German rivers. Although PFCs have been used for many applications for decades, it is only in recent years that their environmental relevance has become apparent and routine analysis feasible. Investigations were carried out by retrospective monitoring of liver and muscle tissue of bream sampled in the years 1995 to 2010 and archived by the German ESB. For the study an HPLC/MS/MS, a procedure was developed that allowed the analysis of 10 perfluorinated carboxylic acids (PFCAs; C5–C14), 5 perfluorinated sulfonic acids (PFSAs; C4, C6–C8 and C10), iso-PFOS (total of the branched isomers) as well as perfluorooctane sulfonamide (PFOSA; linear) and iso-PFOSA (total of the branched isomers). The authors report that the PFC burdens of liver and muscle samples from bream of the rivers Rhine, Elbe, Danube, Saar and Saale were significantly higher than burdens of bream from the reference site Lake Belau. In general, PFC concentrations in liver tissue were clearly higher than in muscle tissue. PFOS, which is classified as persistent, bioaccumulative and toxic, was detected in all bream samples at quite high concentrations. In muscle tissue, levels varied from 5 to 80 ng/g ww and in liver tissues from 60 to 450 ng/g ww. Concentrations of PFOSA were about one order of magnitude lower than those of PFOS (0.2 to 6.5 ng/g ww in muscle and 0.8 to 28 ng/g ww in liver). At most sampling sites both compounds showed decreasing time trends in the investigation period. The other PFSAs and all short-chain PFCAs (C5–C9) were close to or below the limit of quantification. Remarkably, perfluorooctanoic acid (PFOA) – which is often present in higher concentrations in surface waters – was below the limit of determination in most fish samples. Long-chain PFCAs (C10–C14) were found in most bream samples in significant concentrations (0.1 to 3 ng/g ww in muscle and 0.2 to 16 ng/g ww in liver). Most of the PFDA (C10) time series showed increasing time trends.

The study allows a comparison with the investigation by Kwadijk et al. (2010). These authors studied the occurrence of PFOS in eels (*Anguilla anguilla*) collected from Lobith (Rhine) in The Netherlands. This site is near the German ESB sampling site at Bimmen covered by the study by Theobald et al. (2011). According to Kwadijk and co-workers, PFOS levels for eel filet from the Rhine site were in the range 27–120 ng/g ww in the period 1978–2008. From 1999 on, a decreasing trend in PFOS levels in eel was detected. Theobald et al. 2011 report similar PFOS levels of 20–60 ng/g ww for bream muscle tissue for the period 1995–2010 at the nearby Rhine site Bimmen. The downward trend in PFOS levels in recent years was also obvious in the latter study. However, all concentrations are well above a recently proposed EQS of 9.1 ng/g ww in fish (EC 2012).

USAGE OF ESB MONITORING DATA

Joint investigations of limnetic samples on emerging substances by European ESB groups could be a first step towards cooperation. The coverage of different European regions could enhance the applicability of contributions of ESBs to chemicals risk assessment. Monitoring studies with ESB samples may be applied in different contexts and could provide several pieces of information.

Since environmental concentrations measured in biota are correlated to consumption of the respective compounds, retrospective monitoring can be used to verify the success of bans (e.g., for PFOS as described above) or of emission control measures (as e.g., in the case of HBCD).

Analysis of time series of emerging substances in fish from different regions (broad regional coverage, pristine sites and anthropogenic areas influenced at different levels) could give a view of the exposure of the European aquatic environment to substances of concern. The information from pristine regions may be an indication of a long-range transport of the respective compounds. If, beside fish, specimens from other trophic levels were included in the analyses, information on possible biomagnification could be gained (e.g., by determination of a trophic magnification factor for species for which the trophic level is confirmed by stable isotope analysis). Data on long-range transport and biomagnification may be used for the risk assessment of emerging substances if insufficient laboratory data are available (e.g., in the framework of REACH; the use of monitoring data is already implemented as part of the assessment of persistent organic pollutants for the Stockholm Convention).

Specimen banking could also play a role in Water Framework Directive (WFD) related monitoring. For compounds newly classified as priority substances, retrospective specimen banking studies could give information on trends in the past. Retrospective analysis of biota samples from ESB archives could also be used for the identification of chemicals as potential priority substances in the WFD context. If biota samples are analysed retrospectively, this has advantages over analysis in real-time monitoring (where often the between-years variability is high, due to changes of equipment, personnel or even laboratories). Also, the most recent analytical techniques can be applied with limits of determination and measurement uncertainties that are comparable over all sampling years. Thus chemicals which exhibit increasing concentrations in time series for biota samples from several countries and different regions could be identified as a result of cooperation between several European ESBs and assessed further as candidate priority substances.

For some compounds (mercury/methyl-mercury, hexachlorobutadiene, hexachlorobenzene), WFD biota monitoring is already under discussion or even implemented in some countries. In the EU Commission proposal for the amendment of the Directives 2000/60/EC and 2008/105/EC (EC 2012) fish monitoring of even more compounds is considered (e.g., fish-based EQS are proposed for HBCD and PFOS, see above). Thus an archive of additional biota samples currently sampled for compliance monitoring could be the nucleus for new ESBs in countries where currently no ESBs are operated. ESBs are already considered in the guidance on chemical monitoring of sediment and biota under the WFD (EC 2010). It is recognised that ESBs can complement real-time monitoring by retrospective monitoring of emerging substances and by verifying earlier results by renewed analyses applying state-of-the-art methodology. Moreover, archived biota may be used for ecotoxicological research (identification of biological effects in relation to concentrations of toxic substances).

REFERENCES

- EC (2010): Guidance document No 25 – Guidance on chemical monitoring of sediment and biota under the Water Framework Directive. Common Implementation Strategy for the Water Framework Directive (2000/60/EC). Technical Report 2010- 041. European Commission, Office for Official Publications of the European Communities, Luxembourg. http://circa.europa.eu/Public/irc/env/wfd/library?l=/framework_directive/guidance_documents/guidance_monitoring/_EN_1.0_&a=d

NORMAN Association (N° W604002510) - Network of reference laboratories, research centres and related organisations for monitoring of emerging environmental substances.
This Bulletin is produced with the generous support of INERIS.

- EC (2012): Proposal for a Directive of the European Parliament and of the Council amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy. COM(2011)876 final. European Commission, Brussels, 31.01.2012. http://ec.europa.eu/environment/water/water-dangersub/pdf/com_2011_876.pdf
- Koschorreck, J. (Ed.) (2011): Conference for European Environmental Specimen Banks Berlin, 21–22 June 2010. German Federal Ministry for Environment, Nature Conservation and Nuclear Safety, German Federal Environment Agency, and the Norman Network. Berlin, December 2011. http://www.emerging-pollutants.net/public/workshops/workshops2010_esb.htm
- Kierkegaard A, Bignert A, Sellström U, Olsson M, Asplund L, Jansson B, De Wit CA (2004): Polybrominated diphenyl ethers (PBDEs) and their methoxylated derivatives in pike from Swedish waters with emphasis on temporal trends, 1967–2000. Environ Pollut. 130, 187–198.
- Kwadijk CJ, Korytár P, Koelmans AA. (2010): Distribution of perfluorinated compounds in aquatic systems in the Netherlands. Environ. Sci. Technol. 44, 3746–3751.
- Rüdel H, Böhmer W, Schröter-Kermani C (2006): Retrospective monitoring of synthetic musk compounds in aquatic biota from German rivers and coastal areas. J. Environ. Monit. 8, 812–823
- Rüdel H, Müller J, Quack M, Klein R (2012): Monitoring of hexabromocyclododecane diastereomers in fish from European freshwaters and estuaries. Environ. Sci. Pollut. Res. 19,772-783 http://dx.doi.org/10.1007/s11356-011-0604-3
- Sawal, G., Windmüller L., Würtz A., Duffek A., Schröter-Kermani C., Lepom P. (2011): Brominated flame retardants in bream (Abramis brama) from six rivers and a lake in Germany. Organohalogen Comp. 73, 515–518.
- Theobald N., Schäfer S., Baass A-C., Schröter-Kermani C. (2011): Retrospective monitoring of perfluorinated compounds in fish from German rivers and coastal marine ecosystems. Organohalogen Comp. 73, 440–443.

A watch list of emerging pollutants for surface water monitoring in France

Fabrizio Botta, Valeria Dulio, Sandrine Andres, Christine Feray, Anne Morin
INERIS, Parc Technologique ALATA BP 2, 60550 Vernueil-en-Halatte, France
fabrizio.botta@ineris.fr or valeria.dulio@ineris.fr

INTRODUCTION

The Water Framework Directive (WFD) has set up a European list of 41 Priority Substances (PS) which have to be regularly monitored in European waters. Moreover, it requires Member States to establish national lists of substances to be monitored at river basin level. Despite these provisions, it is widely recognised by the scientific community that several substances of emerging concern are currently overlooked and as a result they are not adequately monitored by national authorities. As part of the implementation of the National Action Plan on Micropollutants in the Aquatic Environment (October 2010), the French Ministry of Ecology decided to implement an innovative and comprehensive approach to improve national monitoring programmes under the WFD. This includes the setting-up of a watch list of substances to be investigated at the national level in order to acquire missing information about the level of exposure of emerging contaminants in the aquatic environment and allow regular updating of the list of River Basin-Specific Pollutants to be regularly monitored. Concurrently, an Action Plan on Drug Residues in Water, co-led by the Ministries of Ecology and Public Health, was published in May 2011. This action plan supports prioritisation of pharmaceuticals for which screening studies are needed in view of the implementation of emission reduction measures.

As part of these two action plans a large national screening study is going to take place in spring-autumn 2012 in France. For surface water three campaigns will be performed in the water matrix and one in sediments at about 160 sampling points.For coastal water, one campaign applying passive samplers will be performed at 40 sites, plus sediment analysis at 11 sites. INERIS has been charged with the design and technical implementation of this project for surface water.

SUBSTANCES PRIORITISATION

A National Expert Group (CEP) for prioritisation of substances in the aquatic environment was set up in 2010 under the umbrella of the National Office for Aquatic Environments, ONEMA, in order to organise the overall prioritisation process. For the selection and prioritisation of the watch list compounds, the CEP decided to adopt the main criteria of the NORMAN methodology for prioritisation of emerging substances [1]. That methodology uses a decision tree that first classifies chemicals into six categories, on the basis of the existing knowledge gaps and the actions to be taken by the research community and the public authorities to fill them. The priority within each category is then ranked on the basis of specific indicators, which allows a score to be calculated. The watch list is derived from one of those six categories. About 2400 compounds were considered as potential candidate substances, of which more than 400 are pharmaceuticals and associated metabolites, and about 70 are chemicals used in personal care and household products. The rest are mainly pesticides, biocides and industrial chemicals.

The procedure for the selection of the priority watch list compounds involved systematic collection and validation of Kow, Koc, hydrosolubility, half-life and BCF data for all candidate substances (estimated data were applied when experimental data were not available). Moreover, a PNEC value was assigned to each candidate substance. The values were derived from available experimental ecotoxicity data, or they were estimated, on the basis of a kNN read-across methodology [2], whenever experimental data were lacking.

As regards monitoring data, about 700 chemicals of the starting list of 2400 compounds are already part of monitoring programmes performed by the water agencies, with a database of about 11 million datasets for water and sediment in surface water (years 2007–2009). An exhaustive assessment of the level of adequacy of the existing monitoring data – both in terms of relevant matrix and compatibility between the limit of quantification of the existing data and the environmental protection thresholds (PNEC) (i.e. LOQ <PNEC) – was performed as part of the selection of the watch list compounds.

As a result of the prioritisation process, 460 molecules were assigned a score > 20 out of a maximum score of 40 (221 compounds are relevant in water and 370 in sediment).

NORMAN Association (N° W604002510) - Network of reference laboratories, research centres and related organisations for monitoring of emerging environmental substances.
This Bulletin is produced with the generous support of INERIS.

ANALYTICAL METHODS VALIDATION AND QA/QC ISSUES

In order to ensure proper validation and QA/QC of the analytical methods used throughout the watch list monitoring process a two-step procedure will be followed. In the first screening investigation (national monitoring campaign in 2012) an approach with only a single laboratory per compound is applied, i.e. the analytical work for a given group of compounds will be performed by one single laboratory selected based on its proven capability to analyse this compound. In a second stage, the substances selected for closer scrutiny will be monitored over the following years by the water agencies and the resulting monitoring data will be the basis for the future revision of the list of River Basin-Specific Pollutants for the third WFD management plans. In this second stage the analytical work will be performed by a larger number of laboratories at routine level. AQUAREF, the National Reference Laboratory for Aquatic Environments [3] will ensure the transfer of analytical methods from expert laboratories to routine laboratories. For the analysis of these substances the criteria defined in the NORMAN protocol (V2 level) [4] will be applied in order to ensure thorough validation of the applied analytical methods, including the proof of inter-laboratory transferability.

STATE-OF-THE-ART ANALYTICAL PERFORMANCE

As regards the implementation of the first screening study (national monitoring campaign in 2012), a national analytical working group (including nine French research laboratories) was set up to assess the analytical feasibility for the selected priority pollutants.

Table 1 reports a selection of the molecules prioritised for the monitoring campaign in 2012 (pharmaceuticals and personal care products for analysis in water matrix and / or sediments).

MOLECULE	SCORE
Beta-sitosterol, 17 alpha-Ethinyloestradiol, 17-beta-Estradiol, Closantel, Dimethylpolysiloxane (Dimethicone)	30
Penfluridol	28
Prochlorperazine, Oxyclozanide, Bithionol, Benziodarone, Amiodarone	27
Terofenamate, Piperazine, Ethylhexyl methoxycinnamate, 2-Benzotriazol-2-yl-4,6-di-tert-butylphenol, Pimozide, Niclofolan, Miconazole nitrate, Hydroxyprogesterone caproate, Flunarizine, Econazole, Diosgenin, Diethylstilbestrol, Chlorpromazine, Astemizole, 7,12-Dimethylbenz(a)anthracene	25,5
Timiperone, Tamoxifen, Niflumic acid, Miconazole, Clotrimazole, 4-Methylbenzylidene camphor, Tonalide*, Triclosan	23
Sulfamethoxazole, Sulfamethazine, Propyl-paraben, Phloroglucinol, Oxazepam, Ofloxacin, Norethindrone, Midazolam, Methyl-paraben, Mestranol, Mepacrine chlorhydrate, Lorazepam, Ketoprofen, Fluphenazine, Ethyl-paraben, Estrone, Drospirenone, Diazepam, Dextropropoxyphene, Cyclophosphamide, Carbamazepine, Acetazolamide, Galaxolide*	21

Table 1: List of pharmaceuticals and personal care products included in the campaign (underlined molecules were selected as priority compounds but they were not included in the monitoring campaign because of analytical difficulties).

**Fragrances were excluded from the campaign for logistic reasons.*

Only methods with an LOQ below the PNEC value were accepted.

It is important to highlight that the procedure allowed the identification of the substances of emerging concern for which analytical performance needs to be improved before their inclusion in future screening programmes (for example 17 alpha-Ethinyloestradiol).

SAMPLING SITE SELECTION CRITERIA

Three types of water bodies will be investigated: rivers (140 sites), lakes (20 sites) and coastal water (40 sites). This distribution across the three types reflects the structure of the permanent monitoring network. The choice of sites was made on the basis of previous investigation results [5 and 6] and the following target criteria: at least 20% reference sites, and 16% sites where conditions for good ecological status are not achieved. The remaining 64% were chosen on the basis of land use: urban sites; sites for agricultural activities or breeding; and industrial areas.

CONCLUSIONS

Around 170 substances will be analysed in the national screening study in 2012. Globally, analytical feasibility by the investigated French research laboratories has been confirmed for 56 pharmaceuticals and personal care products.

Beta-sitosterol,17-beta-Estradiol, Closantel, Dimethicone, penfluridol, prochlorperazine and bithionol received the highest scores on the priority list. However, some of them, such as 17 alpha-Ethinyloestradiol or Closantel, displayed a very low PNEC/LOQ performance. Consequently, they will not be included in this surface water screening campaign. The same applies for some selected UV screens, for which the analytical performance is not yet satisfactory.

The results of the monitoring campaign will be analysed in 2013 and will contribute to the further selection of substances to be integrated in the monitoring programmes of the water agencies in the various river basins.

In parallel with this monitoring campaign, as part of the actions planned for 2012–2013 in France, prioritisation of the molecules for which either analytical performance or ecotoxicity data needs to be improved, is under way.

This exercise is planned to be repeated on a regular basis in line with the 6-year cycle under the Water Framework Directive.

REFERENCES

- [1] Methodology for setting priorities among emerging substances in the NORMAN network, 2011. V. Dulio, P.C. von der Ohe, J. Slobodnik, ICCE Conference 2011, Zurich, Oral Presentation
- [2] Schüürmann G. et al. 2011, Quantitative Read-Across for Predicting the Acute Fish Toxicity of Organic Compounds Env. Science and Technology 2011 DOI:10.1021/es200361r
- [3] www.aquaref.fr
- [4] Schwesig et al. A harmonized European framework for method validation to support research on emerging pollutants, Trends in Analytical Chemistry, 2011
- [5] ANSES (2011) Campagne nationale d'occurrence des residus de médicaments dans les eaux destinées a la consommation humaine
- [6] AEAP (2010) Les médicaments dans les cours d'eau du bassin Artois-Picardie : Résultats de la campagne exploratoire

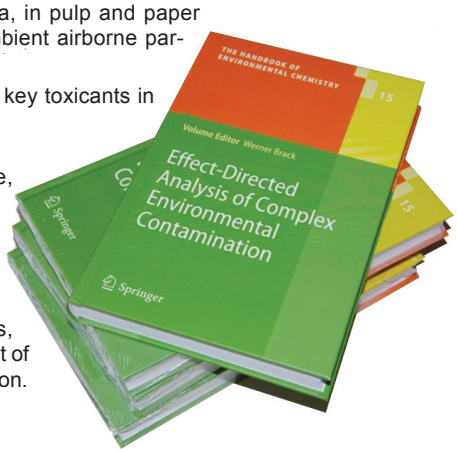
NORMAN Association (N° W604002510) - Network of reference laboratories, research centres and related organisations for monitoring of emerging environmental substances.
This Bulletin is produced with the generous support of INERIS.

Effect-directed analysis of complex environmental contamination

The Handbook of Environmental Chemistry, Volume 15. Volume Editor: Werner Brack,
Springer-Verlag: Berlin, Heidelberg, 2011, 345p, ISBN: 978-3-642-18383-6

Today more than 65 million chemicals are known and registered in the Chemical Abstracts System CAS, of which about 100 000 are frequently used. Both figures are increasing. Many of these chemicals are finally emitted to the environment and may cause adverse effects on ecosystems and human health. Effect-directed analysis (EDA) is a promising tool to identify predominating toxicants in complex, mostly environmental, mixtures: it combines effect testing, fractionation and chemical analysis. In the present book leading experts in the field provide an overview of relevant approaches and tools used in EDA. Its thirteen chapters address the following topics:

- Evolution of the Toxicity Identification Evaluation (TIE) process in the U.S. and recent developments in whole sediment TIEs and the incorporation of bioavailability in EDA and TIE
- Separation techniques and advanced GC–MS, LC–MS and computer tools for structure elucidation in EDA
- Simultaneous screening and chemical characterisation of bioactive compounds using affinity chromatography LC–MS
- Diagnostic tools and their application for EDA of mutagens, endocrine disruptors and AhR-mediated toxicants in aquatic environments including sediments and biota, in pulp and paper mill effluents and in ambient airborne particles
- Ecological relevance of key toxicants in aquatic systems.



This book is a valuable, comprehensive and interdisciplinary source of information for environmental scientists and environmental agencies dealing with the analysis, monitoring and assessment of environmental contamination.

NORMAN MassBank Towards a community-driven, open-access accurate mass spectral database for the identification of emerging pollutants

Tobias Schulze[1], Emma Schymanski[2], Michael Stravs[2], Steffen Neumann[3], Martin Krauss[1], Heinz Singer[2], Christine Hug[1], Christine Gallampois[4], Juliane Hollender[2], Jaroslav Slobodnik[5], Werner Brack[1]

[1] UFZ – Helmholtz Centre for Environmental Research, Department of Effect Directed Analysis, Permoserstr. 15, D-04318 Leipzig, Germany
[2] Eawag, Swiss Federal Institute of Aquatic Science and Technology, Überlandstr. 133, CH-8600 Dübendorf, Switzerland
[3] IPB – Leibniz Institute of Plant Biochemistry, Department of Stress and Developmental Biology,Weinberg 3, D-06120 Halle (Saale), Germany
[4] Linköping University, Department of Clinical and Experimental Medicine, Faculty of Health Science, SE-58183 Linköping, Sweden
[5] Environmental Institute, Okružná 784/42, SK-97241 Koš, Slovak Republic

INTRODUCTION

Organic environmental chemistry focuses more and more on non-target screening of emerging pollutants and identification of unknown compounds such as industrial by-products and transformation products in complex environmental samples (e.g., soils, sediments, surface water, ground water, waste water and biological fluids or tissues). As many of the compounds of interest are polar in nature, liquid chromatography coupled to soft ionisation mass spectrometry is often the method of choice [1]. Improvements in accurate mass and high resolution mass analysers such as time-of-flight (ToF–MS) and Orbitrap mass (FT–MS) spectrometers provide valuable information for the identification of non-target and unknown compounds (e.g., [2–4]). However, a major drawback in the identification of unknowns is the lack of suitable libraries for accurate mass and multidimensional mass spectra (MSn) such as those existing for gas-chromatography (GC) electron impact mass spectrometry (EI–MS) (e.g., NIST [5] and Wiley [6]).

Generally, the low interoperability of MSn from different instrument types and analytical settings (e.g., collision energies, solvents used, and ionisation techniques) was regarded as the main challenge for such MSn libraries. Recent research has proven that standardisation across different mass spectra analysers could be achieved using inter-calibration compounds [7] and/or by setting well-defined experimental conditions for all instruments [8] including multi-stage experiments (e.g., measurement using different collision energies and in positive/negative ionisation mode) [9]. Thus, the first interoperable tandem mass spectra library "MSforID", containing over 9900 mass spectra of over 1000 compounds related to forensics and drugs, was published recently [10, 11]. Further commercially available tools for the vendor-independent evaluation of MSn mass spectra and library search are SmileMS [12] and Mass Frontier™ [13] (http://www.highchem.com).

Community-driven open source approaches for peak deconvolution, mass spectral evaluation and library searches are for instance MzMine [14] (http://mzmine.sourceforge.net) and the web-based MassBank [15]

NORMAN Association (N° W604002510) - Network of reference laboratories, research centres and related organisations for monitoring of emerging environmental substances.
This Bulletin is produced with the generous support of INERIS.

(http://www.massbank.jp). MassBank offers sophisticated, vendor-independent storage and search options for any kind of high and low resolution mass spectra including, for example, EI-MS, ToF-MS and FT-MS. MassBank was recently combined with the in silico fragmentation tool MetFrag [16] (http://msbi.ipb-halle.de/MetFrag) to build up MetFusion (http://msbi.ipb-halle/MetFusion) and linked as a database search option within MzMine (available from version 2.5). These approaches, developed in the metabolomics community, are viable and open access options to overcome problems with different instruments and/or experimental settings to support and enhance the identification of unknown and emerging compounds using conventional and modern mass spectrometers coupled to gas or liquid chromatography.

GOALS

The main goal of the NORMAN MassBank initiative within NORMAN working group 3 'Effect-Directed Analysis' is to implement a community-driven open access mass spectral database for small molecules for the NORMAN network using the MassBank database software. In the NORMAN MassBank, mass spectral records from different instrument types, ionisation techniques and collision energies obtained from standards and environmental samples provided by NORMAN members will be included. However, non-NORMAN members are also invited to contribute to and benefit from the database. Thus, another main objective is to motivate and integrate the environmental chemistry community to share their mass spectra of analytical standards and environmental samples with others to improve the identification of environmental suspects and unknowns.

IMPLEMENTATION OF NORMAN MASSBANK

The NORMAN MassBank server was established in 2011 and is accessible via http://massbank.normandata.eu/MassBank. Further information can be found at the NORMAN databases page (http://www.normandata.eu). Furthermore, the existing NORMAN EMPOMASS database for GC-EI-MS data including provisionally identified and unknown environmental compounds has been integrated into NORMAN MassBank and is now searchable via the NORMAN MassBank web interface. Tools for the conversion of vendor-specific mass spectra to MassBank record format and tutorials will be available during 2012. The site http://www.normandata.eu will be updated regularly with new developments.

CONCLUSIONS AND FUTURE PERSPECTIVES

The mass spectral information obtained from NORMAN MassBank will aid the further development of sophisticated search and classification strategies for the identification of environmental unknowns and, consequently, the prioritisation of emerging compounds. Furthermore, sharing of mass spectral data allows free-of-charge access to thousands of mass spectra for an increasing number of relevant environmental compounds: in contrast to expensive commercial libraries or home-made libraries with a limited subset of compounds. NORMAN MassBank will improve the development of open source tools for the analysis of environmental unknowns, and the ability to check instrument interoperability. The NORMAN Network wants to facilitate the sharing of existing information on knowns in order to free up resources for the identification of unknowns. NORMAN plans to join the MassBank consortium (http://www.massbank.jp), which means that NORMAN MassBank will also be connected to, and searchable via, the main MassBank server.

ACKNOWLEDGEMENTS

This activity was supported financially by the NORMAN Network. Eawag and IPB provided in-kind contributions to the project. The NORMAN MassBank server is hosted by the Helmholtz Centre for Environmental Research GmbH (Leipzig, Germany) as an in-kind contribution to the NORMAN network. We are grateful to Tony Koch, Martin Sand and Guido Schramm for technical assistance.

REFERENCES

- [1] Krauss M, Singer H, Hollender J (2010): LC–high resolution MS in environmental analysis: from target screening to the identification of unknowns. Analytical and Bioanalytical Chemistry 397, 943-951
- [2] Hogenboom AC, van Leerdam JA, de Voogt P (2009): Accurate mass screening and identification of emerging contaminants in environmental samples by liquid chromatography-hybrid linear ion trap Orbitrap mass spectrometry. Journal of Chromatography A 1216, 510-519
- [3] Lübcke-von Varel U, Bataineh M, Lohrmann S, Löffler I, Schulze T, Flückiger-Isler S, Neca J, Machala M, Brack W (2012): Identification and quantitative confirmation of dinitropyrenes and 3-nitrobenzanthrone as major mutagens in contaminated sediments. Environment International in press (doi: 10.1016/j.envint.2012.01.010)
- [4] Kern S, Fenner K, Singer HP, Schwarzenbach RP, Hollender J (2009): Identification of Transformation Products of Organic Contaminants in Natural Waters by Computer-Aided Prediction and High-Resolution Mass Spectrometry. Environmental Science and Technology 43, 7039-7046
- [5] NIST/EPA/NIH (2012): NIST Mass Spectral Library 2011. National Institute of Standards and Technology, US Secretary of Commerce, USA
- [6] Wiley (2009): Wiley registry of mass spectral data 9th edition. John Wiley & Sons, Hoboken, NJ
- [7] Hopley C, Bristow T, Lubben A, Simpson A, Bull E, Klagkou K, Herniman J, Langley J (2008): Towards a universal product ion mass spectral library–reproducibility of product ion spectra across eleven different mass spectrometers. Rapid Communications in Mass Spectrometry 22, 1779-1786
- [8] Volná K, Holčapek M, Kolářová L, Lemr K, Čáslavský J, Kačer P, Poustka J, Hubálek M (2008): Comparison of negative ion electrospray mass spectra measured by seven tandem mass analyzers towards library formation. Rapid Communications in Mass Spectrometry 22, 101-108
- [9] Oberacher H, Pavlic M, Libiseller K, Schubert B, Sulyok M, Schuhmacher R, Csaszar E, Köfeler HC (2009): On the inter-instrument and inter-laboratory transferability of a tandem mass spectral reference library: 1. Results of an Austrian multicenter study. Journal of Mass Spectrometry 44, 485-493
- [10] Oberacher H (2011): Wiley registry of tandem mass spectral data, MSforID. John Wiley & Sons, Hoboken, NJ
- [11] Oberacher H, Weinmann W, Dresen S (2011): Quality evaluation of tandem mass spectral libraries. Analytical and Bioanalytical Chemistry 400, 2641-2648
- [12] Genova Bioinformatics(2011): SmileMS – small molecule identification software for tandem mass spectrometry. John Wiley & Sons, Hoboken, NJ

- [13] HighChem (2008): Mass Frontier™ 5.1. HighChem, Bratislava
- [14] Pluskal T, Castillo S, Villar-Briones A, Oresic M (2010): MZmine 2:modular framework for processing, visualizing, and analyzing mass spectrometry-based molecular profile data. BMC Bioinformatics 11, 395
- [15] Horai H et al. (2010): MassBank: a public repository for sharing mass spectral data for life sciences. Journal of Mass Spectrometry 45, 703-714
- [16] Hildebrandt C, Wolf S, Neumann S (2011): Database supported candidate search for Metabolite identification. Journal of Integrative Bioinformatics 8, 157

What is the optimal strategy for using biomonitoring to assess human exposure to emerging contaminants?

Matthew MacLeod[1] and Martin Scheringer[2]

[1] Department of Applied Environmental Science, Stockholm University, SE 106 91 Stockholm, Sweden
[2] Institute for Chemical and Bioengineering, ETH Zurich, CH 8093, Zurich, Switzerland

Modern analytical chemistry methods make it possible to measure a wide range of chemicals in the human body at very low levels. Analysis of human tissues or fluids to assess levels and trends in human exposure to chemicals is called biomonitoring. The results of biomonitoring studies can generate significant interest among the general population because they directly address one of the primary concerns that people have about chemical pollutants: How much and how many chemicals are accumulating in my body? Currently, biomonitoring programmes are being initiated in jurisdictions all over the world. One important driver of the expansion of biomonitoring efforts is the inclusion of human milk and blood serum as “core media” for monitoring the effectiveness of the Stockholm Convention on Persistent Organic Pollutants. Human biomonitoring is also an attractive method for identifying and characterising exposures to new or unrecognised persistent chemical pollutants.

But biomonitoring alone cannot answer all of the questions about to the mechanism and extent of people’s exposure to a chemical. There is currently a growing realisation that biomonitoring must be complemented by exposure assessments based on “pathways analysis”, in which exposures are calculated by combining measurements of chemical concentrations in exposure media (for example, food, water, and air) with estimates of ingestion or contact rates with those media. Combining the two exposure assessment methods is especially advantageous when dealing with new chemicals, where the number of analysed samples may be small and there may be uncertainties in the reliability of analytical chemistry methods (for example, Trudel et al. 2011).

Conducting large-scale biomonitoring and exposure pathway assessment programmes is labour- and resource-intensive, so it is important to maximise the value and diversity of information that is obtained from such studies. An indispensable tool to help guide the design of exposure assessment programmes is a population-level pharmacokinetic model that describes the uptake and clearance of chemicals from the human body. Such a model was recently developed and described by Ritter et al. (2009, 2011).

Like other population-level models, the Ritter et al. model describes the human body as a single, well-mixed reservoir for chemicals. The amount of chemical that is present in the body (n(t), mol, as a function of time, t) is modelled as the net result of uptake into the body from all exposure pathways (U(t), mol/y) and clearance from the body at a rate characterised by a first-order rate constant (k, y^{-1}):

$$\frac{dn(t)}{dt} = U(t) - k \cdot n(t) \qquad \text{Eq. 1}$$

Equation 1 defines a relationship between the exposures characterised by pathway-based exposure assessment, U(t), and the body burdens of chemicals inferred from biomonitoring, n(t). Specifically, they are related through the intrinsic elimination rate constant from the human body for the chemical, k. Note that k can also be expressed as an equivalent half-life for elimination from the human body, $t^{1/2}$, where $k = \ln 2 / t^{1/2}$. The elimination rate constant is chemical specific, but can be assumed to be the same for all members of the population.

By accepting the mass-balance relationship between uptake and elimination from the body of a chemical that is described by Equation 1, we can state the key considerations for the development of an optimal strategy for human exposure assessment: that a full understanding of the origin of chemicals in humans and the time-scale for clearance of a chemical from the body can only be achieved by accurately characterising all three of U(t), n(t), and k.

The Ritter et al. model solves Equation 1 for n(t) using information about U(t) and k to model body burdens throughout the lifetimes of many representative members of a population. A version of the model that assumes that the entire population has experienced exponentially-declining exposures for their entire adult lives was successfully applied to describe body burdens of DDT and DDE in the Swedish population (Ritter et al. 2009) and a more general version that includes periods of exponentially rising and falling exposures was applied to interpret biomonitoring data for PCBs from the UK population (Ritter et al. 2011). These applications of the model illustrate that there are three dimensions of variability that are important to the understanding of the levels and trends of a chemical present in the members of a population. One dimension is the level and trend in population-average intake of the chemical as a function of time (which is represented by U(t) above). This can only be empirically characterised by pathways-based exposure assessment. The other two dimensions of variability can be empirically assessed using biomonitoring; they are (i) the body burden of specific cohorts, for example females born in a certain region in the same year, as a function of time, and (ii), the body burden in different age cohorts as a function of cohort age at fixed time points. Data of type (i) describe the so-called longitudinal trend of body burdens versus time for a well-defined cohort, and data of type (ii) represent a cross-sectional age-concentration trend at a specific time-point. An example of results from the Ritter et al. model illustrating all three dimensions and fit to data for PCB 153 in the UK population is shown in Figure 1, which is adapted from Ritter et al., 2011.

NORMAN Association (N° W604002510) - Network of reference laboratories, research centres and related organisations for monitoring of emerging environmental substances.
This Bulletin is produced with the generous support of INERIS.

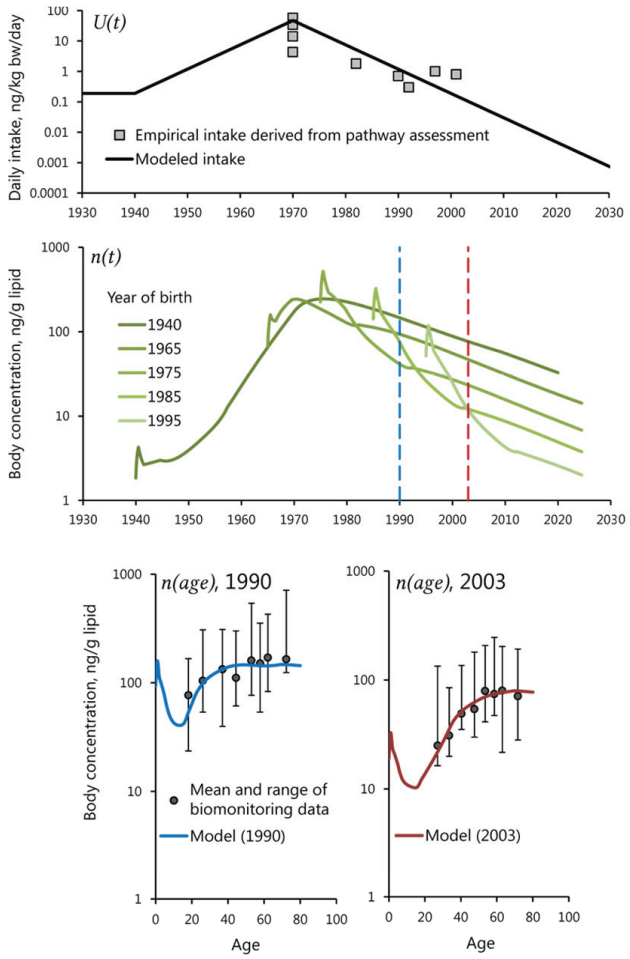


Figure 1: An illustration of the three dimensions of variability in exposure information that can fit with a dynamic population-level pharmacokinetic model. Top panel: Intake as a function of time (U(t)). Middle panel: Longitudinal trends in human body burden as a function of time for cohorts born in different years (each green line represents n(t) for people with the same birth year). Lower panels: Cross-sectional trends in human body burden as a function of age in samples collected at a specified time (n(age) at a constant sampling time). The data and model fit are for PCB 153 in the population of the United Kingdom, and have been adapted from Ritter et al. 2011.

As stated above, an optimal strategy for human exposure assessment will lead to an understanding of the rate of population-level exposure as a function of time (U(t)), the body burden for different age groups of the population, again as a function of time (n(t)) and the average half-life for human elimination (k). This can be accomplished if information about levels and trends in each of the three dimensions described above and illustrated in Figure 1 is retrieved, and fitted with a population-level pharmacokinetic model such as the Ritter model. In other words, an optimised human exposure assessment programme must have components that address 1) the levels and temporal trends of external exposure through exposure pathways analysis, and 2) age-stratified biomonitoring data gathered at at least two time points separated by several years to establish the longitudinal and cross-sectional trends.

The characteristics of an optimised exposure assessment programme identified above lead to an important insight about the utility of biomonitoring of breast milk. Because child bearing and lactation occur in a relatively narrow age range, biomonitoring based only on analysis of human breast milk provides very little information about the variability of body burden with age. Therefore, it cannot be the basis of an optimised exposure assessment. If the goals of a biomonitoring programme are strictly to establish U, n and k, then sampling blood from males and nulliparous females with a range of ages is the optimal strategy since it removes the potential for confounding effects of childbearing on body burdens of persistent substances.

In summary, both biomonitoring data and estimates of population-level intake derived from exposure pathways analysis are needed to build up a complete picture of the uptake and clearance of persistent pollutants by human populations. Biomonitoring studies that include measurements across an age-stratified cross-section of the population provide a valuable dimension of information for fitting population-level pharmacokinetic models. Population-level pharmacokinetic models make it possible to rationalise estimates of levels and trends of intake with the chemical's intrinsic elimination rate constant. This is best accomplished by fitting all three dimensions of the exposure data shown in Figure 1. Therefore, collection of age-stratified biomonitoring data should be preferred over focusing on only one age cohort. In this context, biomonitoring of persistent organic substances is better done in blood than in breast milk.

Several avenues of research hold the potential to further improve the utility of biomonitoring in human exposure assessment. First, there are significant uncertainties associated with extrapolating chemical concentrations measured in blood or other matrices to whole-body burdens, especially for chemicals of emerging environmental and human health interest that are polar or have surfactant-like properties. Additional empirical measurements of the distribution of such substances in different tissues of the body, and improved models that have more detailed descriptions of transport and partitioning in the body are needed to reduce these uncertainties. Second, sampling of blood is an invasive procedure that requires a high level of planning and effort. Development of less-invasive or non-invasive biomonitoring techniques that can be applied across the age structure of the population should be pursued. Especially promising in this regard is monitoring of persistent pollutants in nails and hair (Esteban & Castario, 2009), but significant knowledge gaps need to be overcome to establish robust relationships between levels of contaminants in these matrices and whole-body burdens.

REFERENCES

- Esteban, M., Catario, A. 2009. Non-invasive matrices in human biomonitoring: A review. Environment International. 35, 438 – 449.
- Ritter, R., Scheringer, M., MacLeod, M., Schenker, U., Hungerbühler, K. 2009. A multi-individual pharmacokinetic model framework for interpreting time trends of persistent chemicals in human populations: Application to a postban situation. Environmental Health Perspectives. 117, 1280 – 1286.
- Ritter, R., Scheringer, M., MacLeod, M., Moeckel, C., Jones, K.C., Hungerbühler, K. 2011. Intrinsic human elimination half-lives of polychlorinated biphenyls derived from the temporal evolution of cross-sectional biomonitoring data from the United Kingdom. Environmental Health Perspectives. 119, 225 – 231.
- Trudel, D., Scheringer, M., von Goetz, N., Hungerbühler, K. 2011. Total consumer exposure to polybrominated diphenyl ethers in North America and Europe. Environmental Science & Technology. 45, 2391 – 2397.

NORMAN Association (N° W604002510) - Network of reference laboratories, research centres and related organisations for monitoring of emerging environmental substances.
This Bulletin is produced with the generous support of INERIS.

NORMAN Interlaboratory Study on passive sampling of emerging pollutants

Chemical Monitoring On Site (CM Onsite) organised by the NORMAN Association and European DG Joint Research Centre (JRC) in support of the Common Implementation Strategy (CIS) of the Water Framework Directive (WFD)

Branislav Vrana
Slovak National Water Reference Laboratory, Water Research Institute, Nabr. arm. gen. L. Svobodu 5, 81249 Bratislava, Slovakia
branovrana@googlemail.com

It is now being recognised that passive samplers can play a valuable role in monitoring water quality within a legislative framework such as the European Union's WFD. The time-integrated data from these devices can be used to complement chemical monitoring of priority and emerging contaminants which are difficult to analyse by conventional spot or bottle sampling methods, and to improve risk assessment of chemical pollution. In order to increase the acceptance of passive sampling technology amongst end users and to gain further information about the robustness of the calibration and analytical steps, several interlaboratory field studies have recently been performed in Europe. Such trials are essential to further validate this sampling principle and to increase the confidence of the technological approach for end users.

An interlaboratory study on the use of passive samplers for the monitoring of emerging pollutants was organised in 2011 by the NORMAN association together with the European DG Joint Research Centre to support the CIS of the WFD.

After the intense preparatory work performed in 2010, a team of NORMAN member organisations (Masaryk University, Czech Republic; Cemagref and University of Bordeaux 1, France; UK Environment Agency; Quasimeme and Deltares, the Netherlands; and DG JRC) under the leadership of the Water Research Institute, Slovakia, performed the field sampling exercise from May to August 2011 at the municipal wastewater treatment plant of the city of Brno in the Czech Republic.

Thirty academic, commercial and regulatory laboratories from Europe, North America and Australia participated in the passive sampler comparison exercise and each was allowed to select their own sampler design. All the different devices were exposed at a single sampling site to treated wastewater from the large municipal treatment plant. In addition, for each target analyte class the organisers deployed, in parallel, multiple samplers of a single type which were subsequently distributed to the participants for analysis.

This allowed an evaluation of the contribution of the different analytical laboratory procedures to the data variability. The exercise also covered the aspects relating to the comparison of results between passive sampling and conventional spot sampling. The results obtained allow an evaluation of the potential of different passive sampling methods for monitoring selected emerging organic pollutants:

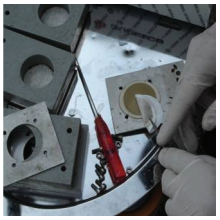
- Polar pesticides (Terbutylazine, Desethylatrazine, Desethylterbutylazine, Atrazine, Carbendazim, S-metolachlor, Diuron)
- Pharmaceuticals (Carbamazepine, Diclofenac, Ibuprofen, Naproxen, Diazepam, Alprazolam, Ketoprofen, Atenolol)
- Steroid hormones: (17-alpha-Estradiol, 17-alpha-Ethinylestradiol, 17-beta-Estradiol, Estriol, Estrone)
- Bisphenol A
- Triclosan
- Fluorinated surfactants (PFOA, PFOS)
- Brominated flame retardants (BDE 28, 47, 99, 100, 153 and 154)

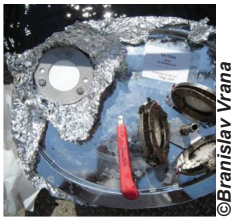
In total, 1057 samplers were deployed at the reference site and distributed for analysis. The exercise was a great learning experience for organisers and participants.

The participating laboratories reported their results by the end of January 2012 and the data treatment phase is currently under way. A dissemination workshop will be organised in Autumn 2012 (organisation by NORMAN and DG JRC as part of the NORMAN-JRC Collaboration Agreement). The results will be used to inform EU Member States about the potential application of passive sampling methods for monitoring these compounds within the framework of the WFD.

It is also proposed as part of the activities in 2012 that an Expert Group (EG) meeting should take place with invited experts in ecotoxicology (Member States' experts for the derivation of EQS in support of WFD) and experts in passive sampling (analytical aspects) to discuss the possible route for making WFD EQS compatible with passive sampling results. The issue of measurement of "whole water" vs "dissolved" concentration in water quality monitoring is a crucial issue for further development and implementation of passive sampling and EDA techniques in compliance monitoring of priority and river basin-specific pollutants. Applicability of passive samplers as "biomimetic" surrogates of monitoring organisms for compliance checking with environmental quality standards of pollutants in biota also needs to be discussed. This issue should therefore be part of discussions in the future NORMAN EG meetings on passive sampling and EDA with a view to preparing proposals for decision-makers.

The dates of these meetings are still to be fixed. NORMAN will provide the necessary financial support to this initiative. For more information: Branislav Vrana at VUVH (branovrana@googlemail.com)





©Branislav Vrana

REFERENCES

- Vrana B. et al. Passive sampling of emerging pollutants in the aquatic environment: state of the art and perspectives – NORMAN Position Paper – 2010 (www.norman-network.net >> Workshops >> Expert NORMAN meetings http://www.norman-network.net/index_php.php?module=public/workshops/workshopsexpert&interface=1024&lang=en).

NORMAN Association (N° W604002510) - Network of reference laboratories, research centres and related organisations for monitoring of emerging environmental substances.
This Bulletin is produced with the generous support of INERIS.

New guidelines for naming perfluoroalkyl and polyfluoroalkyl substances (PFASs) promote a unified understanding

Jana Johansson and Ian T. Cousins*
Department of Applied Environmental Science (ITM), Stockholm University, SE-106 91 Stockholm, SE
*Corresponding author. Email: ian.cousins@itm.su.se

A recent critical review (Buck et al., 2011) presents an overview of terminology, names and acronyms, as well as an organisational hierarchy for PFASs to promote a unified lexicon for use by the global scientific community. The authors believe that the new guidelines for naming PFASs provide an improved understanding of chemical structure, similarities, differences and nomenclature and facilitate a better grasp of uses and origins.

The use of perfluoroalkyl and polyfluoroalkyl substances (PFASs) and surfactants, including the perfluoroalkyl acids (PFAAs) perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA), and polymers made with the aid of PFASs in numerous industrial and commercial applications has been widespread during the last 60 years (Kissa 2001). The consequent emissions have led to a broad range of these substances being detected in the environment (e.g. Yamashita et al., 2005), wildlife (e.g. Giesy and Kannan, 2001; Martin et al., 2004) and humans (e.g. Hansen et al., 2001). The rate of publication in this field has expanded rapidly and there are currently >400 papers per year published on PFASs. In the literature, authors have created terminology, names and acronyms to describe these substances, which are unfortunately inconsistently applied. It is not uncommon that a given compound has been designated by many names and acronyms, or that a given acronym has been used to denote different substances. Occasionally, terms to describe broad groups of substances have mistakenly come to include substances that are very different from one another. At times the scientific literature concerning these substances has thus become confusing. A harmonised terminology that specifically describes PFASs is required in order to promote a collective understanding and meaningful communication between all players concerned: the PFAS industry, the environmental scientific community and the bodies responsible for the regulation of chemicals.

The primary aim of a paper recently published in Integrated Environmental Assessment and Management (Buck et al., 2011) was to recommend a clear, specific and descriptive terminology for PFASs. The paper recommends uses of the terms “perfluoroalkyl”, “polyfluoroalkyl”, “fluorinated polymers”, “fluoropolymers”, “perfluorinated”, “polyfluorinated”, and other phraseologies, as well as the restriction of the acronym PFC exclusively to perfluorocarbons, i.e. substances containing only carbon and fluorine atoms. It is proposed by Buck et al. (2011) that environmental PFASs of interest are best understood by segregation into general families: 1) non-polymer perfluoroalkyl substances (e.g., PFAAs which include PFOS and PFOA); 2) non-polymer polyfluoroalkyl substances (e.g., fluorotelomer alcohols, FTOHs); and 3) fluorinated polymers (including both fluoropolymers e.g. polytetrafluoroethylene (PTFE) and side-chain fluorinated polymers). Furthermore, a set of simple names and acronyms for the families and their individual members are suggested. In this news article it is not possible to reiterate all the definitions contained in Buck et al. (2011). We instead give two important examples of the proposed terminology guidelines. We also include a figure which displays the general families of perfluoroalkyl and polyfluoroalkyl substances (PFASs) with some well-known examples (Figure 1).

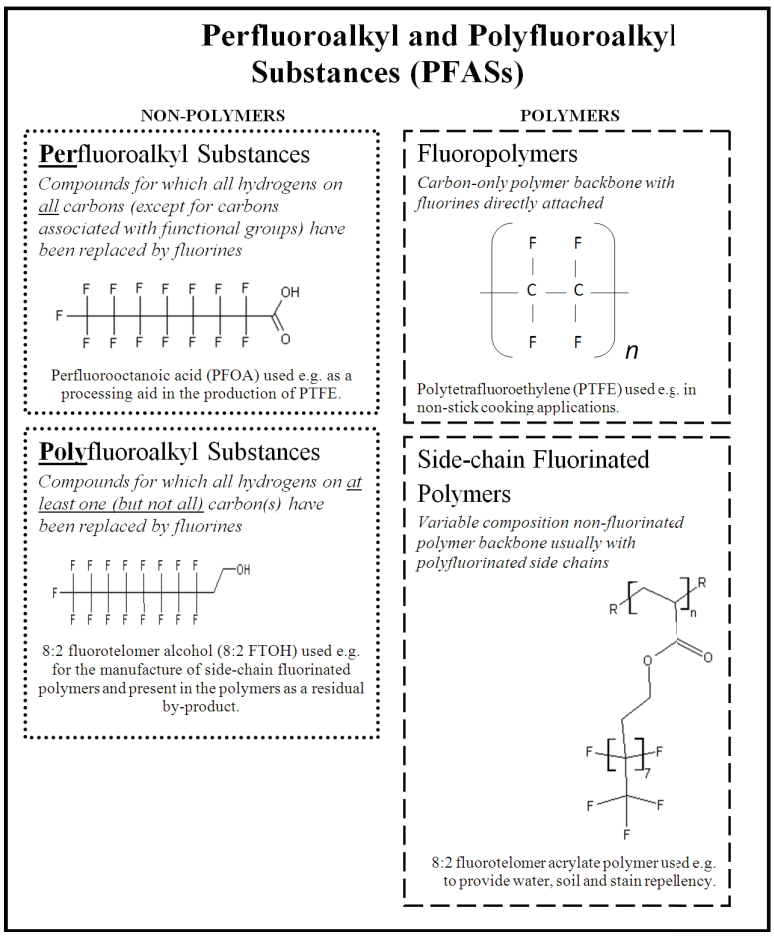


Figure 1: General families of PFASs with some well-known examples

EXAMPLE 1: “PFASS” IS RIGHT AND “PFCS” IS WRONG!

A subset of fluorinated substances are the highly fluorinated aliphatic substances that contain one or more carbon atoms on which all the hydrogen substituents (present in the non-fluorinated analogues from which they are notionally derived) have been replaced by fluorine atoms, in such a manner that they contain the perfluoroalkyl moiety C_nF_{2n+1}—. Buck et al. (2011) refer to these compounds as the “perfluoroalkyl and polyfluoroalkyl substances” and suggest they be denoted by the acronym PFASs. More explicitly, it is recommended that the family of compounds denoted by the acronym PFAS should encompass:

- Perfluoroalkyl substances, defined as aliphatic substances for which all of the hydrogen atoms attached to carbon atoms in the non-fluorinated substance from which they are notionally derived have been replaced by fluorine atoms, except those hydrogen atoms whose substitution would modify the nature of any functional groups present. This usage is consistent with the definition of “perfluoro” and “perfluorinated” provided by Banks et al. (1994, p. 2)
- Polyfluoroalkyl substances, defined here as aliphatic substances for which all hydrogen atoms attached to at least one (but not all) carbons have been replaced by fluorine atoms, in such a manner that they contain the perfluoroalkyl moiety C_nF_{2n+1}— (e.g., $C_8F_{17}CH_2CH_2OH$). Thus, while the general chemical concept of “polyfluorination” embraces compounds containing “scattered” multiple fluorine atoms (such as in $CH_2FCHFCHFCH_2OH$), as well as “grouped” ones (such as in $CF_3CF_2CH_2COOH$), we consider that only those polyfluorinated substances having at least one perfluoroalkyl moiety C_nF_{2n+1}— belong to the PFAS family.

NORMAN Association (N° W604002510) - Network of reference laboratories, research centres and related organisations for monitoring of emerging environmental substances.
This Bulletin is produced with the generous support of INERIS.

The general term "perfluoroalkyl(ated) substance", with the acronym PFAS, was the first to be established as a description of the broad class of highly fluorinated substances observed in the environment (Hekster et al. 2002; Hekster et al. 2003). In addition, many authors started using the acronym "PFC", which has been defined in many different ways and whose meaning is ambiguous. Buck et al. (2011) consider this choice to have been an unfortunate one, as the acronym PFC has been used to designate the perfluorocarbons (United Nations 1998), which is a family of greenhouse gases, in official Kyoto Protocol documents since the adoption of this important international agreement in 1997. Buck et al. strongly urge the scientific community to adopt henceforth the use of PFASs (singular PFAS) as an acronym for "perfluoroalkyl and polyfluoroalkyl substances" and PFCs exclusively for perfluorocarbons.

EXAMPLE 2: "FLUORINATED POLYMERS" AND "FLUOROPOLYMERS" DEFINED

Buck et al. (2011) recommend using the broad generic term "fluorinated polymers" to encompass all polymers for which one or more of the monomer units contains the element fluorine, in the backbone and/or in side chains. Fluorinated polymers may or may not be PFASs, depending on whether or not they contain perfluoroalkyl moieties. It is further recommended, in line with longstanding industry practice, that the term "fluoropolymers" be applied only to a distinct subset of fluorinated polymers – namely those made by (co)polymerization of olefinic monomers, at least one of which contains fluorine bound to one or both of the olefinic carbons, to form a carbon-only polymer backbone with fluorine atoms directly attached to it, e.g., polytetrafluoroethylene (PTFE).

Fluoropolymers should not be confused with another type of commercially important fluorinated polymer, namely the side-chain fluorinated polymers, often used to provide water-, stain- and grease-proofing finishes for textile, leather and paper surfaces. These do not have perfluorinated or polyfluorinated polymer backbones, but are composed of variable composition backbones (acrylate, urethane, or oxetane) usually with polyfluoroalkyl side chains (and possibly also perfluoroalkyl side chains).

A TREASURE TROVE OF INFORMATION

Buck et al. (2011) express in their article a hope that the terminology, names and acronyms suggested will be adopted by the whole "perfluoroalkyl and polyfluoroalkyl substances" community and that this will lead to consensus on usage and the avoidance of misnomers. In this news item we could not even do full justice to the article's treasure trove of information on recommended names and acronyms for 42 families and subfamilies of PFASs and 268 selected individual compounds. The article additionally includes a description of the two main production processes, electrochemical fluorination and telomerization, used for manufacturing PFASs and types of by-products (isomers and homologues) likely to arise in these processes. It further shows how the principal families of PFASs are interrelated as industrial, environmental or metabolic precursors or transformation products of one another. We believe that the article by Buck et al. (2011) will be an invaluable resource and guideline to the community in the coming years, which we expect to continue to be productive years for researchers working on PFASs.

REFERENCES

- Banks RE, Smart BE, Tatlow JC. 1994. Organofluorine chemistry - Principles and commercial applications. New York (NY), USA: Plenum Press. 670 p.
- Buck RC, Franklin J, Berger U, Conder JM, Cousins IT, de Voogt P, Astrup Jensen A, Kannan K, Mabury SA, van Leeuwen SPJ. Accepted for publication. Perfluoroalkyl and polyfluoroalkyl substances (PFASs) in the environment: terminology, classification and origins. Integrated Environmental Assessment and Management.
- Giesy JP, Kannan K. 2001. Global distribution of perfluorooctane sulfonate in wildlife. Environ Sci Technol 35:1339-1342.
- Hansen KJ, Clemen LA, Ellefson ME, Johnson HO. 2001. Compound-specific, quantitative characterization of organic fluorochemicals in biological matrices. Environ Sci Technol 35:766-770.
- Hekster FM, de Voogt P, Pijnenburg AMCM, Laane RWPM. 2002. Perfluoroalkylated substances - Aquatic environmental assessment. The Hague, The Netherlands: National Institute for Coastal and Marine Management (RIKZ). Report RIKZ/2002.043.
- Hekster FM, Laane RWPM, de Voogt P. 2003. Environmental and toxicity effects of perfluoroalkylated substances. Rev Environ Contam Toxicol 179:99-121.
- Kissa E. 2001. Fluorinated surfactants and repellents (2nd edition revised and expanded). New York (NY), USA: Marcel Dekker. 640 p. [In: Surfactant Science Series, 97].
- Martin JW, Smithwick MM, Braune BM et al. 2004. Identification of long-chain perfluorinated acids in biota from the Canadian Arctic. Environ Sci Technol 38:373-380
- United Nations. 1998. Kyoto Protocol to the United Nations Framework Convention on Climate Change [Internet]. [cited 2010 28 September]. Available from: http://unfccc.int/resource/docs/convkp/kpeng.pdf
- Yamashita N, Kannan K, Taniyasu S, Horii Y, Petrick G, Gamo T. 2005. A global survey of perfluorinated acids in the oceans. Mar. Pollut. Bull. 51:658-668.

NORMAN Association (N° W604002510) - Network of reference laboratories, research centres and related organisations for monitoring of emerging environmental substances.
This Bulletin is produced with the generous support of INERIS.

Engineered nanoparticles in the environment

2nd Workshop on "Engineered nanoparticles in the environment; analysis, occurrence and impacts" - NORMAN WG4

Lars Duester
BfG, Federal Institute of Hydrology, Am Mainzer Tor 1, 56068 Koblenz, Germany
duester@bafg.de

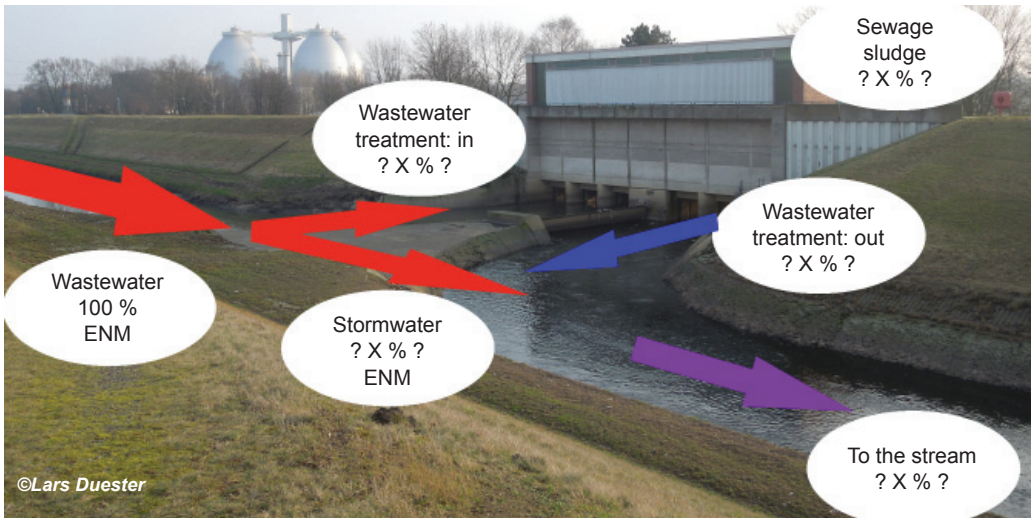
More than 70 participants attended the workshop on "Engineered nanoparticles in the environment - Analysis, Occurrence and Impacts" organised by BfG in October 2010 in Koblenz. During the workshop key questions in the area of nanomaterials, such as the appropriate analytical methods for analysis of engineered nanoparticles (ENPs) in environmental matrices, and their behaviour in the environment were discussed. One year later, a public meeting of interested scientists was held to further clarify the interest in setting up a NORMAN Working Group on engineered nanomaterials and the scope of such a working group. The following four tasks were addressed in presentations during that meeting.

ANALYTICAL METHODS, TASK GROUP I: RALF KAEGI, EAWAG, CH

A large analytical toolbox mainly developed by material scientists is available for the characterisation of engineered nanoparticles (<100 nm, ENPs). However, although these methods are perfectly suited to analyse pure and often highly concentrated suspensions of ENPs, they cannot be applied to detect ENPs in complex matrices, such as surface water, wastewater, ground water, soils or sludge. ENPs are expected to occur in very low concentrations in the environment and they will be largely outnumbered by naturally occurring nanoscale materials, such as nanoclays, iron hydroxides and aggregates of humics/fulvics. The interaction of ENPs with the environmental matrix leads to physical (aggregation) and chemical (speciation) transformations which further complicates the detection of ENP in the environment. Thus, one of the biggest challenges we are facing today is to separate individual fractions of ENPs from the environmental matrix.

LIQUID PHASE INTERACTIONS, TASK GROUP II: RUTE DOMINGOS, INST. SUPERIOR TÉCNICO, PT

Once in the natural environment, it is likely that the properties of the nanoparticles are modified by their interaction with natural compounds. The objectives of this task group were to discuss i) the short- and long-term stability of industrial and natural suspensions, and ii) the possibility of the nanoparticles being relevant carriers for inorganic and organic pollutants. The nanoparticle suspensions are highly dynamic systems: indeed, freshly prepared suspensions of nanoparticles can be observed to change with time. But over what period should they be studied? Do the nanoparticles have the same effect as the colloidal particles that can increase or slow down the mobility of pollutants by orders of magnitude? Adsorption onto some oxide nanoparticles has been found to be important for many heavy metals and may significantly affect their mobility in aquatic environments. But what would be the ENPs that can act as pollutant carriers and how, and to what extent, might ENPs facilitate the transport of the pollutants in the environment?



BEHAVIOUR OF ENPS IN THE ENVIRONMENT, TASK GROUP III: MICHAEL BURKHARDT, UMTEC, CH

The use of engineered nanomaterials (ENMs) in products, their release, transport pathways and environmental behaviour are highly uncertain. So far ENMs have mainly been tested under artificial lab conditions. Only a limited number of experimental results are published, mainly focused on textiles, coatings and mass flow analysis. ENMs present in natural waters are regularly associated with larger particles such as composites. Not a single study has demonstrated the transfer of ENMs to natural water systems in their individual form. Wastewater treatment plants seem to act as excellent barriers for ENM metal oxides, but it is expected that stormwater runoff, landfill leachate and sediments of streams including discharge points might become more environmentally relevant in the future. A sampling strategy is required that is suitable for particular natural flow conditions expected and the particle / substance fate.

ECOTOXICITY OF ENPS, TASK GROUP IV: JOEL PEDERSEN, UNIV. OF WISCONSIN – MADISON, USA

The state-of-the-art knowledge of the toxicity of nano Ag, Au, SiO_2, ZnO, TiO_2 and of carbon-based materials towards different cell lines, bacteria, invertebrates and fish was presented. The need to increase our knowledge about biomagnification and impacts on food webs was emphasised. In future studies the following tasks may be addressed: (i) detailed characterisation of the influence of ENM properties on uptake, distribution and toxicity; (ii) investigation of effects likely to occur at environmentally relevant ENM concentrations; (iii) development of biomarkers of exposure; (iv) evaluation of the utility of high-throughput screening tests; and (v) elucidation of the mechanisms of ENM toxicity as distinct from those of dissolved species.

After in-depth discussion participants decided that WG-4 on Engineered Nanoparticles should address three of the above-mentioned topics (i.e. task groups I, III, IV). In particular, the set of nanomaterials to be investigated would be TiO_2, (future CeO_2), Ag, (Au Reference), C_{60}, (future CNT) with wastewater and the materials from the treatment process, stormwater, surface water and sediments as target matrices.

The set of nanomaterials and matrices will be updated / confirmed each year.

OVERALL GOALS OF THE WORKING GROUP ON ENPS IN THE ENVIRONMENT (WG-4):

- (i) COST Action proposal, Lars Duester, BfG, GER

COST – European Cooperation in Science and Technology – is one of the longest-running European instruments supporting cooperation among scientists and researchers across Europe. It supports networking activities such as meetings, conferences, workshops, short-term scientific exchanges and training schools. COST does not fund the research itself. The COST Action Proposal by the NORMAN group is divided into

NORMAN Association (N° W604002510) - Network of reference laboratories, research centres and related organisations for monitoring of emerging environmental substances.
This Bulletin is produced with the generous support of INERIS.

four work groups: two on emission and fate, one on environmental analytical chemistry and one on toxicity & regulation of ENMs in the environment. If successful, the exchange between the members will be significantly increased and the transfer of scientific information from scientists to the public will be strengthened. Hence, one key task is the publication of position papers by the NORMAN group to support decision-making processes.

- (ii) International Workshop in 2013, Luciana Dini, University of Salento, ITA

  The NORMAN WG-4 on ENPs in the Environment plans to organise a conference on "Ag, TiO_2 and C_{60} nanoparticles in the environment: analysis, occurrence and impacts" to be held in Lecce, Italy in October 2013. With the rapid development of nanotechnology applications, the safety assessment of nano-products has become more important than ever before. The conference will therefore provide an international forum for presentation and discussion. The meeting will focus on the TiO_2, Ag and fullerene-based ENMs and will cover as main topics: i) analysis and analytical methods ii) interactions and behaviour of engineered nanoparticles in the aquatic environment iii) ecotoxicity and regulatory aspects. The purpose of this meeting is to gather scientists, industry & authority representatives and to stimulate discussion on the latest research results, to promote future collaborations and, most importantly, to attract young minds to nanoscience research.

- (iii) Common research, Torsten Klawonn, Fraunhofer – IME, GER

  Investigation of nanomaterials in the environment inevitably requires precise and accurate procedures and analytical methods. In order to evaluate different analytical methods and to exchange expert knowledge within the working group, we will first initiate inter-laboratory comparisons concerning quantification of the total amount of target nanoparticles in different matrices (soil, sediment, sewage sludge and aqueous samples). In this approach an exact amount of nanoparticles is added to the matrix and after possible digestion the amount is quantified by analytical means and the recovery is determined. This straightforward approach makes it possible to validate the applicable procedures and analytical methods needed for basic quantification of added nanoparticles in test systems and to identify the critical steps in this work.

Projects

EDA-EMERGE

Innovative biodiagnosis meets chemical structure elucidation – Novel tools in effect-directed analysis to support the identification and monitoring of emerging toxicants on a European scale (EDA-EMERGE)

FP7-PEOPLE-2011-ITN
Project coordinator: W. Brack, Helmholtz Centre for Environmental Research UFZ

Triggered by an initiative of NORMAN Working Group 3 "Effect-Directed Analysis (EDA) for Hazardous Pollutant Identification", a new Marie Curie Action – Initial Training Network called EDA-EMERGE started in October 2011.

Effect-directed analysis (EDA) is based on the understanding that environmental samples may contain thousands of mostly organic chemicals and that only a fraction of them can be analysed by chemical target analysis. EDA is an integrated approach to focus chemical analysis on those compounds in environmental samples that cause effects. It combines bioassays – and other biodiagnostic tools for effect characterisation – with fractionation procedures to reduce the complexity of environmental mixtures and to isolate toxicants, and chemical analysis and structure elucidation to identify causative toxicants.

EDA-EMERGE aims to train a new generation of young scientists in EDA and other interdisciplinary techniques required to meet the major challenges in the monitoring, assessment and management of toxic pollution in European river basins, considering the enormous complexity of contamination, effects and cause-effect relationships. By integrating innovative mode-of-action based biodiagnostic tools – including *in vitro* tests, transgenic organisms and "omics" techniques – with powerful fractionation and cutting edge analytical and computational structure elucidation tools, a new generation of EDA approaches will be developed for the identification of toxicants in European surface and drinking waters.

Innovative method development by young researchers will be closely interlinked with a joint European demonstration programme and higher-tier EDA and extensive training courses. EDA-EMERGE fellows will learn to organise and run international and interdisciplinary sampling and monitoring campaigns and benefit from the expertise of one of the most experienced private companies in this field. Strong networking between academia, the private sector and leading regulators in the fields of river basin and pollution management ensures the practical relevance of the research and helps to provide excellent employment opportunities for EDA-EMERGE fellows.

The consortium includes two universities (the Free University of Amsterdam and the Technical University of Aachen, RWTH), six research centres (Helmholtz Centre for Environmental Research (UFZ), Institut National de l'Environnement Industriel et des Risques (INERIS), Swiss Federal Institute of Aquatic Science and Technology (Eawag), Rudjer Boskovic Institute (IRB), Norwegian Institute for Water Research (NIVA) and the Italian Istituto Superior di Sanità (ISS)), the European Commission Joint Research Centre (JRC), and five private companies (Environmental Institute, KWR Watercycle Research Institute, WatchFrog, HighChem and gaiac) (Fig. 1). They all are members of, or closely related to, the NORMAN network.

An internationally composed advisory board involving scientists from US-EPA, Environment Canada, the European Environmental Agency and the German Federal Environmental Agency will introduce new perspectives on monitoring, assessment and management of emerging pollutants within and outside of Europe.

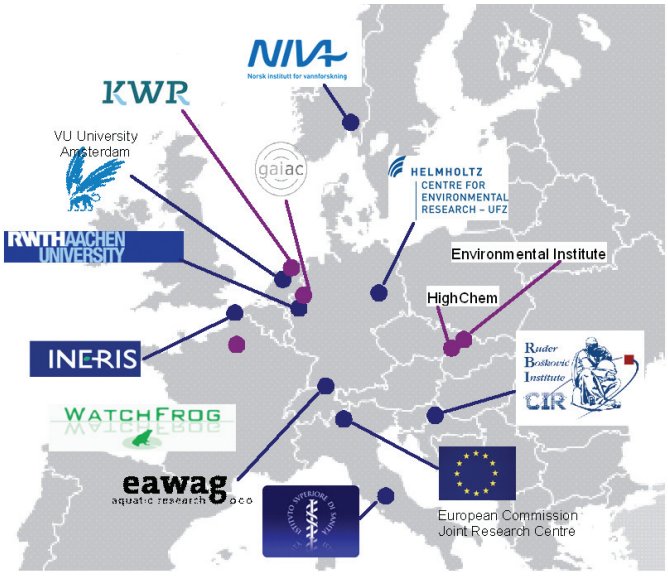


Figure 1: Partner institutions in EDA-EMERGE

NORMAN Association (N° W604002510) - Network of reference laboratories, research centres and related organisations for monitoring of emerging environmental substances.
This Bulletin is produced with the generous support of INERIS.

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

Milestones and achievements in 2011

WORKING GROUPS

• Prioritisation of emerging substances (Working Group 1 - INERIS, FR)

The work of the NORMAN Working Group on Prioritisation of Emerging Substances started in 2010. They key principles of the prioritisation methodology are provided on the NORMAN website http://www.norman-network.net/public_docs/divers/norman_prioritisation_dec2011_vf.ppt

To recap, the NORMAN prioritisation methodology uses a decision tree that first classifies chemicals into six categories, based on existing knowledge gaps (e.g. insufficient information on the effect thresholds of a substance, inadequate performance of the analytical method for quantifying its level of occurrence in the environment).The priority within each category is then evaluated on the basis of specific indicators, e.g. persistence, bioaccumulation potential, toxicological and ecotoxicological properties and, on a risk assessment level, the Frequency of Exceedance and Extent of Exceedance of Predicted No-Effect Concentrations (PNECs).In 2011 the NORMAN IT team (Environmental Institute) has successfully built the methodology into the NORMAN EMPODAT database, thus enabling online automated prioritisation of emerging substances within the various action categories. The results of the application of the presented methodology to the current NORMAN list of emerging substances (www.norman-network.net >> About us >> List) will be published in the course of 2012, after discussion with the Working Group experts. Part of the methodology has been successfully applied to four river basins in the MODELKEY project database (Von der Ohe, P.C. et al.) (http://dx.doi.org/10.1016/j.scitotenv.2011.01.054). The application of the approach revealed the biocide triclosan as one promising candidate for the future list of priority substances (Von der Ohe, P.C. et al.) (http://dx.doi.org/10.1007/s11356-011-0580-7).

Furthermore, the NORMAN scheme is currently used in France as an innovative and comprehensive approach for improving national monitoring programmes under the Water Framework Directive and the regular updating of the list of River Basin-Specific Pollutants (see also, earlier in this bulletin, the dedicated note on a watch list of emerging pollutants in France).

In 2012 NORMAN ecotoxicologists will make a significant effort to improve the data used for the derivation of the lowest PNECs for each substance on the NORMAN list of candidate substances. There is still room for improvement on this point, which is a critical part of the prioritisation methodology. This holds in particular for substances such as the pharmaceuticals for which the standard organisms used in the laboratory ecotoxicity tests appear to be of limited relevance. The study will concentrate on the recent studies including novel endpoints such as behavioural effects, i.e. data about non-standard tests will be collected from the literature, and expert advice will be applied to treat them for the derivation of the Lowest PNEC.

The overall prioritisation work is intended to be repeated on a regular basis as a direct consequence of the continuous revision and updating of the NORMAN list of emerging substances based on the input from the scientific community.

Finally, a comment needs to be made about the Watch List project proposed by DG ENV and JRC in 2011, which should lead to a first pilot study at EU level in 2012. According to the recent Commission Proposal (COM(2011)876) on priority substances in the field of water policy, DG ENV intends to launch a new mechanism to provide the Commission with targeted high-quality monitoring information on the concentration of substances in the aquatic environment. In the context of future reviews of the priority substances list under the Water Framework Directive, it will focus on emerging pollutants and substances for which available monitoring data are not of sufficient quality for the purpose of risk assessment.

The NORMAN prioritisation methodology is fully in line with the objectives of the Watch List project. NORMAN was clearly recognised as a potential contributor in the discussion paper circulated by JRC to the representatives of member states ("Outline of a pilot exercise to investigate the feasibility of a "Watch List", October 2011, DG ENV / JRC). Considering that the first round of the pilot study in 2012 will be mainly aiming to demonstrate the general feasibility of the approach, NORMAN is ready to provide concrete support to this project in 2013. For more information: Valeria Dulio at INERIS valeria.dulio@ineris.fr

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

As part of the achievements of the WG on EDA in 2011 it is worth mentioning: 1) the publication by Springer (Editor: Werner Brack) of the book "Effect-directed analysis of complex environmental contamination" (a summary is provided in this bulletin) and 2) the successful approval of the ITN–Marie Curie, EDA–EMERGE project submitted at the beginning of 2010 as part of the activities of this Working Group.

The EDA–EMERGE project, which started at the end of 2011 (kick-off meeting on 21 November in Stockholm), involves 14 partners from 7 countries with a duration of four years. The project's objectives and the main milestones are illustrated in a dedicated section in this bulletin.

The activities of the EDA–EMERGE project are strictly connected with the activities of the EDA Working Group (for this reason the meeting of the EDA WG took place in Stockholm back-to–back with the kick-off meeting of EDA–EMERGE). In particular the summer school on EDA-related tools (from 25–29 June 2012 at the UFZ in Leipzig), the simplified EDA protocol (January 2013) and the European Demonstration Programme (January–June 2013) are common deliverables of the EDA WG and the EDA–EMERGE project.

Additional activities of the EDA WG are the further development and maintenance of the MassBank database (for details on MassBank, see above) and the organisation of a workshop on "Occurrence, fate and effects of emerging pollutants in the environment – chemical analysis and toxicological assessment" which will take place on 29–30 November 2012 in Amsterdam, The Netherlands (task leader IVM).

• Engineered nanoparticles in the environment; analysis, occurrence and impacts (Working Group 4 - BfG, Koblenz, Germany)

Further to the NORMAN workshop on "Engineered nanoparticles in the environment; analysis, occurrence and impacts" (Koblenz, October 2010) a Working Group meeting took place one year later in Koblenz in order to discuss the interest in setting up a working group on engineered nanoparticles and the scope of such a working group.

After in-depth debates, three task groups will be launched on: 1) Analytical methods; 2) Behaviour of ENPs in the environment; 3) Ecotoxicity of ENPs. The focus for future activities will be on TiO_2, Ag and C_{60}, with a possible future evolution towards CeO_2, Au and CNT. The matrices to

NORMAN Association (N° W604002510) - Network of reference laboratories, research centres and related organisations for monitoring of emerging environmental substances.
This Bulletin is produced with the generous support of INERIS.

be considered will be: wastewater, stormwater, surface water and sediment.The WG also decided to prepare a proposal for a COST action as a first goal for 2012.For further information, see also the dedicated note on "2nd Workshop on Engineered nanoparticles in the environment; analysis, occurrence and impacts" provided in this bulletin (Lars Duester at BfG Duester@bafg.de)

DATABASES

- NORMAN EMPODAT

The continuous upgrading and maintenance of the NORMAN databases are major activities of the NORMAN network. At the end of 2011 the EMPODAT database contained more than 1 million entries from 25 European countries on the occurrence of emerging substances in water, sediment, biota and air matrices. Out of the 706 chemicals identified by NORMAN members as relevant emerging substances, 359 are supported with occurrence data. Information on the ecotoxicity thresholds (lowest PNEC values, measured and/or predicted by Read-Across QSAR modelling) and expected distribution in air/water/soil matrices (via fugacity modelling) was collected for all of the substances. The analytical performance of European laboratories could be judged for more than 400 substances from the Limits of Quantification (LOQs) of the analytical methods provided with the data and the LOQs extracted from the literature. The database also contains an automated procedure for classification of the data based on the supporting QA/QC metadata accompanying the individual data.

A battery of newly upgraded statistical tools allows for a fast overview of the distribution of data by compartment, type of matrix, country and data quality categories. If more detailed information is required, a customised statistics module can be used for personalised substance / parameter searches. Automatically updatable "Substance fact sheets" have been created for each substance, also providing information on the performance of the analytical techniques used.

A specific tool has been developed allowing for on-line automated prioritisation of emerging substances within the various action categories (see text on Prioritisation above and related methodology). Following specific requests, the prioritisation can be carried out for individual European river basins, countries, regions, groups of substances etc. The performance of the automated prioritisation set-up has recently been tested on the Slovak case study (Slobodnik et al., submitted).

Note: Although the NORMAN databases are open to all, the statistical tools, customised statistical module, prioritisation tools and facilities for copying data directly from the "search database" queries are available to NORMAN Association members only.

- NORMAN Massbank for identification of unknowns (UFZ, Leipzig, Germany)

The EMPOMASS database, archiving information from non-target screening using mass spectrometry techniques and tools for identification of unknown substances present in complex environmental samples, was transferred in 2011 to the new MassBank portal. Mass spectrometric data used for identification of "unknown" substances, and thus creating a list of potential candidates to upgrade the current list of emerging substances, are now stored in the NORMAN MassBank database module (see www.norman-network.net //Databases //NORMAN MassBank) or access directly via http://massbank.normandata.eu/MassBank. All tasks carried out in 2011 are described in the "Setting-up of a high resolution mass spectra database for NORMAN" - Status Report, September 2011. The content of the report has been reviewed by three independent experts appointed by the NORMAN Steering Committee. Among the comments received, a recommendation was provided for the organisation of a NORMAN MassBank workshop to demonstrate the functions to stakeholders, to improve the generated tools and encourage participation of a large number of researchers committed to sharing mass spectra in the database. A one-day MassBank workshop for experts interested in getting familiar with this tool will therefore take place at IVM on 27 Nov. 2012 (task leaders: UFZ and EAWAG).

NORMAN plans to join the MassBank consortium (http://www.massbank.jp). NORMAN MassBank will then be connected to and searchable via the main MassBank server. In order to ensure the success of this database as a tool to support identification of unknowns, all NORMAN members agreed at the last General Assembly meeting (Stockholm, 22–23 November 2012) to commit to active sharing of their GC-EI-MS and LC-MS accurate mass spectra. For further information, see also the dedicated note on MassBank provided in this bulletin (Tobias Schulze at UFZ tobias.schulze@ufz.de)

QA/QC ACTIVITIES - INTERLABORATORY STUDIES

- Use of passive sampling for emerging substances

After the intense preparatory work performed in 2010 a team of NORMAN member organisations (Masaryk University, Czech Republic; Cemagref and University of Bordeaux 1, France; UK Environment Agency; Quasimeme and Deltares, the Netherlands; and DG JRC) under the leadership of the Water Research Institute, Slovakia performed the field sampling exercise from May to August 2011 at the municipal wastewater treatment plant of the city of Brno in the Czech Republic. This exercise was organised as "Chemical Monitoring On Site" (CM Onsite) by the NORMAN Association and JRC in support of the Chemical Implementation Strategy of the Water Framework Directive (CIS WFD).Overall 30 participants from commercial, academic and regulatory laboratories from Europe, North America and Australia took part in the study. The following chemical groups were addressed: polar pesticides, pharmaceuticals, steroid hormones, Bisphenol A, Triclosan and perfluoroalkyl compounds. The main aim of the study was the comparison of results from various passive samplers (sent by participating laboratories) exposed to water at a single (reference) site. The exercise also covered the aspects relating to the comparison of results between passive sampling and conventional spot sampling. A dissemination workshop will be organised in Autumn 2012 (organisation by NORMAN and DG JRC as part of the NORMAN-JRC Collaboration Agreement). For more information see also the note provided in this bulletin by Branislav Vrana at VUVH (branovrana@googlemail.com)

- 1st interlaboratory study on the analysis of organic phosphorous flame retardant (PFR)

This first interlaboratory study (ILS) on the analysis of organic phosphorous flame retardant (PFRs) in environmental and dust samples, is led by the experts of IVM (Amsterdam, The Netherlands). In total 15 labs from The Netherlands, Germany, Belgium, Spain, Sweden, Austria, UK, Japan, Canada, US and Norway are participating. The aim of the study is to transfer knowledge on PFR analysis between laboratories, and to investigate how well the laboratories perform.

The ILS included a workshop which was held on 9 December 2011 in Amsterdam. During the workshop the most critical parameters in the analysis of PFRs, i.e. the background contamination, internal standards and the preferred method of analysis (GC-MS or LC-MS) were discussed. The following compounds were included in the exercise: Tri-n-iso-butyl phosphate (TiBP), Tri-n-butyl phosphate (TBP), Tris(2-chloroethyl) phosphate (TCEP), Tris(chloro-2-propyl) phosphate (TCPP), Tris(1,3-dichloro-2-propyl) phosphate (TDCPP), Tris(2-ethylhexyl) phosphate (TEHP), Tris(2-butoxyethyl) phosphate (TBEP), 2-ethylhexyl diphenyl phosphate (EHDP), Tri-cresyl phosphate (TCP), Tri-phenyl phosphste (TPP).

During the workshop a decision was made about the matrices to be included in the study, i.e. a standard solution, spiked fish oil, sediment, and dust (to be analysed in triplicate). It was decided that the laboratories would use LC-MS, GC-MS and GC-FPD for the analysis. The treatment of the results is currently under way. A report for dissemination should be available by June 2012 with a final workshop to discuss with the participating laboratories the results obtained and the report. For more information: Sicco Brandsma at IVM (Sicco.Brandsma@ivm.vu.nl)

- Implementation of NORMAN protocol for methods validation in European standardisation

A major achievement of the NORMAN experts was the publication in 2009 of a common European protocol for the validation of methods for the monitoring (occurrence) and bio-monitoring (effects) of emerging pollutants in environmental matrices. (See Schwesig et al., Trends in Analyti-

NORMAN Association (N° W604002510) - Network of reference laboratories, research centres and related organisations for monitoring of emerging environmental substances.
This Bulletin is produced with the generous support of INERIS.

cal Chemistry, 2011 in references of Fabrizio Botta's paper, above.) The protocol (published on the NORMAN website www.norman-network.net >> QA/QC) has been tested in three case studies as part of the NORMAN project. In 2010 IWW prepared –on the basis of the NORMAN protocol – a New Work Item Proposal which was accepted in 2011 by CEN TC 230, and negotiation is now under way to work up CEN Technical Specifications based on this protocol. (France chairs this activity.).

WORKSHOPS IN 2011

- Workshop on "Data Exchange - Towards a harmonised approach for collection and interpretation of data on emerging substances in the environment in support of European environmental policies" (Environmental Institute, Slovak Republic and UBA, Germany)

The main objective of this workshop was to provide a common forum for the NORMAN Association members, EU Member States and other interested groups for presenting, discussing and streamlining approaches for a harmonised collection and interpretation of data on emerging substances.

Discussion topics included (i) a proposal of the harmonised format of collected data in various environmental matrices allowing for their intercomparison across Europe, (ii) the use of metadata for assessment of quality of data (discussion of the NORMAN scheme) and (iii) possibility for regular and/or automated monitoring data collection at the EU scale.

The potential adoption of the NORMAN approach for prioritisation of emerging substances in the process of selection of future WFD priority substances was discussed in detail.

The discussion tackled questions related to (i) the use of the data in support of European environmental policies and data collection activities carried out by the EEA, DG JRC, DG EUROSTAT and DG ENV and (ii) presentation of the data to the public.

It has been recommended that at the EU level the NORMAN Association should:

- Become the primary data source for emerging substances;
- Provide experiences, data and tools as a basis for the identification/prioritisation of substances of concern;
- Contribute to the architecture of the European data centres dealing with chemicals, including the definition of a harmonised data collection;
- Contribute to the creation of the early warning system for emerging pollutants and subsequent policy actions.

One of the challenging conclusions of the workshop was the need to strengthen the commitment of NORMAN members to sharing of data (mainly monitoring data, but also bioassays, etc.) for the NORMAN EMPODAT database. The achievement of a critical mass of data on emerging substances shared in this common European database is crucial for the statistical treatment that can be performed on these data, it can be beneficial for all members of the network, and should be supported.

8th National Monitoring Conference - Water: One Resource – Shared Effort – Common Future
30 April – 4 May 2012, Portland, Oregon, US

- More information at http://acwi.gov/monitoring/conference/2012/index.html

Forthcoming events

Seminar on Environmental Contaminants organised in cooperation with the Nordic Chemical Group and Working Group for Aquatic Ecosystem: "Today's chemical solutions – problems of tomorrow?"
7 – 8 May 2012, Lund, Sweden

- More information at http://nordicscreening.org/

3rd Workshop on Organosilicones in the Environment
8 – 9 May 2012, Burlington, Ontario, Canada

- For further information download the Workshop flyer on the NORMAN website www.norman-network.net >> Workshops >> Other events

6th SETAC World Congress and SETAC Europe 22nd Annual Meeting
20 – 24 May 2012, Berlin, Germany

- More information at http://berlin.setac.eu/home/?contentid=404&pr_id=403

AWRA's 2012 Summer Specialty Conference on Contaminants of Emerging Concern in Water Resources II: Research, Engineering, and Community Action
25 – 27 June 2012, Denver, Colorado, US

- More information at http://www.awra.org/meetings/Summer2012/contaminants.html

8th Annual LC/MS/MS workshop on environmental applications and food safety
2 – 4 July 2012, Barcelona, Spain

- For further information download the Workshop flyer on the NORMAN website www.norman-network.net >> Workshops >> Other events

4th EuCheMS Chemistry Congress
26 – 30 August 2012, Prague, Czech Republic

- More information at http://www.euchems-prague2012.cz

Wastewater reuse applications and contaminants of emerging concern
13 – 14 September 2012, Limassol, Cyprus

- For further information download the Workshop flyer on the NORMAN website www.norman-network.net >> Workshops >> Norman Workshops

7th European Conference on Pesticides and Related Organic Micropollutants in the Environment
7 – 10 October 2012, Porto, Portugal

- More information at http://pesticides2012.iaren.pt/?seccao=texto

NORMAN Workshop: Occurrence, fate and effects of emerging pollutants in the environment – chemical analysis and toxicological assessment
29 – 30 November 2012, Amsterdam, The Netherlands

- For further information download the Workshop flyer on the NORMAN website www.norman-network.net >> Workshops >> Norman Workshops

>>>>>>>>>>>>>>> Contributing to the Bulletin

If you wish to contribute to a future issue of the Bulletin or announce a forthcoming event, please contact: valeria.dulio@ineris.fr

NORMAN Association (N° W604002510) - Network of reference laboratories, research centres and related organisations for monitoring of emerging environmental substances.
This Bulletin is produced with the generous support of INERIS.