



### WELCOME TO ISSUE N°5 OF THE NORMAN NETWORK NEWSLETTER

*The aim of the activities 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. The NORMAN newsletter is for everyone interested in emerging substances in the environment. This newsletter keeps you up to date on scientific advances in this area and highlights the activities and events of the EU NORMAN Network.*

#### Editorial

## Conclusions of the NORMAN project: for a new beginning of the NORMAN network

**Valeria DULIO**

Scientific Co-ordinator of the NORMAN project – Direction Scientifique - INERIS - France  
[valeria.dulio@ineris.fr](mailto:valeria.dulio@ineris.fr)

Once again, it gives me great pleasure to be writing this editorial for the NORMAN newsletter. On this occasion, the pleasure derives from looking back at what we have achieved together over the past three years, and looking forward to the new NORMAN permanent network.

The NORMAN network has worked very actively since the start of the three-year project and has provided concrete contributions – including its three databases, the organisation of four high-profile workshops, interlaboratory studies and a common protocol for methods validation – to improve the exchange of information and the quality and comparability of data on emerging substances.

The context within which those efforts have been made is well known to us all, but is worth setting out here as a reminder: emerging pollutants are the focus of increasing concern among scientists, regulators and the public in all policy areas and there is widespread awareness of the need to tackle the challenges posed by these substances.

The challenges here are great, because we cannot afford to run the risk of overlooking potential priority pollu-

tants for future regulation; we need a timely answer to the questions posed by public authorities on the potential risks posed by these substances, but the effort required for the improvement of knowledge, collection of information, etc. cannot be left to individual countries. There is, then, general recognition of the need for a permanent and independent panel of experts, recognised at the European level and beyond.

As I see it, a European network will add great value where:

- the public authorities need to be kept right up to date with the progress of research activity (including plans for further research). Progress reports and position papers will therefore be produced by experts working together to arrive at a common view of the state of play;
- the resources required (e.g. for interlaboratory studies on 'difficult matrices') are beyond the reasonable scope of any individual country;
- a substance is identified as emerging, and Working Groups need to be set up without delay.

Thanks to the resources provided by the Commission during these past three years, we have been able to build the infrastructure for this future work. It is there-

fore a natural next step for NORMAN – as an independent and competent forum consisting of an extended network of leading organisations working in the field of emerging contaminants – to continue to support the scientific and technical debate around emerging substances and to provide technical advice to the EC on these very important topics. Thus it was that the meeting on 20–21 October in Paris, organised jointly with the CMA plenary meeting of DG ENV, announced the launch of the new NORMAN permanent network.

Using its close links with the scientific community, Contact Points and reference laboratories in the various countries, the permanent network will carry out systematic collection (and conversion into a common format) of the information that is currently held in many different places and not included in national databases. The network will ensure that, as soon as an emerging substance is identified as a pollutant of concern – thereby requiring regular monitoring – there is sufficient capability across the EU for measuring it at the routine level.

The newsletter has, I believe, contributed to the maintenance of a “constant scientific watch” and to the wider dissemination of information on recent scientific publications, research projects, etc. in the field of

emerging pollutants. We will continue this activity with the “NORMAN Scientific Watch Bulletin on Emerging Substances”, in which we will address various topics, on each of which a NORMAN expert team will prepare a note with an overview of the latest scientific findings, gaps and priority research needs. All this will be produced in the kind of language which will make it accessible to a readership that also includes non-scientists. The bulletin will be disseminated to environment and health agencies, public authorities managing chemical contaminants, etc., and made available on the NORMAN public website.

For a more detailed view of the activities planned for NORMAN in 2009, please take a look at the section of this newsletter headed “Life of the project”, where you will find an extract from the Joint Programme of Activities we presented at the Paris meeting.

As I sign off this time, I express my thanks to all those who have contributed to the success of the NORMAN project and I welcome all who have signed up to our new NORMAN permanent network.

I look forward to working with you.

## Issue 5 – January 2009

EDITORIAL .....	p1
MONITORING AND BIO-MONITORING .....	p2
ENVIRONMENTAL AND HUMAN HEALTH RISK ASSESSMENT .....	p6
RESEARCH PROJECTS / FINDINGS .....	p8
LIFE OF THE NETWORK .....	p13
CALENDAR OF EVENTS .....	p16

## Monitoring and Bio-monitoring

### **Occurrence of organic wastewater contaminants in groundwaters and drinking water**

These papers provide a national-scale summary of Organic Wastewater Contaminants (OWC) in groundwaters and in drinking water sources.

In 2000, USGS sampled 47 groundwaters, representing a variety of geohydrologic environments with potential sources of OWC.

A total of 83 OWCs were analysed, representing numerous chemical groups and different uses. (Veterinary drugs and antibiotics, prescription and non-prescription drugs, sterols [natural compounds], pesticides, detergents, PAHs, COV, BTEX, etc.)

The results are edifying: at least one OWC was found in 81% of groundwater, due to the design of this study (focusing on sampling stations suspected to be affected by animal or human waste contamination). The five most frequently detected compounds include N, N-diethyltoluamide (insect repellent, 35% of samples), bisphenol A (plasticizer, 30%), tri(2chloroethyl)phosphate (fire retardant, 30%), sulfamethoxazole (veterinary and human antibiotic, 23%), and 4-octylphenol monoethoxylate (detergent metabolite, 19%).

These groups (plasticizers, insect repellent and detergent) contributed about 66% of the total measured concentration.

Considering the relationship between pollutant occurrence and well depth, the total of detected compounds significantly decreases as well depth increases. The main sources of contaminant are commonly near the wellhead.

Compared to data collected in US streams, (Kolpin, 2002<sup>1</sup>), fewer OWCs were detected at groundwater sites (35 of 65 target compounds, versus 82 of 95 for surface water sites), and concentrations of OWCs are generally lower in groundwater sites, with concentrations that rarely exceed 1µg/L (versus 67 of 111 on surface water sites).

The second approach covers 25 groundwaters and 49 sources of drinking water. This time 100 targeted chemicals were considered, belonging to the same chemical groups as before and representing several kinds of use (detergent, pharmaceuticals, veterinary drugs, insect repellent, solvents, etc.). Altogether, 63 compounds were detected; the majority of undetected compounds were pharmaceuticals.

In surface water used as a drinking water source, the most detected compounds were cholesterol and β-sitosterols (natural sterols), metolachlor (pesticide), cotinine and 1,7 dimethylxanthine (metabolites of

nicotine and caffeine respectively). In groundwaters, the most detected compounds were tetrachloroethylene (solvent), carbamazepine (pharmaceutical), bisphenol A (plasticizer), 1,7 dimethylxanthine and tri, 2-chloroethyl phosphate (manufacturing additive, fire retardant). Of the 38 pharmaceuticals investigated, 60% were not detected. The part played by transformation and degradation processes is more important in groundwater: compounds are transported into and through the environment as a result of metabolic, photolytic, adsorption and

other attenuation processes that limit input to groundwaters as long as no other source of the contaminant is present in the watershed. It is also possible that the absence of detectable compounds corresponds to the degradation into other compounds that were not targeted. There is also a lack of knowledge concerning the fate of OWCs compounds that can affect groundwater systems, especially emerging compounds such as detergents (and metabolites), pharmaceuticals (veterinary or human uses), and fire retardants.

#### REFERENCES

- [1] Kolpin D. W., Furlong E. T., Meyer M. T., et al. *Pharmaceuticals, Hormones, and Other Organic Wastewater Contaminants in U.S. Streams, 1999-2000: A National Reconnaissance*. Environmental Science and Technology 2002 (36)1202-1211

#### SOURCE:

Barnes K., Kolpin D., Furlong E., Zaugg S., Meyer M., Barber L. *A national reconnaissance of pharmaceuticals and other organic wastewater contaminants in the United States — I) Groundwater*. Science of the Total Environment, 402(2-3) [2008]:192-200.

Focazio M., Kolpin D., Barnes K., Furlong E., Meyer M., Zaugg S., Barber L., Thurman M. *A national reconnaissance for pharmaceuticals and other organic wastewater contaminants in the United States — II) Untreated drinking water sources*. Science of the Total Environment, 402(2-3) [2008]:201-216.

#### REVIEWED BY:

Anne TOGOLA  
BRGM, France  
a.togola@brgm.fr

## Unravelling the sources of Perfluorooctanoic Acid

Perfluoroalkyl carboxylates (PFCAs) have been widely used for numerous applications including metal plating and cleaning, coating formulations, fire-fighting foams, polyurethane production, inks, varnishes, vinyl polymerization, lubricants, gasoline, and oil and water repellents for leather, paper, and textiles<sup>1</sup>. Once in the environment some of the PFCAs may pose long-term health risks since they are persistent and can accumulate in living organisms. PFOA (perfluorooctanoic acid), one of the PFCAs of concern, is frequently detected in the environment and has also been detected worldwide in biota as well as humans. Much research in recent years has focused on unravelling the sources of the PFOA to the environment. Two main hypotheses have been put forward regarding the dominant source of PFOA to the global environment. One, primarily supported by Scott Mabury and colleagues (e.g. see Wallington et al.<sup>2</sup>), is that PFOA in regions remote from point sources are the result of long-range transport of precursors followed by atmospheric oxidation to produce PFOA, which is subsequently deposited. The other hypothesis, first postulated by Prevedouros et al.<sup>1</sup>, is that the industrially-produced PFOA in temperate regions are subject to long-range transport via atmospheric and oceanic currents. Prevedouros et al.<sup>1</sup> published a source inventory for PFOA and concluded that by far the majority of sources to the global environment on a historical perspective (78%) were from the use of PFOA as a processing aid in the manufacturer of fluoropolymers (especially PTFE - polytetrafluoroethylene, which is well known for its nonstick properties; the DuPont trademark is well known as Teflon). The ultimate answer as to what is

the relative importance of different sources will depend on which environment is being studied. The major oceans, for example, will receive inputs both from riverine and atmospheric inputs and it has been convincingly demonstrated<sup>1-3</sup> that direct manufacturing releases are the most important source in this case. Remote inland environments, however, which lack riverine inputs (including inland lakes<sup>4</sup> and the High Arctic<sup>5</sup>) can only receive inputs from the atmosphere. There still remains the uncertainty that atmospheric PFOA can be derived by either direct release from manufacturing facilities and subsequent atmospheric transport or from precursor release, transport and degradation. Armitage et al.<sup>6</sup> have shown that atmospheric transport of PFOA released from manufacturing sources could be a previously underestimated transport pathway. The relative importance of these two atmospheric transport pathways for PFOA is difficult to quantify because of controversy surrounding the correct value of the acid dissociation constant<sup>7-8</sup>. If the pKa of PFOA is 3.8, as stated by Ellis et al.<sup>7</sup>, then atmospheric transport of directly released PFOA will be important because neutral PFOA will be more prevalent in the gas phase, whereas if the pKa is around zero, as argued by Goss et al.<sup>8</sup>, then atmospheric transport of directly released PFOA will be relatively less important because the predominantly ionized PFOA will be rapidly deposited and not revolatilised.<sup>6</sup>

McLachlan et al.<sup>9</sup> measured PFOA in major European rivers and determined that most rivers were not affected by direct manufacturing sources. In the one case where a fluoropolymer manufacturing plant was

located on a river, the River Po, it was clear that this was the major source of PFOA. Indeed McLachlan et al.<sup>9</sup> estimated that the River Po discharge accounted for the majority of riverine flux of PFOA in Europe. Rivers to which there are no direct manufacturing discharges have been shown to contain PFOA (<0.65–23 ng/L)<sup>9</sup> and this raises the question: what are the sources of PFOA in these rivers? The answer is likely to be a combination of wastewater input from municipal and industrial sources as well as runoff.<sup>10</sup> In some regions these two sources can be separated, but in many others runoff is collected and directed through wastewater treatment plants. Recent Japanese studies<sup>10–13</sup> concluded that loadings of PFOA from runoff to rivers were greater than or equal to the loadings from wastewater treatment plants. PFOA present in street dust from urban sources<sup>12</sup> may contribute an additional loading to runoff. Muakami et al.<sup>13</sup> showed that PFOA concentrations were significantly higher in surface runoff than in rainfall, suggesting that PFOA in urban runoff is partially derived from dust deposited on impervious surfaces. Clara et al.<sup>14</sup> analysed PFCAs in wastewaters of municipal and industrial effluents. PFOA was found in nearly equal concentrations in municipal and industrial wastewaters (10–220 ng/L and 1.4–76 ng/L in municipal and industrial wastewater, respectively). The origin of PFOA in municipal wastewaters is unknown but may be from residual PFOA in fluorinated polymeric products still used in household products as stain repellents and waterproof and greaseproof paper coatings. Maybe surprisingly, effluents from the textile and paper industries did not contain especially elevated levels of PFOA. Even rivers and lakes that do not have wastewater inputs will be contaminated with PFOA from

runoff because they are present in precipitation (e.g. PFOA has been detected in North American precipitation at 0.6–89 ng/L)<sup>15</sup> at similar concentrations to those observed in rivers. The ultimate source of PFCAs in precipitation is still uncertain; it could either be from direct manufacturing sources, precursor degradation or a combination of both (see discussion above).

In conclusion, the major source of PFOA to the world oceans is thought to be historically released PFOA, primarily from the manufacture of fluoropolymers such as PTFE. Freshwaters which do not contain direct manufacturing sources will be affected by PFOA-laden municipal and industrial wastewaters and from PFOA-laden runoff. Inland environments (inland lakes, remote streams, soils, the High Arctic) will be primarily affected by atmospheric deposition, but the ultimate origin of the PFOA in the deposition is uncertain; it could be from direct (manufacturing) or indirect (precursor) sources. Research is still needed to properly quantify the relative importance of the different sources/transport pathways. Key chemical markers such as linear and branched isotopes of PFOA and other chain length PFCAs, may help solve the puzzle because the isomer signature and/or PFCA profile have the potential to indicate the manufacturing process (e.g. Electrochemical Fluorination up to 30% branched isomers of PFOA or Telomerisation – 100% linear isomers) and transport pathway<sup>16</sup>. Much of the work to date on source derivation has focused on PFOA and it would be useful to make more accurate source inventories for PFOS and the longer chain PFCAs.

## REFERENCES

- [1] Prevedouros, K., Cousins, I.T., Buck, R.C., Korzeniowski, S.H. (2006) *Sources, fate and transport of perfluorocarboxylates*. Environ. Sci. Technol., 40: 32-44.
- [2] Wallington, T.J., Hurley, M.D., Xia, J., Wuebbles, D.J., Sillman, S., Penner, J.E., Ellis, D.A., Martin, J., Mabury, S.A., Nielsen, O.J., Andersen, M.P.S. (2006) *Formation of C7F15COOH (PFOA) and other perfluorocarboxylic acids during the atmospheric oxidation of 8 : 2 fluorotelomer alcohol*. Environ. Sci. Technol., 40, 924-930.
- [3] Armitage, J., Cousins, I.T., Buck, R.C., Prevedouros, K., Russell, M.H., Macleod, M., Korzeniowski, S.H. (2006) *Modeling Global-Scale Fate and Transport of Perfluorooctanoate Emitted from Direct Sources*. Environ. Sci. Technol., 40, 6969-6975.
- [4] Stock, N.L., Furdui, V.I., Muir, D.C.G., Mabury, S.A. (2007) *Perfluoroalkyl contaminants in the Canadian Arctic: evidence of atmospheric transport and local contamination*. Environ. Sci. Technol., 41: 3529-3536.
- [5] Young, C.J., Furdui, V.I., Franklin, J., Koerner, R.M., Muir, D.C.G., Mabury, S.A. (2007) *Perfluorinated acids in arctic snow: new evidence for atmospheric formation*. Environ. Sci. Technol., 41: 3455-3461.
- [6] Armitage, J.M., MacLeod, M., Cousins, I.T. (2008) *Modeling the global fate and transport of PFO(A) emitted from direct sources using a two-dimensional multi-species model*. Environ. Sci. Technol. (submitted).
- [7] Ellis, D., Li, H., McMurdo, C., Webster, E. (2008) *An Experimental pKa determination for perfluorooctanoic acid (PFOA) and the potential impact of pKa concentration dependence on laboratory-measured partitioning phenomena and environmental modeling*. Environ. Sci. Technol., in press.
- [8] Goss K.-U. (2007) *The pKa values of PFOA and other highly fluorinated carboxylic acids*. Environ. Sci. Technol., 42: 456-458.
- [9] McLachlan, M.S., Holmström, K.E., Reth, M., Berger, U. (2007) *Riverine discharge of perfluorinated carboxylates from the European continent*. Environ. Sci. Technol., 41, 7260-7265.
- [10] Murakami, M., Imamura, E., Shinohara, H., Kiri, K., Muramatsu, Y., Harada, A., Takada, H., (2008) *Occurrence and sources of perfluorinated surfactants in rivers in Japan*. Environ. Sci. Technol.. Article ASAP doi:10.1021/es800353f.
- [11] Zushi, Y., Takeda, T., Masunaga, S. (2008) *Existence of nonpoint source of perfluorinated compounds and their loads in the Tsurumi River basin, Japan*. Chemosphere, 71, 1566-1573.
- [12] Murakami, M., Takada, H. (2008) *Perfluorinated surfactants (PFSs) in size-fractionated street dust in Tokyo*. Chemosphere, In Press, Corrected Proof, Available online 5 September 2008.
- [13] Murakami, M., Shinohara, H., Takada, H. (2008) *Evaluation of wastewater and street runoff as sources of perfluorinated surfactants (PFSs)* Chemosphere, in press.
- [14] Clara, M., Scheffknecht, C., Scharf, S., Weiss, S., Gans, O. (2008) *Emissions of perfluorinated alkylated substances (PFAS) from point sources - Identification of relevant branches*. Water Sci. Technol., 58, 59-66.

#### REFERENCES SUITE

- [15] Scott, B.F., Spencer, C., Mabury, S.A., Muir, D.C.G. (2006) Poly and perfluorinated carboxylates in North American precipitation. *Environ. Sci. Technol.*, 40: 7167-7174.
- [16] De Silva, A.O. (2008) Perfluorocarboxylate isomer analysis as a tool for source elucidation. Ph.D. thesis, Department of Chemistry, University of Toronto, Canada.

#### REVIEWED BY:

**Ian COUSINS**

Department of Applied Environmental Science (ITM), Stockholm University, Frescativägen 50, SE 106 91 Stockholm, Sweden  
ian.cousins@itm.su.se

## **Determination of the solid–water distribution ( $K_d$ ) coefficient for pharmaceuticals, oestrogens and musk fragrance in digested sludge**

The sorption properties of organic compounds affect their fate and their impact in the environment are one of the parameters controlling their removal in sewage treatment plants.

Determination of the affinity of a given molecule to solids is based on its octanol-water partitioning coefficient ( $K_{ow}$ ) and its organic carbon-based coefficient ( $K_{oc}$ ). For pharmaceutical and personal care products (PPCPs), however, recent studies show a deviation from the available  $K_{ow}$  and  $K_{oc}$ , explained by the fact that pharmaceuticals often contain polar functional groups which might interact only with special parts of organic matter or with minerals.  $K_{ow}$  and  $K_{oc}$  appear to be inappropriate to simulate their sorption properties in sludge samples.

Recent developments of the analytical methodology for measuring PPCPs in the sludge allowed the determination of the sorbed quantities.  $K_d$  and  $K_{oc}$  values in primary and secondary sludge have been reported, but no data related to digested sludge could be found. An important fraction of these compounds is eliminated during sludge anaerobic digestion; therefore, having accurate  $K_d$  values in digested sludge would avoid the expensive and time-consuming analysis in the sludge phase. The  $K_d$  values in digested sludge might not be similar to those obtained for primary and secondary sludge as the digested sludge characteristics are different in terms of composition, structure and morphology and as they could be modified during anaerobic digestion (T an pH change) as well as by the pre-treatment methods (alkaline, thermal and oxidative) applied during advanced treatment of sewage sludge.

In order to supply a feasible tool to evaluate PPCPs' fate during sludge treatment, the authors determined  $K_d$  and  $K_{oc}$  for selected molecules in digested sludge.

$K_d$  and  $K_{oc}$  values of Galaxolide (HHCB), tonalide (AHTN), carbamazepine, ibuprofen, naproxen, diclofenac, iopromide, sulfamethoxazole, roxithromycin, estrone (E1),  $14\beta$ -estradiol (E2) and  $17\alpha$ -ethinylestradiol (EE2) were obtained by measuring the concentration of the compounds in the aqueous and solid phase of the effluent of an anaerobic digestion pilot plant run in several operational conditions.

The values obtained in this study are in the same range as those previously published for primary and secondary sludge, but they are significantly higher than those estimated from simple  $K_{ow}$  approaches. The hypothesis is that these approaches describe hydrophobic interactions but fail to predict sorption of polar and ionic compounds. The modelled  $K_{oc}$  were close to or within the lower range of the experimentally determined  $K_{oc}$  for most compounds.

Deviations were observed for iopromide, sulfamethoxazole and roxithromycin, for which the modelled  $K_{oc}$  were 1-3 orders of magnitude lower than the measured ones.

Sorption on digested sludge is a relevant process for musk fragrance and oestrogens; they are 80-99% sorbed on particles, due to elevated total suspended solids concentrations of digested sludge. For pharmaceutical compounds, sorption is of minor importance. No significant influence of the anaerobic digestion operational conditions was observed, contrary to expectations.

#### SOURCE:

Carballa M., et al. 2008. *Determination of the solid-water distribution coefficient ( $K_d$ ) for pharmaceuticals, oestrogens and musk fragrances in digested sludge*. *Water Research*, 42 (1-2): 287-295

#### REVIEWED BY:

**Laurence AMALRIC**

BRGM, France  
l.amalric@brgm.fr

## **Chemical and toxicological assessment of organic contaminants in surface water using passive samplers**

Over the last decade or so, there has been a large increase in publications in the literature on SPMDs.

This paper provides a detailed example of the deployment of two types of passive sampler, SPMD and POCIS, in different watersheds. The extracts from the passive samplers are also examined for toxicity using Microtox and for oestrogenic activity via the YES assay. The level of technical detail in the paper (especially the references to the quality assurance procedures necessary when using these devices) is particularly valuable.

Reference is made to the theory and modelling for deriving water concentrations from the results obtained by each type of device. It was found that the POCIS devices do not lend themselves easily to the incorporation of performance reference compounds – an area for further research, undoubtedly.

Having stressed the importance of a rigorous quality control programme when using passive sampling devices, it was disappointing to find that one set of abnormal results for five compounds was probably due to the wrong amount of solution being added to the SPMD! Perhaps it would have been better if this part of the experiment had been repeated, as a check. In a similar fashion, a very high field blank for one of

the YES assays was reported, but not resolved.

A tentative attempt was made to provide estimated aqueous concentrations, with the warning that these were not definitive values. This highlights the difficulty in deriving such values from passive sampling data. Nonetheless, it would have been useful if spot sampling data (historical values) had been available for comparison purposes, as some of the derived values were at levels measurable in normal spot samples.

A key part of this paper is the linking of the chemical analysis results to the Microtox and YES assays. The results reported here were all negative, for the samples analysed did not contain chemicals at levels high enough to elicit acute toxicity or oestrogenic responses. It was noted that the POCIS matrix blanks had a high background response – ascribed to residual chemicals from the PES membrane. Nailing this one is another area for further research.

In conclusion, this paper provides a high level of technical detail for the deployment of both SPMD and POCIS devices in the field. The extensive list of references also provides the researcher with a good base for acquiring even more detail on the construction and use of passive samplers.

### **SOURCE:**

Alvarez D. A., Cranor W. L., Perkins S. D., Clark R. C. and Smith S. B. *Chemical and toxicologic assessment of organic contaminants in surface water using passive samplers*. *Journal of Environmental Quality*, 37 (3): 1024-1033

### **REVIEWED BY:**

**Ian FOX**  
UK Environment Agency  
ian.fox@environment-agency.gov.uk

## **Tenax extraction as a tool to evaluate the availability of poly-brominated diphenyl ethers, DDT, and DDT metabolites in sediments**

It is increasingly documented that not all of a chemical present in the environment is available for uptake or transformation by biota. In this respect, a distinction is often made between the bioaccessible and bioavailable fractions, with bioavailable material being defined as freely available to cross an organism's cellular membrane from the medium the organism inhabits at a given time, whilst bioaccessible material is "that which is available to cross an organism's cellular membrane from the environment, if the organism has access to the chemical". The bioavailable fraction of a chemical is known to decrease with increasing contact times, and much effort is currently put into developing biomimetic tools to quantify bioavailable and bioaccessible fractions. Depletive extractions of soils and sediments in which the che-

mical activity in the water phase is reduced virtually to zero, thus creating a strong driving force for desorption of (aged) organic contaminants from the solid phase and subsequent transport to the added solid phase, are among the options exploited. Following up on previous research reports, La Cal et al. exploited the use of solid phase extraction with Tenax beans to desorb hydrophobic pollutants from sediments. In general, typical desorption curves are obtained following solid phase extraction of spiked and subsequently aged (12 days) sediments, in which three fractions may be distinguished: a fast, a slow and a very slow fraction. The rapidly desorbing fraction has been shown to correlate with the fraction that an organism can take up or degrade from sediment. The data reported by La Cal et al. confirm previous studies on

desorption of organic contaminants with Tenax. In line with literature reports for other classes of chemicals (such as PAHs and PCBs), it was found that the quickly desorbing fraction is inversely proportional to the hydrophobicity of the chemical. This may in part be explained by slow diffusion kinetics of the more hydrophobic PolyBrominated Diphenyl Ether (PBDE) congeners with higher molecular weight. This correlation has not often been reported before for field-contaminated sediments, as it is hidden by the differences in aging and concentration among pollutants.

La Cal et al. recommend that for a proper assessment of the bioavailability of hydrophobic contaminants such as PBDEs, the whole desorption curve is preferably determined, or at least extraction should be continued until the slow desorbing fraction is reached. This may take several weeks or even months. For pragmatic reasons, la Cal et al. pro-

pose to limit the determinations to the fraction desorbed after 24 h. As the variance in chemical concentrations thus obtained is quite high, and given the nature of the desorption curves, 48 h. of desorption might provide more robust results.

In conclusion, this study nicely shows how physical availability of a released contaminant can be much lower than its total concentration even after a short contact time. Tenax extraction can be used to measure the easily desorbing fraction, providing an improvement over the simple total extraction techniques. When possible, a long contact time between Tenax and the matrix of interest is recommended, but for pragmatic reasons this contact time may be reduced to 1 or 2 days. Bioavailability of hydrophobic organics is inversely proportional to their hydrophobicity (or molecular weight), a factor that needs to be taken into account when assessing potential or actual risks.

#### SOURCE:

Agustina de la Cal, Ethel Eljarrat, Tim Grotenhuis, Damià Barceló. *Tenax (R) extraction as a tool to evaluate the availability of polybrominated diphenyl ethers, DDT, and DDT metabolites in sediments*. Environmental Toxicology and Chemistry, 27, 1250-1256, 2008

#### REVIEWED BY:

**Willie PEIJNENBURG**

RIVM - The Netherlands National Institute for Public Health and the Environment  
WJGM.Peijnenburg@rivm.nl

## **Influence of the coexisting contaminants on bisphenol A sorption and desorption in soil**

The alkylphenolic compound bisphenol A (BPA) is the principal monomer in the production of polycarbonates, epoxy resins, and other plastics. BPA is an anti-oxidant that is non-biodegradable and highly resistant to chemical degradation. In view of its large production volume and hydrophobicity, BPA is expected to adsorb strongly to solid phases in the environment and sorption and desorption are the key factors determining the fate of BPA in the environment. Previous studies have shown that the presence of metals and other organic contaminants may affect the (de)sorption characteristics of BPA. This prompted a (semi-mechanistic) study of the interactions of the metals Pb and Cd and two surfactants on BPA sorption and desorption. The effect of ionic strength was then investigated. This was done by determining sorption isotherms, by sorption column experiments and by flow-through desorption experiments in a column.

All additives were shown to increase BPA sorption. It is speculated by Li et al. that the effect of Pb and Cd is due to aggregation and flocculation of humus in the soil used, thus creating additional soil sorption sites for BPA.

In general, two effects can be expected following addition of (cationic) surfactants:

- 1 – Increase in the apparent water solubility of BPA, or increase in the affinity of BPA for the solution and decrease in BPA sorption to soil.

- 2 – Creation of new phases in the soil-water system with which organic contaminants may become associated: sorption of the monomer of the surfactant to the soil, thus increasing the affinity of BPA for the soil.

Cationic surfactants as used in this study are favourably sorbed to the solid soil matrix; the second mechanism is therefore dominant over the first one and a net increase of sorption of BPA was found upon addition of cationic surfactants.

Ionic strength was found to increase adsorption of BPA, most likely due to a decrease in solubility of BPA upon increasing ionic strength, or to a reduction in the pH of the suspension due to the release of organic matter at high ionic strength.

Desorption of BPA was increased following addition of surfactants. According to Li et al., this is due to increased solubility of BPA and a change of surface tension in the presence of surfactants.

The study of Li et al. nicely shows that, when studying the fate and transport of BPA and other phenolic endocrine disrupting chemicals, it is important to integrate the (site-specific) presence of other contaminants, whilst taking note of the nature of these compounds.

#### SOURCE:

Jinhua Li, Baoxue Zhou, Yangqiao Lui, Qingfen Yang, Weiming Cai. *Influence of the coexisting contaminants on bisphenol A sorption and desorption in soil*. Journal of Hazardous Materials, 51, 389-393, 2008

#### REVIEWED BY:

**Willie PEIJNENBURG**

RIVM - The Netherlands National Institute for Public Health and the Environment  
WJGM.Peijnenburg@rivm.nl

## PERFOOD

### Perfluorinated Organics in Our Diet

**Co-ordinator Prof. Dr. Pim de Voogt**

Institute for Biodiversity and Ecosystem Dynamics  
W.P.deVoogt@uva.nl

The PERFOOD project is likely to be funded for three years by the Food, Agriculture and Fisheries Programme of FP7, and it will start early 2009 under the coordination of Dr Pim de Voogt of the University of Amsterdam.

The PERFOOD project, or PERFluorinated Organics in Our Diet, aims to assess the contributions from food, drinks and drinking water to the daily intake of per- and polyfluorinated organic compounds by the European population, as well as identify the sources of these chemicals in our diet.

PFCs are generally persistent in the environment, and can be found over a broad concentration range and within most parts of the aquatic and terrestrial ecosystems. Food, produced with natural ingredients, and possibly beverages, including drinking water, are likely to be contaminated with PFCs, giving rise to human exposure. Whether or not industrial food processing and packaging may give rise to additional contamination of food and beverages is currently not understood. Whatever the sources, PFCs have indeed been found to be present at a global scale in blood of the general population.

Anthropogenic perfluorinated compounds (PFCs) have recently gained socio-economic and scientific interest. PFCs constitute a newly

emerging group of environmental contaminants, with physico-chemical as well as toxicological properties different from those of other halogenated compounds. Their properties have led to a plethora of successful applications, ranging from dirt and water proofing of furniture, carpets, shoes and clothing, fire fighting foams, lining of food and beverage packaging materials, to electrical print boards, and so on.

PERFOOD brings together the institutes most renowned in Europe and the Globe for their chemical analytical work on PFCs with experts in food consumption and drinking water quality as well as food processing and packaging. The aims of the present project are to develop robust and reliable analytical tools including reference materials for the determination of PFCs in food items, and to use these to (i) qualify and quantify PFCs in our diet, employing a large European sampling campaign; (ii) understand how PFCs are transferred from the environment into dietary items, and (iii) quantify the possible contribution of food/beverage contact materials and food and water processing to the overall PFC levels in our diet. The newly gained knowledge will enable us to evaluate the possible routes, including their relative importance, of human exposure to PFCs via our diet, to assess the role of the technosphere in the contamination of our food, and to identify ways to reduce the PFC contamination of dietary articles.

#### SOURCE:

Webmaster IBED

<http://www.science.uva.nl/ibed/object.cfm/09A93B6A-1321-BoBE-68210EB7AA8D40DB>

## AquaNano

### Transfer and fate of engineered nanoparticles in groundwater

**Co-ordinator H el ene Pauwels**

BRGM – Water Division  
<http://www.ineris.fr/aquanano/>  
h.pauwels@brgm.fr

The increasing use of engineered nanoparticles for industrial and household purposes will inevitably lead to their introduction into different compartments of our environment. Release to the environment may originate from manufacturing facilities, wastewater treatment plants or accidents during transport. It may also have a non-point source origin such as wear from nanoparticle-bearing materials. Whatever the release process, the nanoparticles will finally reach soils or water. Additionally, nanoparticles may also be deliberately introduced to soils or water as a reagent for remediation processes.

Further to transport through soil, groundwater appears to be one of the potential, though not ultimate, receptors. Groundwater is currently largely used as a drinking water resource, and supports groundwater-dependent terrestrial ecosystems as well as surface waters (rivers, lakes). Assessing the risk of groundwater contamination by nanoparticles is hence of the utmost importance, but there is a current lack of knowledge regarding their mobility and reactivity in waters. The mobility and fate of nanoparticles depend on various processes such as coagulation, adsorption, flocculation, dissolution and diffusion, which



in turn depend on the properties of the nanoparticles, the composition of the groundwater and the hydrodynamic conditions. The AquaNano project, funded by the French Agency for Research (ANR), aims to identify the processes involved in the transfer of a selection of engineered particles in groundwater. Nanoparticles being studied include organic (C60) as well as inorganic (CeO<sub>2</sub>, TiO<sub>2</sub>, ZnO) compounds.

The AquaNano consortium consists of four partners with scientific and technical expertise in areas relevant to groundwater protection and/or nanoparticle mobility:

- BRGM – Orléans (France)
- CEREGE- Centre Européen de Recherche et Enseignement des Géosciences de l'Environnement – Aix-en Provence (France)
- INERIS – Institut National de l'Environnement et des Risques – Verneuil en Halatte (France)
- SUEZ-ENVIRONNEMENT – Le Pecq (France)

The approach developed by AquaNano will move from laboratory experiments towards field studies, paying particular attention to the representativeness of experimental conditions. The work focuses on natural waters, which requires the implementation of specific and sophisticated analytical procedures for identifying and quantifying nanoparticles. As far as inorganic nanoparticles are concerned, the natural background levels of both particles and chemical elements which may be significant are taken into account. Experiments on nanoparticle dispersion and ageing are being conducted in waters with a composition similar to that of major European groundwaters. Experiments on particle transport will be conducted at the laboratory, pilot and field scale, allowing both chemical and hydrodynamic aspects to be taken into account. Transport of a few centimetres will be investigated in laboratory conditions. These experiments will involve a wide variety of nanoparticles and will support the selection of nanoparticles for subsequent large-scale experiments: a) pilot-scale experiment for a 3D investigation of the transfer (1 m x 20 cm x 30 cm) in porous media; b) artificial tracer test between an injection site and a pumping well over 10 to 20 m in a fissured aquifer.

## MEDIFLUX

### Modelling pharmaceutical fluxes in hospital sewers

**Co-ordinator Jean-Ulrich MULLOT**

Laboratoire Santé Publique – Environnement. Université Paris Sud 11, Faculté de Pharmacie de Chatenay-Malabry, France  
jumullot@aol.com

Thanks to improvements in analytical capabilities, the presence of pharmaceutical residues in environmental aquatic compartments has become an environmental and public health concern. These products have been detected in wastewaters and/or surface waters at concentrations varying from nanograms to several hundreds of micrograms per litre and it is essential to carry out assessments of environmental and health risks associated with these complex organic pollutants in water resources. It appears unrealistic and inefficient to perform thousands of costly chromatographic analyses to identify and quantify all these compounds. A better approach is to model the behaviour of selected main drug classes in aquatic compartments from the source of pollution to the point of use. In this context, the French “MEDIFLUX programme” was launched to develop a model for the prediction of pharmaceutical loads in hospital wastewater: we planned to compare concentrations of selected pharmaceuticals in hospital sewages to the related estimated concentrations from consumption and pharma-

cokinetics data. It has been decided to focus on hospital wastewater for several complementary reasons:

- hospitals are considered as a major source or “hot spots” for this type of pollution. However, this assumption is not based on objective figures of loads;
- the relative lack of knowledge about pharmaceutical loads in hospital wastewater compared to the huge number of molecules that are administered daily;
- lastly, the knowledge of this hospital pollution could lead to the proposal of pollution prevention strategies at source, such as specific wastewater treatment, separated collection and treatment of urine etc.



To answer these different questions, the MEDIFLUX project has been structured around four consecutive steps.

The first step is the selection of representative target molecules, as it is inconceivable to quantify all the molecules administered in hospitals, but measurements are necessary to calibrate the proposed model. Thus, it was necessary to prioritise and choose target molecules that had been included in the modelling exercise and routinely measured during the project. As far as possible, these molecules should be representative of the wide range of pharmaceuticals administered in hospitals, but should also be the most potentially hazardous for human health if they were to be released in environment. Prioritisation strategies reported in the scientific literature for pharmaceuticals in aquatic environments were reviewed beforehand, to inform the choice of strategy for our study. Finally, 14 target molecules covering 8 pharmaceutical classes were selected according to a scoring method especially developed for and by this project.

The second step is the determination of sampling sites, sampling strategy and data that should be collected during the sampling campaigns to develop the model. Sampling sites have to be representative of all hospital departments and also correspond to the total hospital loads in the public sewer system. Sampling strategy must be adapted to the fugitive nature of pharmaceutical emissions in the sewers. Several variation factors exist and have to be taken into account: day vs. night, week-day vs. Sunday, summer vs. winter etc. Lastly, it is necessary to collect water and pharmaceuticals consumption data during sampling campaigns, which requires close collaboration with hospital teams, even if we try to ease the burden by using existing data when possible. To solve these problems we have developed a specific strategy based on a refrigerated automatic sampling device to obtain 24-hour flow-weighted composite samples.

The third step was to develop and validate specific analytical methods. Identification and accurate quantification of pharmaceutical traces in hospital effluents still remains a challenge because of matrix effects that impair quantification methodology. Most of the pharmaceuticals – or their metabolites – studied present a high polarity and extraction from samples is obtained using SPE cartridges. Analyses are carried out using GC/MS/MS or LC/MS/MS or LC/fluorimetry and matrix effects are controlled in two ways: internal standards (isotopic equivalents of target molecules, if existing) or standard additions method. Validation of methods was carried out in accordance with Commission Decision 96/23/EC.



The fourth step consists of the running of sampling campaigns in accordance with the previously defined sampling strategy. In parallel, predicted concentrations are calculated from collected data using EMEA requirements (EMEA/CHMP/4447/00). Then measured and predicted values will be compared to calibrate and test the validity of the models.

The MEDIFLUX project is run by one academic laboratory (Public Health Environment Laboratory, Faculty of Pharmacy, Université Paris Sud 11) and one analytical laboratory from the French defence medical service with technical and financial support of partners: one private wastewater services company (Suez Environnement), a public authority for wastewater management (SIAAP), a public water basin committee (Agence de l'Eau Seine Normandie), one semi-public company devoted to drinking water supply (Eau de Paris) and three hospitals.

At this time, the first two steps have been completed and definitive results should be available during 2009. Analytical methods have been developed, adapted or implemented for ten pharmaceuticals (5-fluorouracil, cyclophosphamide, ifosfamide, atenolol, sulfamethoxazole, iomeprol, iobitridol, ciprofloxacin, propofol and ketoprofen) and further analytical developments are still ongoing for the remaining molecules. Sampling campaigns began during 2008 and analytical results for the ten products specified above have been obtained. These measured concentrations have been compared to the predicted ones and appeared to confirm the effectiveness of the model.

## **KNAPPE**

### **“Knowledge and Need Assessment on Pharmaceutical Products in Environmental Waters” – Final results**

#### **Co-ordinator Benoit ROIG**

Centre for Industrial Environmental Research, Ecole des Mines d'Alès, France  
benoit.roig@ema.fr

Author of this contribution: Sebastian ZABCZYNSKI Sebastian.Zabczynski@polsl.pl  
Silesian University of Technology - Environmental Biotechnology Department

#### **INTRODUCTION**

The project entitled “Knowledge and Need Assessment on Pharmaceutical Products in Environmental Waters” (KNAPPE), contract n° 036864, was funded under the 6th Framework Programme — Priority 6.3 “Global Change and Ecosystems”.

KNAPPE aimed to carry out a review of the state of knowledge and put emphasis on questions deserving attention by pulling together results of previous and ongoing EU projects and published data from both governmental sources and scientific literature, by involving manufacturers in supplying data on production and use of pharmaceutical pro-

ducts (PPs). These topics of concern included occurrence, detection, fate, behaviour, removal treatments, known environmental and health impacts of these molecules and stewardship approaches. On the basis of these data, the final objective of the project was to identify the relevant priority actions to be taken in the framework of sustainable development, more particularly in terms of reducing the presence, impacts and risk of PPs in the environment (DOW Knappe).

The Knappe project was divided into seven workpackages:

- WP0 – Management and coordination
- WP1 – Occurrence of PPs in the aquatic environment: towards indicators for contamination with pharmaceuticals
- WP2 – Assessment of limits of the current water treatment processes: towards best practices for lowering PPs contamination in the aquatic environment
- WP3 – Develop cornerstones of an EU prevention action
- WP4 – Health and environment impacts/effects of PPs
- WP5 – Eco-Pharmacostewardship and vigilance
- WP6 – Communication, results dissemination and proposition of priority actions.

In this presentation, the main achievements within WP2 “Assessment of limits of the current water treatment processes: towards best practices for lowering PPs contamination in the aquatic environment” will be shown. WP2 underlined the elimination efficiency of conventional treatment processes used in sewage treatment plants and in drinking water production. Additionally, this WP collected data on new processes in development and their combination with existing processes.

#### **REPORT OF THE LIMITATIONS OF CONVENTIONAL TREATMENT PROCESSES FOR THE MOST RESISTANT PPS AND NEW DEVELOPMENTS**

One of the major objectives of WP2 was the comparison of the wastewater and drinking water treatment technologies in regard to pharmaceutical products removal.

Sewage treatment plant (STP) characteristics were taken into account – including reactor configuration, sludge retention time (SRT), hydraulic retention time (HRT), temperature (or sampling season), red-ox conditions, influent and effluent concentration of particular PPs. The data regarding drinking water treatment technologies were collected with emphasis on the process description – including reagent combination (e.g. O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>), reactor volume, molar ratio of oxidants (or irradiation in case of UV), medium (e.g. Milli-Q water, environmental waters), reagent dose, reaction time, pH, temperature.

All pharmaceutical compounds found in the literature were divided into therapeutic groups: antibiotics, anticonvulsants, anti-inflammatories (analgesic),  $\beta$ -blockers, hormones, tranquilizers, X-ray contrast media and lipid regulators.

#### **Wastewater treatment**

##### **Reactor configuration**

In order to compare the efficiencies of various WWTP configurations in removing the reported compounds, the following typical treatments were examined: CASP – Conventional Activated Sludge Processes (N, C, P removal), CASP-C – Conventional Activated Sludge Processes with carbon removal only, SBR – Sequencing Batch Reactor, MBR – Membrane Biological Reactor.

Generally, for CASP and MBR, in some cases only, a slight impact of the reactor configuration could be observed (e.g. for contrast media). The elimination of PPs therefore depends rather on parameters such as SRT, HRT, flow rate etc., as will be shown in the next chapters. Reactor configuration has no impact on the removal of some compounds, which are characterised by: low or no removal (e.g. anticonvulsants), very high removal (e.g. majority of hormones).

##### **Sludge retention time (SRT)**

Sludge retention time (SRT) is defined as the average retention time of sludge flocs before they are removed as excess sludge or lost through the effluent. SRT is a crucial parameter in wastewater treatment, and determines the biodiversity of the sludge, the amount of predominant bacteria in the active biomass and their enzymatic activity.

On the basis of the available literature data, it could be stated that a high removal rate is achieved for the majority of antibiotics and anti-inflammatories with an SRT typical of those used for nutrient removal (10–20 days). Across the range of SRTs, anticonvulsants revealed very low removal rates,  $\beta$ -blockers showed average removal rates and the majority of hormones were removed to a satisfactory level.

##### **Hydraulic retention time (HRT)**

Hydraulic retention time (HRT) can be defined as a measure of the average length of time that a soluble compound remains in a constructed bioreactor (Wikipedia). Like SRT, HRT is also a crucial parameter in wastewater treatment.

All studied compounds can be divided into two groups according to the influence of HRT on their removal rates. PPs with the optimum HRT, which results in the highest elimination rate (antibiotics – HRT < 12 hours; anti-inflammatories – HRT > 12 hours; lipid regulators – 12 < HRT < 25 hours) and groups of PPs where HRT has no impact on their removal rate (X-ray contrast media, anticonvulsants with very low or no removal; majority of hormones - very high removal). Generally, it could be concluded that the optimum range of hydraulic retention time for PP elimination during wastewater treatment would vary from 12 to 25 hours.

##### **Red-ox conditions**

No data regarding the influence of red-ox conditions on the removal of PPs could be found.

##### **Climatic zones**

No influence of climatic zones on the removal of PPs was observed. It is more likely that the removal rates of pharmaceutical compounds depends on their consumption pattern.

##### **Advanced technologies**

Advanced technologies were taken into account, including O<sub>3</sub>, MnO<sub>2</sub>, TiO<sub>2</sub>, TiO<sub>2</sub>/UV, ClO<sub>2</sub>. However, only a few records regarding advanced oxidation processes were found. The majority of substances are very susceptible to ozonation. The only exceptions are tranquilizers, with a reported removal below 40%.

##### **Drinking water treatment**

In most cases ozonation was the most efficient treatment technology. However, the efficiency depends on:

- reagent dose and combination with other oxidants (e.g. H<sub>2</sub>O<sub>2</sub>);
- pH – in most cases, with the exception of e.g. Carbamazepine;
- presence of OH radicals scavengers.

Granular activated carbon is the most effective in relation to compounds with high sorption efficiencies based on their hydrophobicity.

##### **Assessment of the concentrations of pharmaceuticals in sewage sludge**

The sewage sludge originates from the wastewater treatment processes and it can be described as the residue generated during the primary (physical and/or chemical), the secondary (biological) and the tertiary treatment. One of the significant processes in PP removal mechanisms, and directly linked with the treatment of sewage sludge, is sorption. Sorption is regarded as being composed of two distinct reactions: sorption from liquid to the solids and desorption. Sorption equilibrium is reached when the rate of both reactions is equal. A sorption or distribution coefficient (K<sub>d</sub>) is commonly used to describe this process. The K<sub>d</sub> value is the ratio of the sorbed phase concentration to the solution phase concentration at equilibrium. The coefficient is usually distinguished for primary sludge and secondary sludge. It is caused by dif-

ferent properties of the sludges – the composition and pH of the sludge seem to be crucial.

On the basis of the KNAPPE results, it can be concluded that the behaviour of the PPs in sewage sludge is the issue which calls for further investigation. In most cases there are some single records which give a very general overview of the sorption and desorption processes of PPs.

## REPORT OF NEW STRATEGIES TO MINIMISE PPS DISCHARGE

### Possibilities to improve the existing technologies

Current municipal sewage treatment plants are not able to guarantee a complete elimination of pharmaceutical products. Pre- or post-treatment, such as ozonation, activated carbon, UV light or nanofiltration are available solutions, but increase the costs. Moreover, especially in the case of AOPs (Advanced Oxidation Processes), there is a risk of introducing toxic by-products into the environment. That is why major improvements in existing wastewater treatment systems rely on modifications of chosen parameters. It has been proven that the removal efficiency varies with:

- sludge retention time (SRT)
- hydraulic retention time (HRT)
- reactor configuration.

Moreover, since sewer leakage varies from 5 to 25%, simply upgrading wastewater treatment may be insufficient. What is more, if sewer capacity is exceeded with stormwater overflow, there is an unexpected and uncontrolled discharge of PPs directly to the environmental waters.

Therefore, in order to improve the condition of the receiving water and prevent the introduction of PPs into the environment, STPs should be upgraded and removal efficiencies increased at the same time.

### Suggestion of different strategies for pharmaceutical products treatment

As mentioned above, municipal sewage treatment plants are not able to guarantee the complete elimination of pharmaceutical products. Additionally, simply upgrading wastewater treatment may also prove to be insufficient. That is why a wide range of protective actions should be implemented to reduce or minimize the introduction of pharmaceutical compounds into the environment.

#### *Source control*

Source control is one of the solutions to reduce the potential of emerging risks. It focuses mainly on the following modes of action:

- classification of pharmaceuticals,
- minimising the introduction of PPs to the environment,
- targeted therapy instead of prophylactic or empiric consumption of medicine,
- EU regulations.

#### *Source separation*

Source separation and treatment of concentrated waste streams at source may also play a major role as an additional activity to minimize the introduction of pharmaceutical compounds into the environment. This solution is, however, only applicable if:

- treatment before dilution in the sewage system is made more efficient,
- losses during transport in the sewerage system are eliminated.

## ACKNOWLEDGMENTS

The content of this paper was gathered primarily during the EU KNAPPE project “Knowledge and Need Assessment on Pharmaceutical Products in Environmental Waters”, contract n° 036864, which was funded under the 6th Framework Programme — Priority 6.3 “Global Change and Ecosystems”.

## REFERENCES

- [1] Buntner D., Żabczyński S., Miksch K. (2007) *Report of the limitations of conventional treatment processes of the most resistant pharmaceutical products and new development*. KNAPPE Project, Contract 036864.
- [2] Żabczyński S., Buntner D., Miksch K. (2008) *Report of new strategies to minimise PP discharge*. KNAPPE Project, Contract 036864.
- [3] Description of Work (DOW) KNAPPE Project: *Knowledge and Need Assessment on Pharmaceutical Products in Environmental Waters*. Contract 036864.

*The activities of the NORMAN project started officially on 1<sup>st</sup> September 2005, with a kick-off meeting in Paris on 7-8 September 2005. We are laying the foundations on which to build the services that will be provided by the network. The ultimate aim is to meet users' needs in the exchange and production of good-quality and comparable data in a field where data are typically scarce and insufficient for sound decision-making. Below is a summary of the activities carried out so far and forthcoming results. More information on each of these activities is provided on the project website ([www.norman-network.net](http://www.norman-network.net)).*

## Final meeting of the NORMAN project and Launch of the permanent network

The NORMAN project, which started its activities in September 2005 with the financial support of the European Commission (Contract N° 018486), held its final meeting in Paris (French Ministry of Ecology) on 20 October.

The first part of the meeting was dedicated to the presentation of the final results of the project.

The three **interlaboratory studies** (CASE 1 on the analysis of selected natural and synthetic oestrogens and oestrogenic activity in wastewater; CASE 2 on the analysis of non-steroidal anti-inflammatory drugs' residues in environmental samples; and CASE 3 on the analysis of brominated flame retardants in dust) were successfully concluded and the reports are available on the NORMAN website (see page >> QA/QC issues >> Programme of activities).

One of the main purposes of these interlaboratory studies was to test the requirements defined in the three modules that are part of the common scheme developed by the NORMAN network for validation of measurement methods. The feedback from the three interlaboratory studies was therefore used for the improvement of the initial draft of the document, the final version of which can now be downloaded from the NORMAN website (page QA/QC issues >> Validation framework).

It is worth remembering that the **NORMAN scheme for validation of measurement methods** has been developed within NORMAN by biological and chemical experts. It is suitable for the validation of methods for monitoring of pollutants (and/or their effects) in water, air, soil, sediment and biota and it is not restricted to emerging pollutants. Moreover, wherever possible, existing European and international standards and guidelines (e.g. on sampling, terminology, statistics, organisation and evaluation of interlabs/PTs, performance criteria, uncertainty evaluation) have been taken into account.

As regards the next steps for this protocol, negotiations are under way at CEN for its implementation in European Standardisation and a new work item proposal for a technical guidance document will be proposed to CEN TC 230 (Water Analysis). The work under "Mandate M424"

from DG ENTR to CEN will make use of the NORMAN validation protocols where possible. Moreover, reference to the NORMAN validation protocol is integrated in the Guidance Document on Surface Water Monitoring produced by the CMA (Chemical Monitoring Activity) under the co-ordination of DG ENV.

The **NORMAN databases** – EMPOMAP, EMPODAT and EMPOMASS – are accessible from the NORMAN website (page Databases) and will continue to be maintained and further populated with new information and data which will be produced by the members of new permanent network.

An important feature has recently been included in the EMPODAT database: a system that gives a score to the data contained in the database based on the level of the QA/QC information accompanying the data. The data can therefore be sorted into four categories ranging from "data adequately supported by quality-related information" down to "data not supported by quality-related information".

Four **workshops** were organised during the course of the project. All reports are published on the NORMAN website (page >> Workshops). We hope that, with these events, we have been able to improve the EU-wide exchange of information on emerging pollutants among scientists, practitioners and decision-makers responsible for the risk assessment and prioritisation of environmental pollutants.

As a result of the conclusions of these workshops and the other activities of the network, a **Research Agenda** was developed by the network with a list of recommendations for priority research areas to be included under the 7th Framework Programme of DG Research for 2010 and beyond. The NORMAN Research agenda can be downloaded from the NORMAN website at the page >> Workshops.

Further information about the results of the NORMAN project and the future actions that the permanent network will perform in the coming years can be found in the speakers' presentations at the Paris meeting (available on the NORMAN website – page >> Workshops >> Final meeting and Launch permanent network).

## NORMAN Joint Programme of Activities for 2009-2011

NORMAN is now establishing itself as a permanent, self-sustaining network of reference laboratories, research centres and related organisations for the monitoring and biomonitoring of emerging environmental substances.

It operates by organising a number of activities, including Expert Group meetings, Working Groups, workshops, databases and methods validation exercises.

Its Joint Programme of Activities for 2009–2011 was presented at the Launch meeting in Paris on 20 - 21 October 2008. The full text of the programme, which will start in January 2009, can be seen at <http://www.emerging-pollutants.org/public/workshops/paris.htm>

#### **(Extract of the JPA document developed by the network) - NORMAN JPA for 2009-2011**

##### **EUROPEAN PRIORITIES**

The need to look beyond the traditional / conventional target pollutants, when assessing the risks of chemicals to human health and to ecosystems, is now generally recognised as a priority issue in all policy areas at both the European level and the national level in the various European countries.

As part of the implementation of the European Environment and Health Strategy and its Action Plan (COM(2004)416) national competent authorities in the various countries give increasingly higher priority to the need to look at emerging substances and improve the current systems for identifying and addressing new risks to health as they emerge. In the water compartment, the Water Framework Directive plays a key role in the inclusion of emerging pollutants as future priority substances. The work on the revision of the first list of priority substances, which started in 2006 (and is still under way at the time of writing), and the negotiation around the Daughter Directive (EQS Directive), with the proposal from the European Parliament for the inclusion of 30 new substances (including various emerging pollutants) as priority substances, show on the one hand the constant pressure from the public for the inclusion of emerging substances as candidate priority substances, and, on the other hand, the importance of an efficient exchange of information about these substances (level of occurrence in the environment, fate and transport, effects, reliability and comparability of the data, etc. ) in order to facilitate the risk assessment and prioritisation process by the European Commission.

Member States are currently in the process of identifying the substances that are relevant at river basin level (i.e. pollutants which are likely to cause a large number of water bodies within the river basin district to fail the objective of 'good ecological status'). The identification of these substances in the various countries is a hot topic at the moment (with many implications, including economic ones).

Besides the WFD, other programmes (e.g. OSPAR for the marine environment) are identifying new candidate emerging substances and regularly reviewing their priority lists as scientific knowledge advances. Overall the main challenge is to implement tools and approaches to identify the likely causes of ecological impairment (i.e. impact at the level of populations and ecosystems) and in particular, to establish links between chemical and ecological status. A better understanding of these causal links and the implementation of early warning systems is the only way to apply effective corrective measures and predict potential impacts, thereby avoiding a waste of resources.

As regards the air compartment and in particular indoor air, research was focused on lead, asbestos and radon initially (in the 70s and 80s) and on volatile organic compounds (VOCs) in the 1990s. In the past few years, research has been focused on semi-volatile organic compounds (SVOCs), heavier compounds that can be measured both in the indoor air and in house dust. They include many types of compounds from a variety of indoor sources (insecticides, flame retardants, plasticisers...). Interest in the measurement of these compounds indoors is growing, since they are often detected in homes, they are persistent, their metabolites are measured in human blood and urine, and toxicology and epidemiology tend to prove that some of them may be toxic to the human reproductive system and human development. They are therefore considered as indoor emerging substances.

Chemicals are beyond any doubt one of the main stressors threatening the soil ecosystem. A proposal for a Soil Directive received insufficient support at first. But now preparations are underway for a modified proposal in which soil quality will be an important issue.

The new legislation on chemicals in Europe, REACH, requires producers and users of chemicals to show that their products are safe for human health and the environment. This requires, amongst others, that all information on chemicals should be made available and that a thorough risk assessment should be carried out according to the basic philosophy of REACH.

##### **OBJECTIVES OF THE NORMAN JPA FOR 2009-2011**

The NORMAN network is designed to meet the challenges now posed by emerging substances. It will operate via the organisation of a number of activities, including expert group meetings, workshops, databases and methods validation exercises.

The objectives in this Joint Programme of Activities reflect the current priorities at the European and MS level.

*Our goal for 2009-2011* is to stimulate the discussion and build a more structured common approach for the identification of 'emerging' compounds and risk assessment of emerging substances, including all aspects related to the use of chemical and biological integrated approaches for the identification of 'relevant pollutants'. Today we still lack the capacity to capture those substances, which are really emerging in a European context and to distinguish them from those 'believed' to be emerging.

The selection of the proposed actions is made with the following criteria in mind:

- there is a need to keep the public authorities clearly informed about the state of progress of the research activity (i.e. what we have achieved and what more we can expect to achieve). This will entail bringing together experts to arrive to a common understanding on identified topics.
- there are synergies to be derived from a co-operative effort (e.g. interlaboratory studies on 'difficult matrices' where it would be asking too much of a single country and there is a need for international co-operation among laboratories).
- a topic is identified as emerging and Working Groups need to be set up at the earliest moment.

In the light of those considerations and the identified policy needs, we have set the following priorities for this 2009-2011 JPA.

##### **ACTIONS**

1. Provide a system for prioritisation to identify which substances deserve higher priority for further investigations based on agreed criteria, such as their (eco)toxicity, persistence, bioaccumulation, spatial and temporal distribution, occurrence levels, use, etc.

A Working Group on '**Prioritisation of emerging substances**' will be organised for the development of a set of criteria allowing for prioritisation of emerging substances and their allocation to clearly pre-defined categories (e.g. substances for which info is not yet sufficient, substances for which there is evidence of hazard but analytical performance is not yet satisfactory) along with a yearly update of the NORMAN list of emerging substances in close cooperation with all NORMAN partners.

2. Closely follow the progress of research on identification of the toxicants that are causing the observed effects and bridge the gap between chemical and ecological status, and prepare a common position to be transferred to policy-makers and environmental managers.

A workshop on 'Emerging pollutants in the WFD: Support for identification of river basin specific pollutants through NORMAN – MS strategies and needs' will be organised, addressing the MSs' needs in their strategies for the identification of the relevant pollutants of concern.

The metabolisation of the target substances (i.e. the metabolites / degradation products that should actually be monitored for the different categories of substances) is a hot topic when discussing emerging contaminants and their associated risks. Metabolites or degradation products may be more toxic or persistent than the parent compounds. **NORMAN will organise a workshop on the topic of metabolites.**

NORMAN will organise an **Expert Group meeting on "Toxicity profiling (in vitro, in vivo assays, and omics): the state of the art and the perspectives"** to define what is today the position of the leading experts on this specific topic, with publication of a final position paper. These tools can be used in combination with statistical clustering methods to provide specific information on toxicity profiles of environmental matrices to assess the risks of environmental pollution, and information on the modes of action of substances in samples. In combination with TIE/EDA approaches, it can allow the identification of the toxicants that are causing the observed effects. Toxicity profiles can also be transformed to hazard profiles by linking e.g. in vitro to in vivo and field effects OR "hot-spots" and reference locations.

3. Define and standardise the interpretation of the results of monitoring with bioassays. When using bioassays, what we can and cannot say about our water quality and how decision-makers can use the results of these tools (e.g. in future implementation under the WFD).

Closely linked with the above-mentioned Expert Group meeting, NORMAN will organise a **Working Group on "The use of bioassays in monitoring programmes: interpretation of results"** to organise, based on the experience of the different experts, common exercises to "calibrate / validate" the proposed bioassays / biomarkers in controlled semi-field experiments (e.g. in mesocosm and experimental ditch facilities) and get to the definition of a harmonised approach for the interpretation of the results.

4. Harmonise work in the area of passive sampling, and bring together the disparate research groups to develop sound validation procedures for all aspects of the use of passive sampling devices, including laboratory calibration, handling, field deployment, chemical analysis or toxicological analysis and data interpretation.

The application of passive samplers opens new perspectives in the design of monitoring programmes and ecotoxicological assessments. Passive samplers show a great potential in the identification of emerging pollutants (e.g. in combination with bioassay-directed chemical analysis), in the assessment of their bioavailability and bioaccumulation as well as in the in situ measurement of time-weighted average concentrations over extended periods. The state of the art and the performance achieved in the use of passive samplers for emerging chemicals, in particular for polar compounds, will be the object of an **Expert Group meeting** and a science note in the **Scientific Watch Bulletin in 2009**, followed by the organisation of a common **interlaboratory study in 2010**.

5. Inform environmental managers and policy-makers about the possible benefits deriving from the implementation of environmental specimen banks (ESB) as tools for the retrospective monitoring of emerging pollutants.

This method involves collecting and storing biota samples from freshwater, marine and terrestrial environments.

The application of direct effects assessment on ESB samples is an ideal tool in identifying effects of emerging substances.

ESB also offers the following advantages for exposure assessment:

- Concentration trends can be identified by analyses of appropriate biota samples from different levels of the trophic system allowing the identification of emerging pollutants
- Even small temporal changes or slight regional differences of concentrations become obvious due to standardised samples
- The monitoring data can be used as a basis for the justification of political measures (e.g. banning of pollutants with accumulation potential)
- Monitoring results allow the assessment of results of political measures taken in the past (e.g. use restrictions for TBT)

The topic of **environmental specimen banks** will be the subject of regular science notes in the **Scientific Watch bulletin**.

6. Find synergies in collaboration, so as to reduce the use of resources for harmonisation and validation of analytical methods.

NORMAN has identified **pharmaceuticals** and **PFC** as two topics that are already at quite an advanced stage ('mature emerging substances') but that justify a collaborative effort. Depending on the resources available either one or two **interlaboratory exercises** will be organised in **2009**.

In the case of pharmaceuticals this means harmonising routine laboratory methods for handling substances identified as relevant, with a view to including these substances in future monitoring programmes.

In the case of PFC, matters are less advanced: the choice is determined by the need to have reliable data to support research results on the risks associated with these contaminants – the exposure, fate and availability of which are still poorly understood.

7. Address emerging issues at the earliest possible stage.

For **engineered nanoparticles (ENP)**: exposure, fate & availability are poorly understood. An important issue in ENP literature is that exposure is not known. Currently, no methods are available to quantitatively detect ENP levels in the environment. Further, there are currently no ENPs in the environment. So, the primary question is: What future ENP levels can be anticipated, based on production volumes & fate processes? The organisation of an **Expert Group meeting** on engineered nanoparticles is proposed for **2010**, to address, amongst others, behaviour of nanoparticles in the water environment, interaction with other chemicals, nanoparticles fate and exposure modelling.

## Forthcoming events

### **INTERNATIONAL CONFERENCE XENOWAC 2009 - XENOBIOTICS IN THE URBAN WATER CYCLE**

11 → 13 March 2009, Paphos, Cyprus

This conference is organised in the framework of the European Commission Cost Action 636 Xenobiotics in the Urban Water Cycle. For more details: <http://www.xenowac2009.com/>

### **5<sup>th</sup> WORLD WATER FORUM - BRIDGING DIVIDES FOR WATER**

16 → 22 March 2009, Istanbul, Turkey

The World Water Forum, organised every three years by the World Water Council in close collaboration with the authorities of the hosting country, is the largest international event in the field of water. For more details: <http://www.worldwaterforum5.org/>

### **3<sup>rd</sup> INTERNATIONAL PASSIVE SAMPLING WORKSHOP AND SYMPOSIUM (IPSW 2009)**

27 → 30 May 2009, Prague, Czech Republic

Sessions will be assigned to the key topics reflecting the development and application of passive samplers in air, sediments/soils and water. IPSW 2009 will host several satellite workshops, including an expert group meeting dedicated to passive sampling techniques for monitoring emerging pollutants organised by NORMAN. For more details: <http://animaracio.com/ipsw2009>

### **SETAC EUROPE 2009 - SESSION ON ENVIRONMENTAL SPECIMEN BANKING**

31 May → 4 June 2009, Göteborg, Sweden

This session aims to bring together researchers from established environmental specimen banking programmes in Europe, North America, and Asia to present and discuss the latest results regarding temporal changes in concentrations of emerging contaminants in their regions through use of banked specimens. For more details: <http://goteborg.setac.eu>

### **MICROPOL AND ECOHAZARD CONFERENCE 2009**

8 → 10 June 2009, San Francisco, California, USA

For this new edition of the conference the International Water Association (IWA) has partnered with the Groundwater Resources Association of California (GRA) for the organisation of this three-day event on the latest developments in the detection, risk assessment, treatment and regulation of micropollutants and hazardous substances in water systems. For more details go to <http://www.grac.org/micropol.asp>

### **ICCE 2009 - 12<sup>th</sup> EUCHEMMS INTERNATIONAL CONFERENCE ON CHEMISTRY AND THE ENVIRONMENT**

14 → 17 June 2009, Stockholm, Sweden

This conference invites oral and poster contributions illustrating the importance of a range of priority, novel issues related to chemicals and the environment. Particularly welcome are presentations on emerging issues for all sessions. For more details: <http://www.chemsoc.se/sidor/KK/icce2009.htm>

### **FINAL CONFERENCE OF THE EU FP6 SOCOPSE PROJECT - FUTURE APPROACH TO PRIORITY AND EMERGING SUBSTANCES IN EUROPEAN WATERS**

24 → 25 June 2009, Maastricht, The Netherlands

The conference will give an overview of the project results and discuss the next generation of river basin management plans with a special focus on Priority and Emerging Substances in Europe and how to plan for reduced emission of these substances into the aquatic environment. For more details: <http://www.socopse.eu>

### **EMCON 2009 - 2<sup>ND</sup> INTERNATIONAL CONFERENCE ON OCCURRENCE, FATE, EFFECTS, AND ANALYSIS OF EMERGING CONTAMINANTS IN THE ENVIRONMENT**

4 → 7 Aug 2009, Fort Collins, Colorado, USA

In March 2007, the first EmCon conference (EmCon2007) was held in York (United Kingdom). Because of the remarkable success of the 2007 conference and the numerous advances made within the topic of emerging contaminants, we invite you to attend EmCon2009 in Fort Collins, Colorado. This four-day event will focus on the most recent developments and findings concerning the occurrence, fate, effects, and analysis of Emerging Contaminants in the Environment. Flyer of the conference [291 kB].

Abstracts must be submitted before February 1, 2009.

For further information go to <http://www.emcon2009.com>

NORMAN is funded by the European Commission, DG Research, under the Sixth Framework Programme – Priority 6.3 “Global Change and Ecosystems”. Contract N° 018486. This newsletter does not represent the opinion of the EU Commission. The EU Commission is not responsible for any use that might be made of the data appearing within this newsletter.

## Contributing to the Newsletter

I would like to thank all of you who have contributed to the issues of the NORMAN Newsletter. The publication of the first issue of the Scientific Watch Bulletin is planned for June – July 2009.