



WELCOME TO ISSUE N°4 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

Emerging Contaminants in the Environment: How Can We Identify the Problems?

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In recent years there has been increasing concern over the less well-studied 'emerging contaminants' (ECs) such as metabolites, transformation products (formed in the environment and treatment processes), human pharmaceuticals, veterinary medicines, nanomaterials, personal care products and flame retardants. Many of these substances have been shown to be released to the environment and in the many monitoring studies that have looked for them, representatives have been detected in surface waters, groundwaters and drinking waters.

Alongside the monitoring, studies have been performed to explore the effects of a range of emerging contaminants at the biochemical, cellular, whole organism, population and community levels. While many of the data that have been produced on different classes of emerging contaminants indicate that many pose a small risk to ecosystems and human health, there is some evidence that selected emerging contaminants could affect human and environmental health. For example, the non-steroidal anti-inflammatory drug diclofenac was found to be responsible for the decline in populations of vulture species in Asia; the antiparasitic drug ivermectin has been shown to affect invertebrates at concentrations lower than those that could occur in the aquatic

environment; ethinylestradiol has been associated with endocrine disruption in fish; and there is concern that long-term exposure to antibacterial pharmaceuticals may be contributing to the selection of resistant bacteria.

However, we have still only detected a small proportion of ECs that are likely to occur in the environment and we have information on the ecotoxicological effects of an even smaller number of these. It is probably therefore timely to begin to tackle the issue of emerging contaminants in the environment in a more systematic way than we are doing at present. In order to do this we should begin to work towards a better characterisation of: 1) what emerging contaminants are released to and formed in the environment; 2) the occurrence, fate and transport of emerging contaminants in the environment; 3) effects on organisms and the implications in terms of ecosystem functioning. This information could then be used to expand current monitoring programmes to quantify those emerging contaminants that are likely to pose the greatest risk to environmental and human health. The use of ecological monitoring, biomarker assessment and effects-directed analysis could also provide valuable information. A useful approach to these challenges might well reflect the considerations I set out below.

IDENTIFYING INPUTS OF EMERGING CONTAMINANTS TO THE ENVIRONMENT

A good first step in focusing work on emerging contaminants is to identify what substances are being released to the environment and what substances are being formed in the environment. This information is often very difficult to obtain but can be extremely helpful in prioritising monitoring and testing requirements, steering analytical method development and informing the design of ecotoxicity studies. In the past we have successfully used a range of sources of information such as usage amounts and patterns, product composition data, usage surveys and life cycle analysis to evaluate the potential for environmental exposure. Other approaches such as remote sensing may also provide valuable information on potential pressures in a catchment. As a result of REACH, our understanding of the use of chemicals in Europe will improve, as companies will be required to provide data on amounts used. Metabolites and environmental transformation products are a special case, as they are formed either during the use of a product or following release into the environment. The transformation pathways of many substance classes (e.g. pharmaceuticals and plant protection products) have been well characterised and information from these types of studies has been used to develop prediction systems for identifying potential transformation pathways of a 'new' molecule. While these approaches are still not yet fully developed and evaluated, in the future they could provide a very valuable tool for identifying transformation products that could occur in a particular system.

IDENTIFICATION OF HIGH RISK ECS

We must not forget that something will not cause an impact solely because it is released to the environment. To determine whether an EC is likely to pose a risk to the environment we really need to assess the potential for exposure as well as the likely effects. For many ECs, experimental data on fate and effects in the environment are limited or non-existent, although this situation is changing as a result of new regulatory initiatives (e.g. REACH, requirements for environmental risk assessment of pharmaceuticals). We do, however, have a number of simple models available for estimating exposure in different environmental systems and, as long as the level of usage of a substance is known, these models often perform reasonably well for certain substance classes. New analytical technologies (e.g. time of flight technologies) also provide a powerful tool to identify and semi-quantify emerging contaminants in real environmental systems. By using the information on potential inputs to a system, it should be possible to focus the analysis on the emerging contaminants of most interest. We also have a number of tools available for estimating the effects of a substance, including: read-across techniques, QSARs and expert systems. By using exposure models and effects prediction approaches in combination, we can begin to home in on those substances that are likely to pose the

greatest risk in a particular situation. The main problem is that for many classes of emerging contaminants, the predictive models are inappropriate. For example, exposure models do not yet exist for assessing the fate of engineered nanoparticles, and good quality QSARs are not always available for predicting ecotoxicity of some chemical classes. But as REACH begins to have an impact, this situation is likely to improve. Our understanding of risks of ECs would also improve through more sharing of data (e.g. between scientists working in the area and industry), including negative data that may never find their way into a scientific publication.

MONITORING OF THE ENVIRONMENT

As ecosystems are so complex, it is probably impossible to predict the impact of a substance on the actual environment based on laboratory studies and modelling alone. The approaches described above should therefore go hand-in-hand with biology-based monitoring programmes in the real environment. For example, ecological monitoring will provide an indication of the impacts on structure and functioning of a system. This approach is already employed in surface water assessment in many countries but perhaps we should begin to expand the monitoring to other systems (e.g. soil systems). Monitoring of biomarker responses might also be appropriate, although the link between biomarker response and ecological functioning is often not clear. In instances where impacts on an ecosystem are observed, the use of effects-directed analysis may help to identify stressors - both emerged and emerging.

CLOSING COMMENTS

Over the past ten years there has been a significant increase in the amount of work on emerging contaminants in the environment. Priority lists have been developed for many ECs in different regions, information has been produced on effects of many substances on aquatic and terrestrial organisms and monitoring data has been produced for a wide range of geographies; alongside this, there have been significant advances in the regulatory testing requirements of many ECs. The studies often only consider one aspect and are not always joined up. It now seems timely to begin to consolidate the information to begin to establish which ECs we should be most worried about, in order to focus our future monitoring and research. It would also be of benefit to begin to consider the many ECs that have been ignored to date and to begin to consider which contaminants could become an issue in the future as a result of e.g. climate change and land use changes. While this will be challenging, I believe that, through the development of better mechanisms of data collation and sharing and the improvement of modelling approaches, this could be achievable. Clearly the NORMAN network has an important role to play in achieving this goal and in communicating the conclusions to the regulatory community and the general public.

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Fate of pharmaceutical and personal care products (PPCPs) during anaerobic digestion of sewage sludge

Anaerobic digestion has proven to be an efficient technique for stabilising sewage sludge. Mesophilic anaerobic digestion is the most widely used process for treatment of primary and secondary sludge generated by sewage treatment plants. Because of increased demands on sewage sludge treatment (especially hygienisation and sludge reduction), the mesophilic process is being increasingly supplemented or complemented with a thermophilic treatment at 55 °C instead of 37 °C. Thermophilic treatment accelerates biochemical reactions and increases the efficiency of organic matter decomposition.

This study investigated whether there is a difference in removal of 13 pharmaceutical and personal care products during thermophilic or mesophilic treatment. This was done in laboratory-scale batch reactors with a contents of 10L each. Experimental data on the removal of the chemicals spiked were obtained by means of a novel methodology taking into account the fraction of the chemical sorbed to sludge.

Mass balance calculations revealed five groups of pharmaceutical and personal care products:

- chemicals with very high removal efficiencies (> 85 %) such as Naproxen, Sulfamethoxazole, Roxithromycin and oestrogens;
- chemicals with high removal efficiencies (>60%), such as Galaxolide, Tonalide and Diclofenac;
- chemicals with medium removal efficiency (40–60%), such as Diazepam and Ibuprofen;
- chemicals with low removal efficiency (< 20%), such as Iopromide;
- persistent chemicals such as carbamazepine.

Elimination of oestrogens, Diazepam and Diclofenac was found to occur only after sludge adaptation, and in general no influence of sludge retention time or temperature was observed.

SOURCE:

Carballa M, Omil F, Ternes T and Lema JM. *Fate of pharmaceutical and personal care products (PPCPs) during anaerobic digestion of sewage sludge*. Water Research 41(10) [2007]: 2139-2150.

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Dechlorane Plus: Another flame retardant contaminating the European environment?

Dechlorane Plus is a chlorinated flame retardant with major applications in industrial polymers used for coating electrical wires, cables, and connectors as well as in plastic roofing material. It was developed as a replacement for Mirex. Mirex was used as a flame retardant and a pesticide, but banned in the 1970s due to its adverse environmental effects. The structure of Dechlorane Plus is similar to that of Mirex; it is formed by the reaction of two hexachlorocyclopentadiene molecules with cyclooctadiene (1, 2).

In 2006 Hoh et al. reported the discovery of Dechlorane Plus as an environmental contaminant (1). They identified it in ambient air samples collected around the Great Lakes. The concentrations were similar to the concentrations of another flame retardant of environmental concern, decabromodiphenyl ether (BDE-209), at the two sampling stations on Lake Erie, with means of ~20 and 34 pg m⁻³, while they were considerably lower at the stations further west. Sediment cores were

also analysed, and again the highest concentrations of Dechlorane Plus were found in Lake Erie, which at their peak were similar to the concentrations of BDE-209. This led the authors to hypothesize that a major production facility of the compound located in Niagara Falls is a major source of Dechlorane Plus to the environment.

Three recent papers have provided further insight into the extent and causes of environmental contamination with Dechlorane Plus. Qui et al. (3) studied its levels in a sediment core from Lake Ontario, downstream of the production facility. The levels were very high (up to 300 ng/g d.w.), ~10 times greater than in Lake Erie, and they greatly exceeded the levels of all brominated flame retardants combined. Some 20 tonnes of Dechlorane Plus were estimated to be stored in the sediments of Lake Ontario. This is compelling evidence that the production facility has been a major source of contamination.

This issue was pursued further by Qui and Hites (4), who used tree bark as a passive sampler of atmospheric contamination. They found a strong gradient of Dechlorane Plus concentrations in the bark; they decreased by 4 orders of magnitude from the vicinity of the production facility to remote sites ~1000 km distant. The spatial distribution was well described by a one dimensional Gaussian diffusion model. This indicated that the production facility was a strong atmospheric source, and that Dechlorane Plus is subject to atmospheric transport over long distances.

The occurrence of Dechlorane Plus in the indoor air environment was explored by Zhu et al. (2). They analysed 69 dust samples collected from residential homes in Ottawa, Canada, and detected Dechlorane Plus in all samples. The concentrations were highly variable, ranging from 2.3 to 5683 ng g⁻¹. The median concentration was 30 to 40 times lower than the median concentrations of BDE-99 and BDE-209. Nevertheless, this work indicates that Dechlorane Plus is present in the indoor environ-

ment. It suggests that it, like the brominated flame retardants, is released from products, and that indoor air could be a major vector of human exposure.

The tree bark study of Qui and Hites (4) gave the first indications of the occurrence of Dechlorane Plus in Europe. One sample from Germany and one from Italy were analysed. Both contained Dechlorane Plus at a concentration at the lower end of the range measured in the USA. The concentrations were comparable to those of the lower brominated PBDEs in the same samples. This suggests that Dechlorane Plus is also an environmental contaminant in Europe. At this point one can only speculate whether the primary source is long-range atmospheric transport, release from products, or emissions from production or processing facilities. Given the similarity of Dechlorane Plus to other known POPs such as aldrin and heptachlor, and the lack of experimental toxicity data (2), it would seem prudent to further investigate this chemical.

REFERENCES

- [1] Hoh E, Zhu L, Hites RA. *Dechlorane Plus, a chlorinated flame retardant, in the Great Lakes*. Environ. Sci. Technol. 40 [2006]: 1184-1189.
- [2] Zhu J, Feng YL, Shoeib M. *Detection of Dechlorane Plus in residential indoor dust in the city of Ottawa, Canada*. Environ. Sci. Technol. 41 [2007]: 7694-7698.
- [3] Qui X, Marvin CH, Hites RA. *Dechlorane Plus and other flame retardants in a sediment core from Lake Ontario*. Environ. Sci. Technol. 41 [2007]: 6014-6019.
- [4] Qui X, Hites RA. *Dechlorane Plus and other flame retardants in tree bark from the northeastern United States*. Environ. Sci. Technol. 42 [2008]: 31-36.

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Environmental and human health risk assessment

Effects of the UV filter benzophenone-2 on reproduction in fish

UV protection is becoming increasingly important. Amounts of UV filters added to sunscreens and cosmetics are increasing because, in general, higher sunlight protection factors are currently used. As UV filters are also increasingly used for the protection of a large variety of materials such as textiles, and because of their typical usage patterns, UV filters are increasingly reaching the environmental compartments. Because UV filters are photostable and often lipophilic, with log K_{ow} up to 7, they are relatively stable in the aquatic environment and have the potential to bioaccumulate. It is therefore not surprising that UV filters such as benzophenones have been detected in wastewater, surface water, soil, sediment and raw drinking water, as well as in fish.

These findings raise concerns about possible adverse effects on aquatic biota, especially regarding endocrine disrupting effects, as many wastewaters have been demonstrated to have oestrogenic activity. Effects on reproduction can therefore not be ruled out.

Recent studies show that several UV filters may have an oestrogenic activity in humans; and in the aquatic environment they have become a matter of concern, based on both in vitro and in vivo studies.

In this study, the endocrine disrupting potential of 2-benzophenone in fish was investigated. In vivo oestrogenic activity such as vitellogenin

induction and further oestrogenic and androgenic effects – including secondary sexual characteristics such as the formation and number of nuptial tubercles (decrease in male fish as an indication of a potential oestrogenic effect versus formation of tubercles in females as an indication of a potential androgenic effect) – were assayed for this purpose. It is shown for the first time that 2-benzophenone has dose-dependent effects on vitellogenin plasma concentrations, secondary sexual characteristics, gonad histology and fecundity in reproducing fathead minnows. The lowest observed concentration for the most sensitive parameters was 1.2 mg/L. In the environment, however, typical levels

of UV filters such as 2-benzophenone are in the order of up to 40 µg/L, which implies that in itself no adverse effects are likely to occur. It should be noted, however, that although ambient levels of UV filters are much lower than the effect levels derived in this study, additive interactions have been shown for hormonally active compounds such as UV filters. It is therefore concluded that 2-benzophenone may contribute to potential effects on fish reproduction, and the authors of this contribution therefore conclude by stating that their work offers “novel information for the hazard and risk assessment of widely used UV filters”.

SOURCE:

Weisbrod CJ, Kunz PY, Zenker AK and Fent K. *Effects of the UV filter benzophenone-2 on reproduction in fish*. Toxicology and Applied Pharmacology 225(3) [2007]: 255-266.

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Determination of pKa values of active pharmaceutical ingredients

Pharmaceuticals are a class of emerging chemicals that typically comprise various functional moieties. In turn, these moieties determine the fate (and effects) of pharmaceutical ingredients in the environment. Most active pharmaceutical ingredients have acidic and/or basic functionalities and one of the characteristic parameters of relevance in this respect is the dissociation constant. The ionization state of a chemical is controlled by solution pH and acidic dissociation constants (i.e. Ka-values), and the resulting cationic, neutral or anionic chemical species often have vastly differing properties with respect to, for instance, water solubility, volatility, and chemical or biological reactivity. It is then the extent of ionization that determines the absorption, distribution, metabolism and excretion of a chemical in biological systems and in the environment. It is thus of importance to be capable of reliably determining pKa values of ionizing chemicals such as active pharmaceutical ingredients.

This paper aims to review the methods available for determining pKa-values and it provides an overview of pKa-values that are typically found for various classes of pharmaceuticals, such as sulfonamides, tetracyclines, quinolones, macrolides, β-blockers, and anti-inflammatories.

Experimental techniques discussed for determining dissociation constants include:

- potentiometric titration, being the standard technique for decades;
- spectrophotometric methods, including UV-VIS and multi-wavelength spectrophotometry combined with target-factor analysis to deduce pKa-values for components containing more than two dissociation sites;
- NMR titration, albeit that this method has not yet been applied for active pharmaceutical ingredients;
- liquid chromatography;
- capillary electrophoresis;
- combined methods.

Computational methods are then discussed.

The paper presents a clear overview of the possibilities of reliably determining and calculating pKa-values, combined with a clear explanation of the theoretical back-ground to ionization and assessing the degree of association of chemicals in general and pharmaceuticals in particular.

SOURCE:

Babic S, Horvat AJM, Mutavdzic Pavlovic D and Kastelan-Macan M. *Determination of pKa values of active pharmaceutical ingredients*. TrAC Trends in Analytical Chemistry 26(11) [2007]: 1043-1061.

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Adapting an ambient monitoring programme to the challenge of managing emerging pollutants in the San Francisco Estuary

This article describes the regional monitoring programme in the San Francisco Estuary and the way in which this was adapted in order to respond to the challenge of managing emerging pollutants. This example is actually taken by the authors to show the general need for traditional monitoring programmes to be improved in recognition of the need to develop a proactive approach for the surveillance of emerging pollutants.

At the beginning of the article, the authors recall that the term 'emerging pollutants' refers to synthetic organic compounds or manufactured natural compounds where growing evidence suggests that adverse effects at environmentally relevant concentrations could occur but whose environmental releases are not regulated, and which are not routinely screened for their presence in water, sediment or tissue (and, we would like to add, all other environmental matrices according to the definition of the NORMAN network – Ed.).

While over seven million organic and inorganic compounds that have been indexed by the American Chemical Society's Abstract Service in their CAS Registry are commercially available, most pollution monitoring programmes focus only on those chemical compounds for which regulatory benchmarks exist, and have been traditionally considered responsible for the most significant human and environmental risk. There are numerous examples of chemicals whose acute and chronic adverse effects on human health and on ecosystems have been recognised only after they had been certified for widespread commercial use and often the time lag between initial indications of harm and actual management is considerable – more than 37 years in the case of PCBs. Clean-up and mitigation measures can be very expensive, especially for compounds that can persist in the environment for decades and therefore the authors stress that a proactive monitoring approach is advisable in order to avoid some of the costly mistakes of the past.

In the San Francisco Estuary a limited set of known pollutants was regularly monitored and compared against the existing water quality standards.

In 1998, a forensic analysis of archived chromatograms, together with the assessment of the chemical and toxicological properties of candidate compounds (e.g. potential for endocrine disruption, induction of cytochrome P450 1A1 and 1A2, etc.) was carried out, followed by the evaluation of more recent data from San Francisco Bay. An extensive monitoring programme was performed on water, sediment and bivalve tissue samples, using gas-chromatography-mass spectrometry (GC-MS) in full-scan mode. The authors (1) describe the scientific and analytical bases of this new monitoring approach, including their limitations; (2) summarise the approaches used and results obtained from the forensic retrospective; (3) present the monitoring data on emerging pollutants obtained from the analysis of wastewater, sediment, storm water, runoff and biota.

But the most interesting part of the article is the authors' analysis of this experience and the discussion of their suggested next steps for the development of monitoring programmes and research that could assist in the implementation of a more holistic approach to pollution prevention and control for the management of emerging pollutants. Thanks to this two-year extensive monitoring programme, a variety of synthetic organic compounds which had previously not been targeted for analysis were identified as pollutants of concern at the level of concentration found in the San Francisco Bay and were therefore placed on a non-regulatory 'watch list' slated for increased monitoring and assessment activities. An example are the PBDEs. The authors stress that in the US no comprehensive framework exists to encourage risk reduction before full proof of harm is available. The data from toxicological literature, together with the evidence of the widespread presence in the environment of PBDEs shown by the monitoring programme conducted in the San Francisco Bay, rapidly brought these pollutants to public attention.

The relatively rapid response of the regulatory system with regard to PBDEs, compared to the slow regulatory response time to emerging pollutants in the past, is a hopeful sign of possible closer feedback between science and environmental management.

There are other areas for improvement in our ability to deal effectively with the wide variety of chemicals entering the market. For example, great benefits would be gained from a more holistic exposure assessment that would include interactions between multiple stressors and evaluate cumulative and synergistic effects. A strong need exists to further evaluate the use of biomarkers as management tools and incorporate them into potential benchmarks for anticipating effects. The use of biomarkers as indicators of exposure to the total numbers and quantities of stressors is increasing as a monitoring tool. However, the environmental management system is currently not equipped to use such information as a trigger for action.

The article closes with a plea for the implementation of an appropriate mix of monitoring, evaluating sources and fate, methodological improvements and modelling to prevent and control pollution from emerging substances before they become a burden for future generations. The article also contains quite interesting details of the properties of some important families of emerging pollutants and their effects (polybrominated diphenyl ethers, phthalates, p-nonylphenol, triphenylphosphate, nitro and polycyclic musks).

The arguments and the recommendations proposed by the authors based on this case study are important lessons that are also applicable in Europe and should be considered in view of the progress that will be possible thanks to the implementation of REACH.

SOURCE:

Hoenicke R, Oros DR, Oram JJ and Taberski KM. *Adapting an ambient monitoring program to the challenge of managing emerging pollutants in the San Francisco Estuary*. Environmental Research 105(1) [2007]: 132-144.

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Mass spectrometry for identifying pharmaceutical biotransformation products in the environment

Among emerging contaminants, pharmaceuticals belong to a group of increasing interest, due to their rising consumption and important biological activity. The fate and behaviour of those substances, considered as pseudo-persistent compounds (due to a continual input into the aquatic systems) have been more and more documented, especially the part played by WWTP. Indeed, WWTP are considered as a major source of the environmental pollution by pharmaceuticals, although WWTP treatment steps remove pharmaceutical residues. Depending on the treatments, compounds could be more or less mineralised, degraded, or could pass through treatment steps unaltered.

Enzymatic processes occurring during biological treatment steps are an important part of the degradation and transformation phenomenon, but breakdown-products could have different properties (toxicity, persistence, polarity, etc.) from those of the parent compounds.

On the other hand, there is a lack of data on these 'new products', mostly because of difficulties in their identification, which requires the application of advanced instrumental methods, given the numerous transformation products, the high variability in chemical structures and, in many cases, the lack of commercial standards. Developments in instrumental technologies, such as liquid chromatography with mass spectrometry (LC-MS), can improve the feasibility of this highly complex task: screening for trace levels of unknown compounds in complex media (WWTP effluent) and identifying them.

The authors present the different new technologies dealing with mass spectrometric technologies, along with their capabilities and potential. Single MS coupling does not give sufficient information to confirm the chemical structure of an unknown, even if the chemical structure seems to be in agreement with the mass spectrum library (not available for all compounds). It's why MS/MS or MSⁿ technologies are used more for this kind of task.

TRIPLE QUADRUPOLE TECHNOLOGY (QQQ-MS)

This technology is used more for selective and sensitive quantification of target compounds. However, preselection of fragments is required, which leads to a loss of qualitative information. For structure elucidation, there are neutral loss scan, precursor ion scan or product ion scan modes. But QQQ is less sensitive in scan mode than other technologies. QQQ technology has been successfully used for identification of carbamazepine biodegradation products and metabolites [1; 2].

ION TRAP TECHNOLOGY (IT-MS)

Three dimensional quadrupole IT-MS allows MSⁿ, which is particularly attractive in identifying new compounds, since it provides fragmentation pathways that give a lot of information concerning the chemical structure of the unknown product. Even if quantification is less reliable with ITMS than with QQQ or QqToF, IT has higher sensitivity.

IT has been used for identification of microbial transformation products of naproxen [3], biodegradation product of trimethoprim [4] and iopromide [5]. A new technology coupling quadrupole and linear Ion trap (Qq-LIT), has recently been created; it combined QQQ capabilities with the scanning performances of IT. There is no published data yet available, but this technique is a promising one for the identification of unknown compounds in environmental samples.

TIME OF FLIGHT INSTRUMENTS (TOF AND QqTOF)

ToF instruments measure the mass dependent time that ions of different m/z ratios take to move from the entrance of the analyser to the detector. Full scan sensitivity, high mass resolution and mass accuracy (error lower than 2mDa) provided by ToF-MS are especially suited for the identification of trace level unknowns. QqToF reveals the elements of all product ions obtained, giving information for the elucidation of elemental structure of an unknown product. This apparatus has been already implemented for the determination of diclofenac biotransformation products [6].

CONCLUSION

The technological advances and developments achieved in hyphenated MS techniques are still under investigation for identification of unknown biodegradation products in environmental studies. The evolution of apparatus combining MS² techniques (QQQ or LIT) with high resolution mass spectrometer (ToF or Fourier transform) or apparition of hybrid systems such as LITQ-MSⁿ-FT (that combines Linear Ion Trap and Fourier transform mass spectrometer) will allow sufficient data to be gathered for the elucidation of the chemical structure of pharmaceutical or other organic pollutants' degradation products in complex environmental matrices.

If these analytical fields of investigation are still in development, the main drawbacks are the high costs of this new kind of apparatus, which will nevertheless become more and more vital in environmental research.

REFERENCES

- [1] D.F. Zhong, L.L. Sun and H.H. Huang, Acta Pharmacol. Sinica 24 (5) (2003), p. 442
- [2] X.S. Miao, J.J. Yang and C.D. Metcalfe, Environ. Sci. Technol. 39 (19) (2005), p. 7469
- [3] Kosjek, E. Heath, D. Žigon, B. Kralj, Identification of diclofenac's biodegradation product by quadrupole/orthogonal acceleration time-of-flight mass spectrometry (2007) submitted
- [4] F. Zhong, L.L. Sun and H.H. Huang, Acta Pharmacol. Sinica 24 (5) (2003), p. 442
- [5] S. Pérez, P. Eichhorn, M.D. Celiz and D.S. Aga, Anal. Chem. 78 (2006), p. 1866
- [6] P. Eichhorn, L. Ferguson, S. Pérez and D.S. Aga, Anal. Chem. 77 (2005), p. 4176.

SOURCE:

Kosjek T, Heath E, Petrovic M and Barcelo D. *Mass spectrometry for identifying pharmaceutical biotransformation products in the environment*. TrAC Trends in Analytical Chemistry 26(11) [2007]: 1076-1085.

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Using semi-permeable membrane devices as passive samplers

Over the last decade or so, there has been an increasing interest in and use of passive sampling devices, such as Diffuse Gradient Thin-film (DGT) and semi-permeable membrane devices (SPMD). Over this period, there has been a five-fold increase in publications in the literature on SPMDs.

This paper provides a timely review of the current technology and techniques for deploying SPMDs, including their use in monitoring emerging pollutants. In general, the paper is an accurate reflection of SPMD technology, although it does contain some unnecessary repetition. There is a serious contradiction in the paragraph that goes from pages 709 to 710, concerning the relative uptake rates by mussels and SPMDs.

Several references are made to the high cost of triolene-filled membranes but it represents a small fraction of the overall costs of analysis. In addition, more emphasis should be given to the delicate nature of LDPE membranes, which are prone to tears during handling (especially when being installed into the cages) and deployment. Unsurprisingly, any damage to the membrane renders them unusable.

The authors recognise that SPMDs can be used for air monitoring, but do not mention that it is therefore essential that any non-water-borne absorption is monitored so that it can be taken into account during the data analysis stages. The use of field blanks (second SPMDs that are stored in sealed tins at all times except when the deployed SPMDs are

exposed to the air, such as during preparation, deployment, retrieval, etc.) is advisory. These may then be analysed in tandem with the deployed sample membranes allowing potentially misleading data to be avoided.

The paper outlines the relative advantages and disadvantages of the different types of SPMDs, offers comparisons with active sampling systems and, in table 2, provides a very useful list of the different compounds that have been sampled using SPMDs.

The authors refer to the issues of attempting to adopt sampling rate models recreated from laboratory-generated data. The influence of both environmental and deployment circumstances on uptake should not be underestimated and makes the full calibration of SPMDs especially challenging. These areas require more research to provide solutions. In the meantime, SPMDs can be utilised to identify emerging pollutants, accumulated from extremely low concentrations, allowing us to tailor future analysis accordingly.

In conclusion, this paper provides a good, unbiased overview of the construction, deployment and analysis of SPMDs. It covers their use for both water and air monitoring, for a wide range of pollutants. The authors anticipate that new applications will be found for SPMDs and that the devices themselves will be improved. Calibration of SPMDs remains a major challenge, for the future.

SOURCE:

Esteve-Turrillas FA, Pastor A, Yusà V and de la Guardia M. *Using semi-permeable membrane devices as passive samplers*. Trends in Analytical Chemistry 26(7) [2007]: 703-712.

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Analytical techniques in studies of the environmental fate of pharmaceuticals and personal-care products

Despite the title of this article, readers will be very disappointed that the emphasis of the text is not directed towards analytical issues but is mainly focussed on the occurrence and fate of pharmaceuticals and personal-care products in the environment. Further emphasis is also placed on the development and need for pharmaceuticals and personal-care products and how different countries adopt different approaches towards their regulatory control. In the attempt to cover most pharmaceuticals and personal-care products in all environmental matrices, the authors have done themselves a disservice in that generalised statements have been made and sufficient detail not

provided to enable an analyst to grasp the real understanding of the analytical issues that need to be considered for the monitoring of these emerging substances in the environment. In addition, the article, in my opinion, is biased towards highlighting the [potential] dangers of these substances being present in the environment rather than concentrating on the analytical challenges that face analysts in detecting them. Also, whilst the article stresses that no proof of the toxic effects of pharmaceuticals has been presented, their possible effects are a cause for concern and much of the text directs the reader, in my view, to focus on this rather than concentrate on the analytical challenges.

The authors point out the obvious fact that there is no single analytical method to detect all pharmaceuticals, but that more attention is being paid to issues of labour and time consumption, and the burden to the environment associated with analytical procedures. Intuitively, one would not expect a single method for the analysis of all pharmaceuticals to be the most appropriate method. Whilst one method for analysing many pharmaceuticals is a laboratory desire for increasing efficiency or for screening purposes, it is highly unlikely to satisfy monitoring requirements where a high degree of accuracy and reliability is needed to enable confident decisions to be made.

Notwithstanding these criticisms, the article presents a very brief overview of some of the analytical techniques that have been used to date to detect pharmaceuticals and personal-care products in different environmental matrices, together with scant details of the concentrations determined, although I found the reporting of different concentration units somewhat confusing. There is also a brief summary of sampling issues, some of the detail I would question. For example, I would disagree with the statements that the most frequently used primary step in sampling analysis is separation of suspended matter by centrifugation, and the distances quoted for sampling river waters, and tributaries or waste waters.

Finally, the authors describe some details of HPLC and GC techniques, mainly coupled with MS detection, used for determining pharmaceuticals and personal-care products as sample extracts. Whilst details of the use of internal standards for quantification are included, the fundamental factor that the internal standards used should not be present in the original sample is omitted.

As an analytical chemist, solely interested in the analytical issues surrounding the challenges that face all analysts in detecting and determining trace levels of pharmaceuticals and personal-care products in different environmental matrices, I found this article, as suggested by the title, somewhat uninformative and disappointing.

SOURCE:

Kot-Wasik A, Debska J and Namiesnik J. *Analytical techniques in studies of the environmental fate of pharmaceuticals and personal care products*. Trac-Trends in Analytical Chemistry 26(6) [2007]: 557-568.

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Research projects / findings

COST Action 636: Xenobiotics in the Urban Water Cycle

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<http://cost636xenobiotics.er.dtu.dk/>



Hazardous chemicals such as many of the xenobiotic organic compounds are of increasing concern in urban water management, since water supply, urban drainage and wastewater treatment systems were originally designed solely to solve other problems (supply of potable water, flood prevention and sanitation). There is therefore a need to understand, in an integrated manner, the sources, flow paths, fate and effects of hazardous chemicals on both humans and the environment. The main objective of COST Action 636: Xenobiotics in the Urban Water Cycle is to assess the role of xenobiotics in the urban water cycle and to set up strategies for minimising their impact on humans and ecosystems (COST Action 636, 2008). COST Action 636 provides the tools for the integration of



knowledge and experience at the European level to create a critical mass required to assess the role of xenobiotics in the urban water cycle. The action includes a multi-disciplinary approach with discussions and exchange of knowledge among experts and stakeholders on the specific topics listed below.

COST - European Cooperation in the field of Scientific and Technical Research - is the oldest and widest system for research networking in Europe (COST, 2008a). It is based on an inter-governmental framework for cooperation on research, agreed following a Ministerial Conference in 1971. The goal of COST is to ensure that Europe holds a strong position in the field of scientific and technical research through the support of European cooperation and interaction between European researchers. It aims to strengthen non-competitive and pre-normative research in order to maximise European synergy and added values. To emphasise that the initiative came from the scientists and technical experts themselves and from those with a direct interest in furthering international collaboration, the founding fathers of COST opted for a flexible and pragmatic approach. COST activities have in the past paved the way for Community activities and its flexibility allows COST Actions to be used as a testing and exploratory field for emerging topics. The funds provided by COST support the co-ordination costs of the research networks (Actions), while the research funding for the networks is a responsibility for others (nationally and EU). The member countries participate on an 'à la carte' principle and activities are launched on a 'bottom-up' approach. One of its main features is its built-in flexibility. This concept clearly meets a growing demand and, in addition, it complements the Community programmes.

30 countries (COST, 2008b) have signed up to participate in COST Action 636: Xenobiotics in the Urban Water Cycle. This includes more than 250 scientists and practitioners from more than 120 different departments, companies and municipalities in the 30 countries. The action started in March 2005 and will be finalised by organising an open conference: International Conference on Xenobiotics in the Urban Water Cycle (XENOWAC 2009) in Cyprus in March 2009 (XENOWAC, 2008).

There are > 100,000 xenobiotics on the market in the European Union. Approximately 30,000 of these are 'everyday' chemicals i.e. estimated to be used in volumes over 1 ton each year. It has been estimated that 70,000 xenobiotics may potentially be hazardous for humans and/or ecosystems. In order to fulfil the goal of COST Action 636 – to assess the role of xenobiotics in the urban water cycle – information is needed with respect to the sources, flow paths, fate (transport, treatment, natural attenuation) and impact on humans, livestock and in the environment. Furthermore, it is necessary to have suitable tools such as

chemical analytical methods or eco-toxicological test methods for collecting the information that is needed and assessing the potential risk. The work in the action is organised in the following sub-topics which also correspond to the four working groups (WG):

1. identification, sources and fluxes;
2. methods for treatment;
3. impact assessment;
4. analytical issues.

These working groups organise meetings and identify and exploit possibilities for the exchange of research ideas and research staff between the participants.

During autumn and winter 2007/2008, Working Group no. 4 'Analytical issues' organised an interlaboratory exercise on oestrogens in water samples. The objective was to assess the laboratories' testing capability to perform analysis of steroid oestrogens (17 - ethinylestradiol, 17 - estradiol, Estrone, Estriol, and 17 -estradiol) from different types of water samples (tap water, surface water, untreated and treated wastewater). Eleven laboratories, both commercial laboratories and research institutions, from different EU countries participated. The interlaboratory exercise was coordinated by the working group chairs Ester Heath of the Josef Stefan Institute, Slovenia, and Frank Sacher of TZW, Germany. The samples were prepared by a team lead by Henrik R. Andersen and Hans-Christian H. Lützhøft at the Technical University of Denmark. The statistical evaluation and reporting was performed by Liliana Cruceru of ECOIND, Romania. This illustrates nicely how collaboration has been established between different partners in Europe. The results will be presented at international conferences and on the COST Action 636 webpage.

Working Group no. 4 is also involved in the preparation of a handbook for students and practitioners regarding analyses of different kinds of xenobiotics in water samples. The handbook will comprise the full chain from taking representative samples, preparation and analyses, to finally performing proper data evaluation. The handbook will also include the basics in quality assurance of chemical analysis.

Working Groups no. 1 'Identification, sources and fluxes' is about to finalise a special issue in the journal *Water, Air and Soil Pollution*. The topics in focus are 'Sources and fluxes', and the special issue will include some of the most interesting scientific papers that have been discussed during the meetings in this working group.

For more information regarding activities in 2008 and 2009, please, visit the webpage (COST Action 636, 2008).

REFERENCES

- COST, 2008a: <http://www.cost.esf.org/index.php>
- COST, 2008b: http://www.cost.esf.org/index.php?id=205&action_number=636
- COST Action 636, 2008: <http://cost636xenobiotics.er.dtu.dk/>
- XENOWAC, 2008: <http://www.xenowac2009.com>

NANOSH

Inflammatory and genotoxic effects of engineered nanomaterials

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<http://www.ttl.fi/Internet/partner/Nanosh/>



NANOSH is an EU FP6 STREP-funded three-year research project started in November 2006.

Nanotechnologies are rapidly growing technologies that provide new and innovative solutions in many industrial sectors. They will have a major impact on the everyday life of people in both industrialised and developing countries. As the use of engineered nanoparticles continues to expand, the number of exposed workers continues to increase, and exposure becomes an issue in many different industrial fields. It is therefore understandable that society is demanding more and better information on the possible health effects of engineered nanoparticles and on the significance of these effects. Of all nanotechnology research, only about one percent targets the exposure to engineered nanoparticles or the health effects of these particles, and about 99% is focused on the development of novel nanoparticles and nanotechnologies. As a consequence, the gap between the progress of the technology and safety information is growing rapidly.

The NANOSH project focuses on occupational exposure to nanoparticles and their health effects. The overall goal of the project is to delineate exposure and health effects of selected nano-sized particles relevant to the occupational environment. The consortium consists of seven partners with scientific and technical excellence in research areas relevant to nanoparticles and their effects:

- FIOH - Finnish Institute of Occupational Health, Helsinki, Finland;
- LMU - Institute for Surgical Research, University of Munich, Germany;
- CIOP - Central Institute for Labour Protection, National Research Institute, Warsaw, Poland;
- TNO - Netherlands Organisation for Applied Scientific Research, Zeist, Netherlands;
- HSL - Health and Safety Laboratory, Buxton, UK;
- DGUV - BGIA - BG Institute for Occupational Safety and Health, Sankt Augustin, Germany;
- ULEIC - Cancer Biomarkers and Prevention Group, University of Leicester, UK.

The main objectives of the NANOSH project can be divided into two categories:

- characterisation and exposure: characterisation of nanoparticles and definition of exposure levels in laboratory conditions and in workplaces;
- health effects: assessment of the genotoxic, inflammatory and microcirculatory effects of nanoparticles.

In more detail, the scientific and technological objectives of the project are:

- particle and exposure characterisation:
 - exposure levels of commercially relevant nanoparticles under laboratory conditions and in selected workplaces;
 - particle size distribution, dissolution, agglomeration properties, surface area and surface activity of various nanoparticles;
- genotoxicity of nanoparticles:
 - nanoparticle-induced oxidative DNA damage in lung cells;
 - nanoparticle-induced DNA strand breakage in pulmonary cells;
 - nanoparticle-induced chromosomal damage in pulmonary cells;
- pulmonary inflammation induced by nanoparticles:
 - direct effects of nanomaterial exposure on pulmonary inflammation;
 - modulatory effects of nanomaterial exposure on the development of allergic asthma;
 - nanomaterial-induced inflammatory responses in pulmonary cells;
- effects of nanoparticles on microcirculation:
 - the effects of nanoparticles on microvascular thrombus formation;
 - potential prothrombotic and proinflammatory effects of nanoparticles in the microvasculature;
 - the role of nanoparticles in consequences of post-ischaemic injury.

The occupational hygienic task is to characterise the levels of exposure to specific engineered nanoparticles in certain selected workplaces. Exposure levels are evaluated under laboratory conditions and during the manufacture of the particles. The particles are characterised with respect to their morphology and particle-size distribution, surface activity, and potential for agglomerate formation.

The main health effects being assessed are the effects in target organs. The analysed effects include genotoxicity and inflammatory responses in airways. Genotoxicity, a short-term indicator of potential carcinogenicity, is assessed in pulmonary tissue, by measuring oxidative DNA damage, DNA strand breakage and chromosomal damage. The parameters which will evaluate pulmonary inflammation include alterations in the panorama of pulmonary inflammatory cells as well as expression of biochemical markers of inflammation, i.e. cytokines and chemokines, and markers of cell death. To assess the effects of nanoparticles on the vasculature, the potential of nanoparticles to induce proinflammatory or prothrombotic effects in the microcirculation of experimental animals is explored.

The safety risks of nanoparticles have become a topic of much debate among health-care and medical researchers worldwide. It is crucial to the industries that the risks and liabilities of adopting new technologies should be under control. Assuring the safety of new nanomaterials will be a crucial prerequisite for successful promotion of nanotechnological innovations and their applications in the future. The NANOSH project aims to create a reliable and sound foundation for the assessment of safety of production and consumption of nanoparticles, thereby encouraging nanotechnological advances to support the European national economies, as well as the prosperity and wellbeing of citizens of the EU Member States.

Swiss-Romanian Co-operative Research Programme

Co-ordinator Prof. Walter GIGER

GRC, Giger Research Consulting, Zurich, and Eawag, Duebendorf, Switzerland

<http://www.estrom.ch> or <http://www.cnmp.ro/estrom.php>



The ESTROM programme was launched in March 2004 jointly by the Swiss National Science Foundation, the Swiss Agency for Development and Cooperation and the Romanian Ministry for Education and Research.

ESTROM had the following characteristics:

- orientation on relevant problems of a national dimension: the problems addressed by ESTROM have a socio-political background. They have been converted into scientific questions and are now entrusted to the scientific community for exploration;
- inter- and transdisciplinarity: the combining of different scientific disciplines and the involvement of all relevant stakeholders, from researchers to end-users, to ensure a well-founded overall approach to the solution of the defined problems;
- added value: ESTROM is not only the sum of individual projects, but rather co-ordinated and guided research aimed at creating additional stimulus and insights above the individual project level;
- transfer of results into practice: ESTROM is implementation-oriented, and requires special efforts to be made to inform the targeted groups and the public about achieved results and their possible use in practice.

The aims of the ESTROM programme were to:

- improve understanding of the environmental effects of water contamination due to chronic or acute anthropogenic effects;
- evaluate the adverse effects of water contamination on the ecosystem and human health;
- develop models and realistic solutions for the rehabilitation of the environment at selected locations, taking into account the improvement of the socio-economic status of the affected region;
- create a basis for decision-making regarding: the minimisation of negative effects of water contamination; the protection and improvement of the aquatic eco-systems and drinking water supply; sustainable, socio-economic development and improvement of the quality of life in Romania.

From a broader perspective, ESTROM aimed to create a decision basis for industry and regulators on how to avoid the negative impact of today's environmental contaminants. In the pursuit of this goal, ESTROM aimed to identify pertinent aquatic pollutants and to suggest mitigating actions.

ESTROM encompassed scientific studies on inorganic and organic water pollutants, focusing on measuring environmental exposure and evaluating inputs, fate and behaviour in wastewater and in ambient waters. Measured environmental concentrations and evaluation of potential negative effects will be the basis for the assessment of risks to the environment and human health.

Major questions addressed were:

- what is the magnitude of exposure of the environment and of people in Romania?
- what are the hazards and risks to human health?
- what measures should be taken for the protection of the environment and of people?

Nine Swiss-Romanian research partnerships were established under this programme (see list below and Figure), Approximately 60 researchers were involved, mostly working in Romania. The projects started in spring 2005 and lasted 30 months. The projects increased Romanian research capacities in this scientific field, through the funding of doctoral students and exchange of scientists. Furthermore, the programme offered funding possibilities for implementing the research results.

AREAS OF APPLICATION OF THE RESULTS

Exposure assessment

Development of reliable and robust methods for qualitative and quantitative measurements of organic and inorganic water contaminants in discrete aqueous and solid samples as well as by online measurements in aquatic systems, i.e. in wastewaters, ambient waters, sludges, particulates, sediments and soils.

Analytical determinations of organic and inorganic chemical contaminants in the aquatic environment in order to recognise and apportion inputs and occurrences of contaminants in municipal and industrial wastewaters, elucidate fate and behaviour in wastewater and drinking water treatment and assess residual amounts in ambient waters such as rivers, lakes, groundwaters and drinking water.

Investigations should focus on environmental pollution by dangerous substances as defined by the European Water Directive, persistent organic pollutants including pesticides and heavy metals, petroleum and emerging contaminants such as pharmaceuticals, endocrine disruptors or biocidal products. The research projects should particularly focus on high sophistication in procedures, analytical quality control and the application of mathematical modelling techniques for developing concepts of sample collection and for the interpretation of measured results.

Evaluation of the impact of the dynamics of particulate matter and sediments

Particles and sediments in aquatic systems are primarily not considered as pollutants per se. However, due to their character as reactive surfaces (particles) and their potential as sinks and archives (sediments) they play a crucial role within a 'cycling of polluting substances'. Therefore, if conclusions are to be drawn on the transport, distribution and depositional processes of pollutants, particles have to be considered in order to assess their potential harm. As sediments often serve as a sink for dangerous substances, they may in turn become a source of secondary pollution after their deposition. Besides, sediments are useful archives for the reconstruction of polluting events and widespread spatial distribution of polluting substances to assess remediation measures.

Wastewater treatment

Assessment and optimisation of the treatment of industrial and municipal wastewaters regarding specific contaminants, production facilities and end products.

Assessment of human health effects

Assessment of public health effects of water (well water, surface water) as regards pollution by nutrients, pesticides, heavy metals. In particular, the results of this programme will be applied for improving the situation regarding water pollutants in Romania by recognising critical points of chronic or acute contamination.

This interdisciplinary programme addressed questions such as the magnitude of exposure of the environment and of people in Romania, the hazards and risks to human health, or the measures to be taken for the protection of the environment and of people. From a broader perspective, ESTROM aimed to create a decision basis for industry and regulators seeking to avoid the negative impact of today's environmental contaminants.

The outcomes of this programme should help the Romanian authorities to cope with activities of the European Union with respect to the implementation of the Water Framework Directive and derived measu-

res regarding dangerous substances. It is also hoped that ESTROM contributes to measures connected to the Stockholm Convention on Persistent Organic Pollutants (POPs).

International Conference

The International Conference ESTROM 2008 will be held in the Romanian Academy in Bucharest on 3–5 September 2008. The ESTROM 2008 Conference will include presentations by Romanian ESTROM researchers and reputable scientists from several European countries. It is planned to publish a special ESTROM Issue in the journal *Environmental Science and Pollution Research*.

ESTROM PROJECTS:

Chemical, Biological and Ecotoxicological Assessment of Pesticides and Persistent Organic Pollutants in the Bahlui River, Romania POPIASI

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- 2 Alexandru Ioan Cuza University Iasi, Faculty of Biology, Centre of Expertise for Sustainable Exploitation of Ecosystems, Iasi, Romania
- 3 EPFL, Ecole Polytechnique Fédérale de Lausanne, Environmental Science and Technology Institute, Ecublens, Switzerland

Environmental Exposure of Pharmaceuticals in the Somes Valley Watershed, Romania PHARMSOMES

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- 2 Iuliu Hateganu University of Medicine and Pharmacy, Cluj-Napoca, Romania
- 3 Eawag, Dübendorf, Switzerland

Trihalomethane Formation During Water Disinfection in the Four Drinking Water Treatment Plants of the Somes River Basin, Romania WAQA

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- 2 Institute of Public Health Cluj-Napoca, Cluj-Napoca, Romania
- 3 University Babes-Bolyai Cluj-Napoca, Faculty of Physics, Cluj-Napoca, Romania
- 4 Water and Sewerage Company Cluj, Cluj-Napoca, Romania.
- 5 Garda de mediu, Comisariatul Judeean Cluj, Cluj-Napoca, Romania
- 6 Eawag, Dübendorf, Switzerland

Historical Record of Mercury Contamination in the Sediments of the Babeni Reservoir, Olt River, Romania ORSED

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- 2 Institute F.-A. Forel, University of Geneva, Versoix, Switzerland

Integrated Environmental and Socioeconomic Assessment of Impacts by Mining Activities – A Case Study in the Certej River Catchment, Romania EIMAR

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Heavy Metal Contamination in the Vicinity of an Industrial Area near Bucharest NEPOLL

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Development of an Integrated Water Quality Management System with Application to the Ialomita River Basin, Romania INWAQ

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Eutrophication of Lake Tasaul, Romania: Proposals for Rehabilitation TASAUL

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Water and Sediment Dynamics Affecting Nutrient Cycles and Greenhouse Gas Emissions in the Danube Delta WASEDY

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Occurrence and behaviour of pharmaceuticals and musk fragrances in the Somes River before and after upgrading the municipal wastewater treatment plant of Cluj-Napoca

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<http://www.estrom.ch/> and <http://www.cnmp.ro/estrom.php>

Pharmaceutically active substances are a class of new, so called 'emerging' contaminants, which has led to increasing concern about potential environmental risks. After excretion substantial amounts of unchanged pharmaceuticals and their metabolites are discharged into domestic wastewaters and, if they are not removed during wastewater treatment, these substances will eventually reach ambient waters. Discharge of the effluents from wastewater treatment plants (WWTPs) into the receiving waters results in a further dilution of the pharmacologically active substances which occur at concentrations up to the high ng/L range. The concentrations in surface waters are very dependent on the contribution of the wastewater flow to the receiving water flow, and therefore of the dilution of the wastewater that occurs.

The Somes River Basin is in the north-west of Romania (Figure 1). The Somes Mic originates south of Cluj-Napoca and merges at Dej with the Somes Mare to form the Somes, which flows into the Tiza in Hungary and later into the Danube. The Somes receives a variety of organic wastes from urban areas, factories and individual households, as well as treated and almost untreated wastewater effluents from several municipal WWTPs. The Cluj-Napoca WWTP is the largest WWTP in Transylvania and serves a residential population of around 350,000 inhabitants. Between 1998 and 2003 the WWTP was upgraded and equipped for nutrient removal. Sampling campaigns were conducted before (April 2003) and after (September 2006) the upgrade of the Cluj-Napoca WWTP.

The Pharmaceutical and Personal Care Products (PPCPs) were selected on the basis of consumption at the regional scale, reported aquatic toxicity and the suitability of the GC/MS method for the determination of the compounds at trace levels: caffeine (stimulant), carbamazepine (anti-epileptic), pentoxifylline (anticoagulant), cyclophosphamide (cytostatic), ibuprofen (analgesic) and galaxolide (musk fragrance).

The concentrations in the Somes River varied from below 10 ng/L up to 10 µg/L. A substantial decrease of the exposure in the Somes River was observed due to the upgrade of the municipal WWTP in Cluj-Napoca. The concentrations in the river stretch between Cluj-Napoca and Dej (Somes Mic) varied greatly: caffeine (230–9700 ng/L), carbamazepine (30–70 ng/L), galaxolide (10–310 ng/L), and ibuprofen (30–120 ng/L). Cyclophosphamide and pentoxifylline could not be detected in the Somes River after the upgrade of the Cluj-Napoca WWTP. The concentrations and loads of caffeine decreased by one order of magnitude after the upgrade of the Cluj-Napoca WWTP, whereas the levels of persistent carbamazepine remained almost unchanged within expected temporal variations (Figure 2).

The relative contribution of treated and untreated wastewater in surface water may be assessed by measuring chemical indicators. Recalcitrant pharmaceuticals such as carbamazepine are suitable as chemical markers for estimating the relative contribution of wastewater to surface water. Caffeine is efficiently eliminated in WWTPs and is therefore a suitable indicator for surface water pollution by raw sewage and barely treated wastewaters. During the second campaign the loads at Dej of the recalcitrant carbamazepine increased by a factor of 2 compared to the first sampling site. The concurrent increase of the caffeine load by a factor of nearly 5 refers to a discharge of untreated wastewater into the Somes. Because the increase of the load occurred after the confluence of the Somes Mic and the Somes Mare, this increase must be due to the discharged of untreated wastewater deriving from Bistrita, Nasaud and Beclean. These data support the improvement of existing WWTPs and implementation of new ones where necessary in order to reduce the discharge of contaminants in the Somes Valley River Basin.

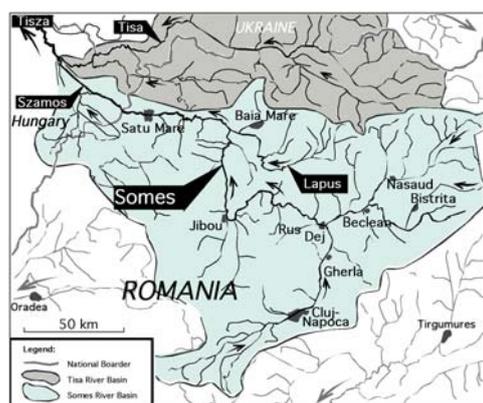


Figure 1. Map of the Somes River Basin. For the shown results, river samples were collected at 3 sites: downstream of Cluj-Napoca, downstream of Gherla and upstream of Dej, after confluence of Somesul Mic with Somesul Mare.

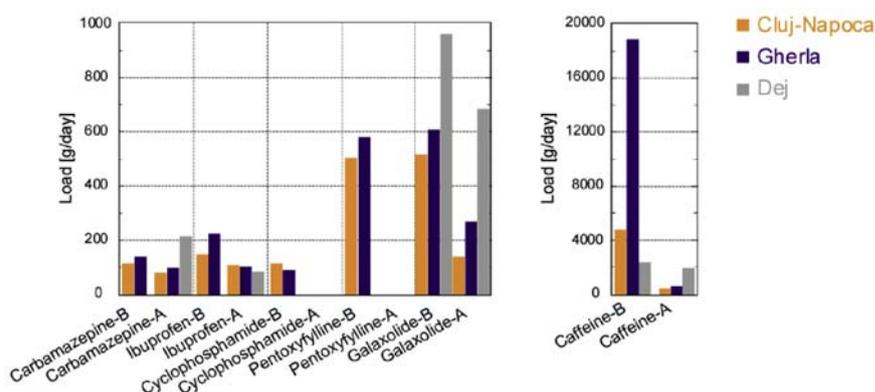


Figure 2. Loads of the studied compounds in the Somes River Basin before (B) and after (A) the upgrade of the WWTP Cluj-Napoca

FURTHER READING:

- Moldovan Z (2006): *Occurrences of pharmaceutical and personal care products as micropollutants in rivers from Romania*. Chemosphere 64, 1808-1817.
- Moldovan Z, Schmutzer G, Tusa F, Calin R, Alder AC (2007): *An overview of pharmaceuticals and personal care products contamination along the River Somes watershed, Romania*. J. Environ. Monit. 9, 986-993.
- Moldovan Z, Chira R, Alder AC (2008 (submitted)): *Environmental Exposure of Pharmaceuticals and Musk Fragrances in the Somes River before and after upgrading the Municipal WWTP Cluj-Napoca*. ESPR - Environ. Sci. Pollut. Res.

Life of the network, NORMAN Activities

The activities of the NORMAN project started officially on 1st 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).

NORMAN CONTACT POINTS

The appointment of four new Contact Points brings to 23 out of 45 the number of European countries where a NORMAN National Contact Point has been appointed.

We would like to thank:

- Martin Schlabach from the Norwegian Institute for Air Research - NILU - in Norway;
- Ott Roots from the Estonian Environmental Research Institute – EERI - in Estonia;
- Sebastian Zabczynski from the Silesian University of Technology Environmental Biotechnology Department – SUT EBD - in Poland;
- Branislav Vrana from the Slovak National Water Reference Laboratory, Water Research Institute – VUVH - in Slovakia

for their commitment and the valuable contribution that they will provide in the exchange of information on emerging substances within the NORMAN network.

Representatives from Denmark, Estonia, Finland, Italy, Poland, Romania, Slovakia, Sweden and Ukraine participated as Contact Points in the 4th NORMAN workshop, organised in Lyon immediately before the plenary meeting.



EXCHANGE OF INFORMATION

Workshop on 'Integrated chemical and bio-monitoring strategies for risk assessment of emerging substances' (Lyon, France: 17-18 March 2008)

The workshop was organised by Cemagref – Agricultural and Environmental Engineering Research Institute – in France. With 110 participants, this workshop brought together experts from different communities (the scientific community, environmental water managers and decision-makers, regulators) and offered a precious opportunity to debate existing protocols and experiences in the application of strategies integrating chemical and biological methods and the concrete possibilities and limitations today for their application in the framework of the current legislation (in particular, the Water Framework Directive), to complement chemical-driven risk assessment approaches.

The workshop programme included 19 presentations and 15 posters organised in three sessions:

- prioritisation of emerging substances for field monitoring and risk assessment;
- effects-driven approaches for field monitoring and risk assessment of emerging pollutants;
- integrated approaches within risk assessment strategies for monitoring risks from emerging pollutants at local and large scales.

The book of abstracts and the speakers' presentations are already available on the NORMAN site at: <http://www.norman-network.net> >> Workshops. The workshop report will be published by July 2008 on the same website.

This was also the last workshop organised by NORMAN under the EC Contract. The NORMAN network intends to continue these activities as a permanent, self-sustaining network with the organisation of workshops and expert group meetings on topics of priority interest. The programme of activities for 2009 is in preparation and the title of the next NORMAN workshop will be announced on the NORMAN website as soon as the programme is approved.

NORMAN DATABASES

The EMPOMAP database now contains 182 entries: 56 experts (6 entries in draft), 28 organisations (5 in draft) and 98 projects (10 in draft) dealing with emerging substances.

Registration in this database is open to all experts around the world working in the field of emerging substances. We reiterate our invitation to such experts to register their expert profile in the database and to contact INERIS (valeria.dulio@ineris.fr) for registration of relevant research in the field of emerging substances.

The EMPODAT database now contains about 6000 entries and the further datasets ready for uploading mean that a total of 8500 will soon be available on the database.

Both the EMPODAT and EMPOMASS databases are accessible to NORMAN partners only.

The databases are still not available on the public website since they are still in test mode; they will be publicly available in the last phase of the project (May 2008). However, there has been no restriction on access

and use of the databases; all NORMAN partners and organisations willing to join and collaborate with the network have received from the working team at EI detailed instructions for access and use of the database. Other interested organisations are invited to contact us if they are interested in visiting the databases and helping us to improve them.

REVISION OF THE LIST OF FREQUENTLY DISCUSSED EMERGING SUBSTANCES – NORMAN LIST

The current list of emerging substances (available on the NORMAN website <http://www.norman-network.net> >> About us >> Emerging substances >> List) is under revision with the expert advice of all NORMAN partners.

The current definition of 'emerging substances' and '- pollutants' are published as part of the NORMAN Glossary of Terms. The question arises whether this definition needs also to be improved. This was discussed at the recent plenary meeting of the NORMAN network – 19 March in Lyon. Actually the conclusion of the discussion was that it is probably not possible to agree on a precise list of criteria for the classification of a substance as an emerging substance / pollutant. There are various levels of 'maturity' for a substance to be referred to as an 'emerging substance' (e.g. there are substances that have been discussed only recently and about which we know very little, and there are substances that are already at quite an advanced stage and that are likely to become regulated substances quite soon). The network should not spend too much time and efforts in the revision of the definition, but rather carry out a regular updating based on the present definition and meaningful expert judgement.

One clear principle, however, is that regulated substances, such as the Priority Substances under the WFD are not emerging substances even if we do not have a lot of data available for some of these substances. Nevertheless, there is an interest in including selected priority substances in the database when the associated compounds / degradation products or isomers of these substances are on the list of emerging substances. A typical example are the organotin compounds, where the tributyltin (TBT) is regulated as a PS under the WFD and the associated compounds monobutyl-tin and the dibutyl-tin are on the list of emerging substances.

QA/QC ACTIVITIES

Methods validation protocols

The current version of the NORMAN validation protocol (available as a draft on the NORMAN website at <http://www.norman-network.net> >> QA/QC issues >> Validation framework) is under revision. The improvement of the protocol will be made taking into account the results of the three case studies (interlaboratory studies) organised during the project. To this purpose a questionnaire has been developed and dis-

seminated to the partners of the CASE study. The deadline for submission of feedback by the CASE partners is the end of March (Deadline 31st March).

In the meantime work has started at the CEN level (TC 230) for the implementation of the NORMAN protocol in standardisation. Moreover, NORMAN was presented at the meeting of the CEN / SABE (Scientific Advisory Board Environment) on 3 April in Athens.

The NORMAN Case studies (1, 2 and 3) are about to be finalised and the final reports will soon be available on the NORMAN website:

- **case 1:** Oestrogens in sewage treatment effluents – the final report is expected by the end of April 2008;
- **case 2:** Non-steroidal anti-inflammatory drugs – the evaluation of the data of the 2nd interlaboratory study is still on going; the final data evaluation and the report of the 1st and 2nd interlaboratory study will be ready for the 2nd Interlaboratory meeting, which is planned for 19 May 2008 in Ljubljana (SI);
- **case 3:** Brominated flame retardants (DecaBDE) – the report of the 1st and 2nd interlaboratory exercise on decaBDE is expected by April 2008.

NORMAN FOLLOW-UP: ESTABLISHMENT OF THE PERMANENT NETWORK

Work is proceeding to ensure that NORMAN becomes a self-sustaining permanent network after the expiration of the NORMAN EC contract. After the last October plenary meeting in Amsterdam, a call for expressions of interest was launched on the NORMAN website and about 40 positive replies were received by the end of December 2007 / beginning of January 2008. The list of the organisations that have already expressed an interest in joining the network is regularly updated on the NORMAN website (Homepage).

All organisations that had expressed an interest in becoming members of the future network were invited to participate in the NORMAN plenary meeting of 19 March 2008 (Lyon), which included the following points on the agenda:

- the presentation of the proposals received so far for activities to be carried out in 2009;
- the presentation of the outline of the future NORMAN statutes.

The plan is to create the NORMAN network as a non-profit association under French Law. The Activity Plan of the network for 2009 is in preparation and will be presented at the final meeting to be held under the NORMAN EU contract. That meeting, which will take place in September / October 2008 (date still to be announced) will also be the kick-off meeting of the new NORMAN permanent network.

More details about the implementation of the NORMAN permanent network are available at:

http://norman.ineris.fr/index_php.php?module=public/about_us/fo_low_up&menu2=public/about_us/about_us

Forthcoming events

1ST INTERNATIONAL WORKSHOP FLUORINATED SURFACTANTS: NEW DEVELOPMENTS

26 → 28 June 2008, Idstein, Germany

For further information and registration go to <http://pft.fh-fresenius.de>

DIOXIN 2008

17 → 22 August 2008, Birmingham, UK

28th International Symposium on Halogenated Persistent Organic Pollutants

Further information and registration at <http://www.dioxin2008.org/>

EUROPEAN AEROSOL CONFERENCE

24 → 29 August 2008, Thessaloniki, Greece

The 2008 European Aerosol Conference is organized, under the auspices of the European Aerosol Assembly (EAA), by the Hellenic Association for Aerosol Research (HAAR). In this EAC 2008 special emphasis will be put on the topic "Nanoparticles".

More information about the conference at the page <http://www.eac2008.org/>

INTERNATIONAL ESTROM CONFERENCE

3 → 5 September 2008, Bucharest, Romania

For more information go to: <http://www.estrom.ch>

2ND EUCHEMS CHEMISTRY CONGRESS

16 → 20 September 2008, Torino, Italy

For more information go to: <http://www.euchems-torino2008.it/site/home.asp>

4TH EUROPEAN DETERGENTS CONFERENCE

15 → 7 October 2008, Würzburg, Germany

For more information download the flyer on NORMAN website

5TH EUROPEAN CONFERENCE ON PESTICIDES AND RELATED ORGANIC MICROPOLLUTANTS IN THE ENVIRONMENT

11th Symposium on Chemistry and Fate of Modern Pesticides

22 → 25 October 2008, Marseille, France

For more information go to: http://www.univ-provence.fr/document.php?project=pesticides_2008

INTERNATIONAL CONFERENCE ON SAFE PRODUCTION AND USE OF NANOMATERIALS

3 → 7 November 2008, Grenoble, France

This conference is organised by the Integrated NANOSAFE2 project, funded by the European Commission under FP6.

More information at <http://www.nanosafe.org>

9TH EUROPEAN MEETING ON ENVIRONMENTAL CHEMISTRY - EMEC9

3 → 6 December 2008, Girona, Spain

Organised on behalf of the European Association of Chemistry and the Environment (ACE)

More information on the EMEC website at <http://www.udg.edu/deqata/mma/emec9>

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»»»»»»»»»» **Contributing to the Newsletter**

If you would like to contribute to a future issue of the newsletter or announce an upcoming event, you can contact the newsletter co-ordinator at corinne.mandin@ineris.fr

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