NORMAN WORKSHOP REPORT

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Sampling and analysis of emerging contaminants in the aquatic environment: current and future challenges

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Brief workshop report

On the 1[t] and 2 March 2012 approximately 80 scientists gathered in Oslo to discuss the challenges and pitfalls related to the sampling of contaminants of emerging concern (CECs). The objective of the workshop was to discuss and evaluate whether the approaches currently in place are effective for the sampling and analysis of emerging contaminants, to develop a framework for identifying the next generation of emerging compounds and see what new contaminants are emerging. These objectives provided three workshop themes that formed the basis of three sessions:

1. How do we effectively sample for emerging compounds?
2. How do we identify the next generation of emerging compounds?
3. What are the next generation of emerging compounds?

The first two sessions were based on a number of invited presentations followed by a panel discussion. For Theme 3, participants were invited to present their candidates for the next generation of emerging compounds following a keynote presentation on transformation products. The presentations and the workshop programme are available here[1].

Session 1. How do we identify the next generation of emerging compounds?

This session set out to establish whether we have the necessary tools and approaches in place to successfully identify the next generation of emerging compounds. *Werner Brack* (UFZ, DE) provided an overview of whether we focus on the right chemicals in terms of monitoring and assessment. Werner highlighted the fact that historical sediment contamination with non-polar priority POPs is a problem (accumulation in the food chain, effects on top predators), but many substances we should be concerned about are CECs, polar in nature. They include frequently used personal care products, biocides, pesticides etc. Werner noted that these CECs are bioavailable, affect ecosystems and their services, some may possibly be mutagenic or disrupt endocrine systems and that identifying them should involve integrated biological and chemical analytical approaches. A big challenge that lies ahead is to identify the unknown toxicants. Effect-directed analysis (EDA) is one approach for the identification of unknowns and a newly developed structure elucidation strategy for unknowns appears promising. There is an increasing importance of predictive models and computer tools in the identification of unknowns. Werner pointed out that there is an urgent need for the advancement of predictive models together with innovative analytical tools, spectral databases, multivariate tools (pattern recognition) and biodiagnostic tools (omics).

Steve Rowland (University of Plymouth, UK) provided an insight into his group's work on the identification of unknowns in unresolved complex mixtures, using naphthenic acids from oil sands process water (OSPW) as an example. Steve demonstrated how GCxGC-MS with

[1] http://www.norman-network.net/index_php.php?module=public/workshops/workshops2012_oslo&menu2=public/workshops/workshops&interface=1024&lang=en

normal and reverse phases was a useful technique for resolving complex mixtures, including "humps" containing toxicants and compounds modelled to be toxic.

Jana Weiss (IVM VUA, NL) described accurate mass screening techniques for "known unknowns" in environmental samples using high resolution Mass Spectrometry. Jana's approach was also based on the integration of chemical analysis and effect-based tools in the form of EDA, and showed that expanded fractionation before identification is useful because of the complexity of environmental samples. Accurate mass determination for the identification of "known unknowns" was shown to be promising and non-exclusive. In addition chromatograms can be saved for future evaluation, for example for retro-analysis of newly identified CECs. Finally she encouraged the sharing of data and in particular library spectra.

Martin Scheringer (ETH Zurich, CH) presented his group's work on the Screening for PBT Chemicals among the "Existing" and "New" Chemicals of the EU, recently published in ES&T (Strempel et al., 2012). He presented a PBT screening of approximately 95000 chemicals based on a comparison of estimated P, B, and T properties of each chemical with the P, B, and T thresholds defined under REACH. The screening procedure was also performed on a set of 2576 high production volume chemicals and a set of 2781 chemicals from the EU's former list of "new chemicals" (ELINCS). In the set of 95000 chemicals, the fraction of potential PBT chemicals is around 3%, but in the ELINCS chemicals it reaches 5%. The most common structural elements among the potential PBT chemicals were identified. Analysis of the P, B, and T data for all chemicals considered here shows that the uncertainty in persistence data contributes most to the uncertainty in the number of potential PBT chemicals.

Jan Christensen (University of Copenhagen, DK) proposed contaminant profiling as a set of next-generation analytical tools to deal with contaminant complexity. Pattern recognition coupled with chemometric tools (refered to as Chemsic) was demonstrated between different complex samples, such as oils, and were also suitable for comprehensive GCxGC analyses. It was summarised that contaminant profiling is one way to deal with contaminant complexity, complementary to conventional quantitative analysis of selected contaminants.
The panel discussion for this session was focused on whether we have the necessary tools to identify the next generation of CECs. The key points are summarised as:

- Tools are available but they are not sufficiently developed, especially modeling-based solutions. There is a need to improve fractionation techniques as used in EDA.
- Disappointing that there is so little information available for a majority of chemicals, especially when they have been on the market for a long time. There is a need for more basic work, like half-life investigations.
- Increased collaboration between research groups as well as industry is required to provide better data.
- Response based controls should be more directly linked to monitoring data in regulatory monitoring.
- Reliance upon acute toxicity data for PBT assessments means that a number of other toxicity pathways and endpoints are excluded. There are important toxicity pathways that are still unknown and contribute to T.

Session 2: How do we effectively sample for emerging compounds?

Christopher Harman (NIVA, NO) kicked off the second session on the sampling of CECs with a presentation on passive methods for the sampling and *in situ* extraction of emerging contaminants. The presentation introduced the concept of passive sampling, the devices available and their application. The polar organic compound integrative sampler (POCIS) was described as useful for investigative monitoring, but results are semi-quantitative and currently lacking an exposure correction method and uptake model. It was stressed that we cannot simply copy the theory from hydrophobic passive sampling for use with polar samplers. Emerging hydrophobic or medium polar compounds may be sampled by existing samplers such as low density polyethelene (LDPE) and silicone rubber with a performance reference compound (PRC) approach. It was also noted that passive samplers can generate environmentally relevant extracts for ecotoxicology testing.

Christoph Ort (Eawag, CH) explained to the audience the additional uncertainties introduced to occurrence data through sampling. CECs (and all other pollutants) in sewers and rivers are subject to substantial short-term variations and therefore robust sampling protocols are required for their accurate quantification. Modelling the systems under investigation is a valuable tool to minimise sampling errors and maximise data quality. Calculating the CEC load will reveal more about fate and transport in an environmental system than concentrations alone. When it comes to sampling in rivers it was suggested that the discharge (variable dilution) should be analysed and the expected concentration range estimated in order to determine the appropriate number of samples needed (assuming constant load). Again loads should be calculated and not just concentrations. If the load is not constant then more samples are required. For assistance with understanding the uncertainties in a sampling plan, an online helper is available at http://www.samplinghelper.com.

Katrina Borgå (NIVA, NO) moved on to discuss the challenges in field sampling and design when it comes to understanding the bioaccumulation of CECs. The advantage of field based studies when studying CEC bioaccumulation is that the exposure concentrations and times are more realistic, there are multiple exposure routes and processes as well as ecosystem related variables (e.g. spatial/temporal, benthopelagic coupling, temperature, nutrients) being considered. The challenges associated with such studies are that: 1) they usually are "snap shots" in time where one cannot assure steady state, 2) the exposure history is not known, 3) you are dealing with a more heterogeneous population, and 4) it is difficult to quantify the bioavailable concentration and potentially low concentrations and sample size.
In terms of reducing variability, the importance of good quality data was stressed. The transformation and normaliszation of raw data is also a very important consideration. Other sources of variability in metrics include biotransformation, bioavailability, uptake routes, species-specific differences and environmental and food web specifics.

Bård Nordbø (Norwegian Climate and Pollution Agency, NO) told the audience about the Norwegian screening programme, the purpose of which is to map emissions, levels in nature and risk from emerging pollutants in Norwegian and Arctic environments. Examples were provided of the CECs that have been included (brominated flame retardants (HBCDD and PBDE), perfluorinated organic compounds (PFOS, PFOA), chlorinated paraffins (MCCP, SCCP), DEHP (diethylhexylphtalate), bisphenol A, nonyl- and octylphenols, siloxanes, 'emerging' brominated flame retardants, phosphororganic flame retardants, selected pharmaceuticals and personal care products, teflu- and diflubenzurons and sucralose). The results are used in local, national and international measures. Reports are available from http://www.klif.no/no/Publikasjoner/Publikasjoner/.

The panel discussion for this session was focused on whether we have the necessary tools to effectively sample CECs. The key points are summarised in two main conclusions:

- A chemical could be toxic without being taken up by an organism. Passive sampling devices are excellent to detect free dissolved concentrations. This is proportional to chemical activity.
- Passive samplers should be considered for inclusion in specimen banks.

Session 3: What are the next generation of emerging compounds?

Session 3 was opened by *Thomas Ternes* (Federal Institute of Hydrology, DE) who introduced **transformation products (TPs) as new CECs in the water cycle**. Pharmaceuticals and personal care products were used as an example and the key questions addressed were how to identify the relevant TPs (toxic, persistent) formed using analytical, modelling and ecotixicological approaches as well as the technological challenges in avoiding the formation of (toxic) TPs and how to remove TPs. A number of examples were provided of where pharmaceutical metabolites and TPs had been identified in the water cycle. It was concluded that: 1) biological wastewater treatment does not currently lead to a removal of emerging pollutants, but causes the formation of a multitude of polar biological and chemical TPs, with some TPs even reaching drinking water, and 2) there needs to be a lot of time and independent techniques to elucidate and confirm the complete chemical structure of an unknown molecule including its stereochemistry. . It was emphasised that strong oxidants used for disinfection are prone to form (halogenated) TPs (disinfection by-products) and that non-toxic TPs can be transformed into toxic TPs. The overall message was that TPs are new, emerging, frequently unknown contaminants.

The remainder of the third session was filled with suggestions for the CECs of the future. This began with an update of the Norman Interlaboratory study (ILS) on passive sampling of emerging pollutants by *Branislav Vrana* (Water Research Institute, SK). The ILS had 30 participants who measured a variety of pesticides, pharmaceuticals, flame retardants, endocrine disrupters, fluorinated surfactants and brominated flame retardants in passive sampling devices. The results of the study will be available in the autumn of 2012. *Merete Grung* (NIVA, NO) proposed **amines used in CO_2 capture and their transformation products** as possible CECs of the future. These amines can result in the formation of carcinogenic TPs and it is currently not fully understood what risks these pose. *Marlen Vasquez* (University of Cyprus, CY) continued on the theme of **pharmaceutical TPs** and suggested that the effects of pharmaceutical transformation products formed during treatment can go beyond toxicity. These effects were highlighted to be genotoxicity and the retention of anti-microbial activity. *Neville Llewellyn* (Centre for Ecology and Hydrology, UK) highlighted the presence of **cytotoxic drugs** in sewage effluents. They are released from wastewater treatment works and they are present in the water cycle posing an as yet non-quantified risk to human and environmental health. *Katherine Langford* (NIVA, NO) suggested the **chitin synthesis inhibitors, diflubenzuron and teflubenzuron**, used to treat sealice during intensive fish farming as future CECs. In Norway, levels in fjords where fish farming occurs have been shown to be sufficiently high to affect non-target crustaceans, such as shrimp and crab. *Patrick S. Bäuerlein* (KWR, NL) introduced **engineered nanoparticles (ENPs)** as potential CECs in drinking water and its sources. Evidence was provided that ENPs are released into the environment but little is known about their behaviour, although toxic effects have been demonstrated. There is currently a paucity of data regarding ENP occurrence and KWR are currently working on methods to quantify their occurrence in the environment. **Polyfluoroalkylphosphates (PAPs) and perfluorinated phosphonic acids (PFPAs)** were suggested by *Sandra Huber* (NILU, NO) as CECs. PAPs are ammonium salts of perfluoroalkyl

substituted phosphoric acid esters, whilst PFPAs are precursor compounds for perfluorocarboxylic acids (PFCAs). Examples were provided where these chemicals had been shown to be released into the environment, but in general there was little information on their occurrence, fate and effects. *Axel Möller* (Helmholtz-Zentrum Geesthacht, DE) provided a convincing case for **non-PBDE halogenated and non-halogenated flame retardants** as global CECs. These PBDE replacements were shown to occur in the global marine atmosphere (and seawater) with the traditional alternative BFRs (hexabromobenzene (HBB), pentabromotoluene (PBT), and 2,3-dibromopropyl-2,4,6-tribromophenyl ether (DPTE)) present at levels similar to or higher than PBDEs, with organophosphate flame retardants, especially TCPP and TCEP, typically 1–3 magnitudes higher than PBDEs. **HBB and PBT (and pentabromoethylbenzene)** were further supported by *Hans Peter Arp* (NGI, NO), who reported their occurrence and partitioning in the Norwegian environment. He reported high particle sorption of HBB, yet little removal during wastewater treatment, and stressed the importance of the TPs of brominated flame retardants. He suggested that labs currently analysing for PBDEs should include HBB, PBT and PBEB in their analyses. The final group of future CECs presented were **azaarenes and azaarones** by *Pim de Voogt* (University of Amsterdam, NL). Their occurrence was shown in Dutch coastal zone sediments. They result from the oxidation of nitro-PAHs from petrogenic and pyrogenic sources.

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