Network of reference laboratories for monitoring of environmental substances

BULLETIN

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WELCOME TO ISSUE N°1
OF THE NORMAN NETWORK BULLETIN

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

Editorial

A new NORMAN, a new Bulletin

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Welcome to the first issue of the NORMAN Bulletin on emerging substances, which is part of the Joint Programme of Activities of the NORMAN network.

Following the success of the NORMAN Newsletter published during the NORMAN project, we have decided to continue this activity aimed at keeping managers and decision-makers up to date on scientific advances, although we propose a slightly different format for this Bulletin.

We will address, in each issue, various topics of significance in the field of emerging substances, with the aim of bringing together for each topic the results of relevant, recently published scientific studies, giving an overview of the latest findings, gaps and priority research needs – in accessible language.

The Bulletin is addressed primarily to environment and health agencies and public authorities managing environmental risk policies.

This year we have chosen to publish five notes, on highly debated topics such as per- and polyfluoroalkyl compounds (PFAs or also commonly known as PFCs) and bisphenol A (BPA), as well as on less frequently monitored substances such as siloxanes. For PFCs and BPA, concerns about the ecological and human health risks associated with their occurrence in the environment and in consumer products have been put forward by scientists and regulatory agencies quite extensively during the last decade, but important questions are still open, such as those about the relevance to human health of so-called "low-dose effects" (for BPA) and the human exposure pathways (for PFCs). These open questions are closely related to the reliability of analytical data and the developments in analytical measurements, which is the object of the second note on PFCs. Siloxanes are substances of increasing concern. They have been the object of thorough screening in the Scandinavian countries and could soon become the object of increased monitoring in other European countries, too. We have also proposed a note on another substance – sucralose - which has "emerged" only recently and on which questions and the state of the discussion are still in an early phase. The final topic, which will also feature in the 2010 Bulletin, is the environmental specimen banks. In our opinion, they deserve close attention because they are a precious source of retrospective data on potential exposures and environmental concentration trends, which can be extremely helpful in assessing the relevance of emerging substances. Moreover, their potential as a tool is not yet fully exploited.

We will be running with this new version of the Bulletin as an experiment this year. We plan to include in future editions an additional section dedicated to research projects. Moreover, the position papers produced by the network to reflect the common position of the experts on important topics treated in the Joint Programme of Activities of the network will also be included in the Bulletin.

Any remarks and suggestions for improving this Bulletin will be most welcome.

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Environmental specimen banking

Environmental specimen banks as tools for the retrospective monitoring of emerging pollutants

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NEED FOR ENVIRONMENTAL MONITORING

Currently there is a lack of knowledge regarding the fate and effects of many chemicals released into the environment either as products or accidentally. This was the main reason for enacting Europe's new chemicals regulation REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals; Regulation EC 1907/2006 http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2006:396:0001:0849:EN:PDF). An important part of the assessment is the estimation of potential environmental exposures. REACH came into force along with a change of paradigm by transferring responsibility for the risk assessment from regulatory authorities to industry. Thus, in the future it is likely that it will be necessary to conduct monitoring studies to check the plausibility of exposure scenarios submitted by producers and importers.

Generally, monitoring of chemicals in the abiotic and biotic environment provides important information for their risk assessment. Together with effect data from laboratory (eco)toxicity tests, this exposure information can be used within the management process for hazardous chemicals. Experience shows that problems with chemicals have often arisen after they had been in use for years. For example, chemicals with endocrine disrupting properties or polyfluorinated compounds were recognized as hazardous only after decades of commercial use. Moreover, chemicals can often not be detected in the environment because of the limitations of analytical methodology (for example, this was the case for polar compounds such as pharmaceuticals, before LC/MS became available as a routine method). As a result, retrospective data on potential exposures and environmental concentration trends are helpful for the assessment of the relevance of a given compound. Based on such considerations the idea of environmental specimen banks (ESBs) was developed.

ESB HISTORY

As early as the 1960s, several countries set up ESBs in response to increasing emissions of chemicals, e.g., Sweden (Odsjö 2006) and Japan (Tanabe 2006). In the USA an ESB was launched in 1979 (Becker and Wise 2006) and in Germany routine operation of an ESB started in the 1980s after extensive previous research (Gies 2007).

Milestones for ESB development were international symposia in Vienna (proceedings: Sci Total Environ 1993, 139-140), Stockholm (Chemosphere 1997, 34, 9/10), and Charleston, USA (J Environ Monit 2006, 8, 8). Several scientific ESB publications report time trends for emerging contaminants in different ecosystems. Such data are used to support risk assessments of chemicals. More information on existing ESBs is available at the website of the International Environmental Specimen Bank Group (http://www.inter-esb.org/).

WHAT EXACTLY IS AN ESB?

The German ESB uses the following definition: An environmental specimen bank is an archive of representative environmental and human samples which are collected at regular intervals (human cryobanking will not be covered here; for an example see Wiesmüller et al. 2007). The unique feature of ESBs – storing biological and abiotic samples under conditions which assure that their chemical information content does not change over decades – allows the retrospective analysis of plant and animal specimens as well as of abiotic media such as soil or suspended particulate matter from freshwaters.

A key aspect in ESB concepts is the standardisation of all working steps to ensure that changes in chemical concentrations are due to real responses to actual chemical levels in the environment and not to variations of methods. Work steps are often described in standard operating procedures (SOPs) which have to be followed strictly (see German ESB SOPs at http://www.umweltbundesamt.de/specimen/upb22.htm or US National Biomonitoring Specimen Bank SOPs at http://www.hml.nist.gov/MESB.htm).

EXAMPLES OF ESB APPLICATIONS

ESBs have already generated essential data for the exposure assessment of many chemicals by retrospective analysis. Studies of the Swedish ESB on archived guillemot eggs from the Baltic Sea reported concentration trends of brominated flame retardants (Sellström et al. 2003) and perfluorinated compounds (Holmström et al. 2005). ESB data were also used to monitor the success of banning uses of chemicals. For example, data from the German ESB revealed that levels of organotin compounds decreased after regulations were enacted (Rüdel et al. 2007, Rüdel et al. 2009b). Compliance with voluntary renunciations

of chemical use by industry associations could also be proved in some cases (e.g.: alkylphenols/alkylphenol monoethoxylates in freshwater and marine biota, Wenzel et al. 2004; synthetic musk fragrances in freshwater fish, Rüdel et al. 2006).

CURRENT ACTIVITIES

Sessions on environmental specimen banks were run during the SETAC world conference in Sydney in August 2008 and the SETAC Europe conference in Gothenburg in June 2009. Topics related to emerging pollutants were:

- Temporal and spatial trends of new and legacy POPs in German marine ecosystems (Schroeter-Kermani et al. 2009, German ESB): Classic POPs bioaccumulate easily in lipid-rich marine bird eggs, and are therefore good indicators of chemical burdens in the marine environment. Concentrations of PCBs, DDT and HCB significantly decreased until the end of the 1990s, but seem to have levelled off in recent years. Recently, archived herring gull eggs from two decades were investigated for fluorinated and brominated compounds to verify the effectiveness of regulatory and voluntary use restrictions. In the case of perfluorooctanesulfonate (PFOS), so far neither use restrictions declared by industry nor legal measures issued by the European Union have decreased concen-trations of the perfluorinated compounds in gull eggs. Levels in eggs from the North Sea were varying and concentrations in eggs from the Baltic Sea even increased significantly over the last two decades. In contrast, the European ban on the flame-retardants Penta-BDE and Octa-BDE seems to be effective. Preliminary results reveal a more than 50 percent decrease in concentrations of both substance groups in gull eggs. In contrast, there is no clear temporal trend for Deca-BDE.

- Retrospective monitoring of methyltriclosan in freshwater fish covering the period 1992–2008 (Ruedel et al. 2009a, German ESB): This poster gives an update on a monitoring study performed in 2004 revealing that levels of methyltriclosan had increased over a period of 10 years up to 2003 (Böhmer et al. 2004). However, data for the period 2004–2008 now show that methyltriclosan concentrations in fish are no longer increasing, and may even have decreased recently. It is assumed that this is a result of a voluntary renunciation of the use of the parent compound triclosan in washing and cleaning agents by the member companies of the German Cosmetic, Toiletry, Perfumery and Detergent Association (IKW) as announced in 2001.

- Conceptual considerations for environmental specimen banks (Koschorreck 2009, German ESB): The use of ESBs is discussed considering that risk assessors need support with reliable information on both time trends and the biomagnification potential of (emerging) substances. Whereas existing regulatory concepts extrapolate biomagnification from laboratory studies and modelling, ESBs can generate more meaningful information from wildlife, e.g. biomagnification factors.

- Brominated Flame Retardants in Asian Waters: Monitoring Studies Using Archived Samples from es-BANK, Ehime University, Japan (Tanabe et al. 2008a, b). The results indicate that environmental levels of PBDE and HBCD have increased significantly during the last 30 years. In samples from Japan, where usage of some commercial PBDE products was voluntarily discontinued in the 1990s, environmental PBDE levels seem to be constant or slightly decreasing since then. However, concentrations of HBCD revealed an increasing trend. In recent years HBCD levels appear to exceed those of PBDE, reflecting increasing usage of HBCD.

CONCLUSION

ESBs could play an important role, especially in the assessment of emerging substances. Past studies showed correlations between consumption patterns of compounds and tissue concentrations in biota. After banning or phasing out compounds, their concentrations in potentially exposed biota decreased (e.g., organotins, alkylphenols). The use of archived biological samples allows very fast analysis of samples from different years and regions. They are analysed in one laboratory under similar conditions, allowing the detection of small differences between years and sites. The results of such retrospective monitoring could help to assess the relevance of the compound in question (levels and trends). Together with ecotoxicological information, these exposure data are helpful in deciding whether a compound has to be considered as an emerging substance. Several banks in Europe already have the capacity to be used in this way. Thus the potential is present – banks should be used more broadly for the assessment of potential emerging substances.

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Siloxanes in the Nordic Environment

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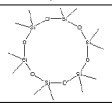
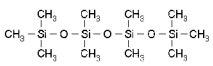
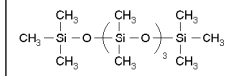
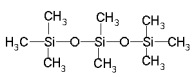
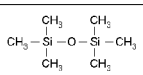
This science note brings together the outcome of recent studies within the field of siloxane contamination in the Nordic environment. It highlights the most important findings and identifies the major conlusions from these studies, as well as future research needs.

SILOXANES - EMERGING SUBSTANCES OF INCREASING INTEREST

Siloxanes are chemical substances containing units with the general formula R2SiO, R representing a hydrogen or a hydrocarbon group. They may be straight chains or cyclic compounds and vary in weight from a few hundred to several hundred thousand g/mol. The siloxanes of main interest from an environmental perspective are the volatile methylsiloxanes, having a short SiO backbone, in particular the cyclic siloxanes known as D4, D5 and D6 and the linear siloxanes, MM (or HMDS), MDM, MD2M and MD3M (Table 1). Out of these commercially used siloxanes, D4 (CAS: 556-67-2), D5 (CAS: 541-02-6), and MM (CAS: 107-46-0) are chemicals of high production volume within the European Union. The first two are the most commonly used siloxanes in the Nordic countries (Kaj et al., 2005b). Recent activities within the Nordic area have focused on investigating the environmental occurrence of the above-mentioned siloxanes, which are used in a large number of industrial and consumer products such as fuel, car polish, cleaners, anti- foaming agents, car waxes, personal care and biomedical products. The widespread use of siloxanes, their broad application, high volatility and potential for toxic effects have raised concerns about these compounds within various disciplines of environmental science. Recent studies indicate that they may be found everywhere in the environment.

Table 1. Nomenclature for siloxanes of recent interest

Abbreviation	Name	CAS #	Structure
D4	Octamethyl-cyclotetra-siloxane	556-67-2	
D5	Decamethyl-cyclopenta-siloxane	541-02-6	
D6	Dodecamethyl-cyclohexa-siloxane	540-97-6	
MM(HMDS)	Hexamethyl-disiloxane	107-46-0	
MDM	Octamethyl-trisiloxane	107-51-7	
MD2M	Decamethyl-tetrasiloxane	141-62-8	
MD3M	Dodecamethyl-pentasiloxane	141-63-9	

RECENT ACTIVITIES WITHIN THE NORDIC AREA

As early as the year 2000, Paxéus and co-workers published a study on the occurrence of organic contaminants in landfill leachates, where MM and D4 were detected at levels of 2–106 and 1–2 µg/L, respectively. In 2005, the Nordic work on siloxanes started off on a larger scale with two parallel screening studies, one in Sweden, financed by the Swedish Environmental Protection Agency (Kaj et al., 2005a) and one in the Nordic environment, financed by the Nordic Council of Ministers, NMR (Kaj et al., 2005b). The main objective with the screening studies is to get a snapshot of the contamination status of the chemicals of interest, in order to identify hot spot areas and fields where continued investigation is needed. Simultaneously, the Danish Environmental Protection Agency undertook an extensive literature review on the Danish consumption of siloxanes, their toxicity and possible alternatives (Lassen et al., 2005). The Danish consumption of siloxanes was estimated at 2400 – 3800 tonnes/year, based on consumption figures from Western Europe. The inventory included in total about 150 different siloxanes and siloxane derivatives. The Nordic screening study focused on the substances listed above, and the highest consumption was reported in Denmark. The Nordic screening study found high levels of mainly D5 in areas of high population, near municipal sewage treatment plants (STP), and frequently in biotic samples, indicating potential for uptake in biota. Particularly high levels of D5 were found in cod liver in the inner Oslofjord. Results are listed in Table 2.

Table 2. Levels of siloxanes in different environmental matrices in the Nordic environment (Kaj et al., 2005b)

Substance	Air (µg/m³)	Water (µg/L)		Sludge (ng/g dw)	Soil (ng/g dw)	Sediment (ng/g dw)	Biota (ng/g ww)
		Sewage/ industrial*	Coastal/ Watercourse				
MM/HMDS	<0.004	<0.0005-0.14	<0.0005-<0.0006	<0.5-<3	<0.1	<0.02-<0.7	<0.4
MDM	<0.008	<0.0005-0.014	<0.0005-<0.0006	<1-64	<0.1	<0.02-<0.7	<0.3
MD2M	<0.006	<0.0005-0.078	<0.0005-<0.0006	1-450	<0.1	<0.02-29	<0.4 – 1.1
MD3M	<0.02	<0.004-0.23	<0.002-<0.004	3-550	<0.1	<0.02-57	<0.5
D3	n.a**	n.a	n.a	n.a	n.a	n.a	<50-90.4***
D4	0.08-4.0	<0.06-3.7	<0.04-<0.09	96-960	<6-<10	<3-84	<5-70
D5	0.05-19	<0.04-26	<0.02-<0.05	1100-89000	<3-<5	<2-2000	<5-2200
D6	0.02-2.1	<0.04-3.8	<0.02-<0.05	220-11000	<2-<4	<1-170	<5-74

* Samples represent influent and effluents to and from sewage treatment plants, landfill leachate and industrial storm water
** n.a = not analysed
*** Detected levels were below limit of quantification.

Since the screening studies, research has continued with several follow-up studies, in particular in Norway and Sweden. These studies include e.g:

- *In-depth studies of volatile methyl siloxanes in foodstuffs and sludge and in- and outgoing water from a municipal treatment plant (Kaj et al., 2007)*. Siloxanes were generally not detected in foodstuffs, but one sample of liver pâté contained detectable amounts of D3 and D4. Measurements performed at a municipal STP indicated a reduction of 68%, and 95 % of D4 and D5/D6 respectively. 21% (D4) and 30% (D5/D6) of the reduced amounts were found in the sewage sludge. The studied STP had a high load of D5 (490 g/d) compared to other Swedish STPs, with a clear contribution from the incoming water stream – largely derived from industrial sources – indicating a local siloxane source somewhere along this inflow line.

- *Detailed investigation of siloxane contamination in the Inner Oslofjord (Schlabach et al., 2007)*. This study confirmed the high levels in cod liver found in the Nordic screening study (1500 – 2000 ng/g ww as compared to 2200 ng/g ww), but other biotic samples (blue mussel, flounder) showed much lower levels (3.3 – 27 ng/g ww). On the lipid weight basis, too, the cod liver and the cod stomach content contained high levels of D5 compared to other species. It was hypothesized that this discrepancy between aquatic species is a result of the physical-chemical properties of D5 and the release pattern. The main emission source of D5 in the Oslofjord area is likely to be the Bekkelaget STP, which emits water to the deeper water layers in the fjord. As a result of their high Kow (logKow,D5 = 5.7), siloxanes will rapidly bind to particles and deposit to sediments, where they may contribute to the exposure of sediment-dwelling organisms and their predators (e.g. cod). Any freely dissolved siloxane is likely to volatilise, thus leaving the surface water and surface water living organisms (mussels, flounder) fairly uncontaminated.

- *Evaluation of toxic effects of siloxanes (Greve et al., 2008)*. Study carried out by the National Food Institute at the Technical University of Denmark, investigating the toxic effects of siloxanes as a group in order to set a health-based quality criterion for ambient air. Toxic effects of D3, D4, D5, D6, and HMDS were studied using a 'read-across' method, which is based on structural similarity and its relation to toxicity. The linear siloxane HMDS appeared to have lower potential for liver toxicity, but higher potential for lung toxicity, than the cyclic substances. Decreasing toxicity with increasing chain length was also indicated. An ambient quality criterion of 0.01 mg/m³ was derived, based on lung toxicity, and including a safety factor of 250.

- *Measurements of siloxanes in digested sludge (SEPA, 2009)*. Preliminary results indicate that cyclic siloxanes were strongly dominated by D5, which varied between 5200 and 27000 ng/g dw, but no temporal trend was found for the years 2004–2008. For the linear siloxanes, sludge levels appeared to increase between 2004 and 2008 in all STPs but two. MD3M was dominant among the linear siloxanes, with levels between 16 and 440 ng/g dw.

- *Analysis of siloxanes in biogas from sludge digesters at Stockholm Water (Wahlberg, personal communication)*. This is an on-going study measuring siloxanes in the gaseous by-products of digestion chambers treating municipal sewage sludge in Stockholm, Sweden. Preliminary results show levels of the sum of D4, D5, D6, MM, MDM, MD2M and MD3M of 21–73 mg/m³, of which D5 accounted for 74–95 % and the linear siloxanes accounted for 1–4 %. The overall aim with this study is to investigate the possibility for cleaning the gas in order to use it as fuel.

- *Interlaboratory comparison of siloxanes in codfish collected in the Oslofjord (Durham et al., 2009)*. Three different laboratories parti-

cipated in this intercomparison exercise, of which NILU was one. The results confirmed earlier reported levels (Kaj et al., 2007, Schlabach et al., 2007). Statistical differences were observed for individual substances and laboratories, and methods for extraction and liver processing were somewhat different between the different labs. In general, however, a good level of agreement between the three labs was obtained concerning the liver concentrations of siloxanes.

- *Evaluation of Swedish screening data in air and deposition (Palm Cousins et al., submitted)*. Siloxanes represent one substance group which has been subjected to a methodological evaluation of organic chemicals that have been included in the Swedish EPA's screening programme between 2000 and 2005. The aim was to identify which substances or groups of substances should be prioritized for long-term atmospheric monitoring. Based on this assessment, siloxanes were not considered to belong to the chemicals of highest priority for inclusion in long-term air monitoring. D4 was listed under chemicals that should be "kept under surveillance", whereas the need for atmospheric monitoring of D5 and D6 was considered to be less important.

FINAL REMARKS AND CONCLUSIONS

The above-mentioned studies indicate that siloxanes are generally occurring contaminants in the Nordic environment. The dominant substance in environmental samples is the cyclic siloxane D5 (Decamethylcyclopentasiloxane). The main emission routes appear to be via diffuse sources ending up in sewage water and storm water streams, thus generating elevated levels in sediments and biota near STP effluents and in densely populated areas. Substantial amounts can also be found in municipal sludge, which may be of concern if the sludge is meant to be put to agricultural use. Foodstuff does not seem to be an important exposure route for humans. Siloxanes are also found in air, but the various samples analysed could not clearly indicate the major sources to the levels found in this matrix. It was suggested that air sampling along an urban-rural gradient, or with increasing distance from an STP plant, may generate answers as to which sources are of major importance for atmospheric levels of siloxanes. The evaluation of substances included in the Swedish EPA's screening programme concluded that there is no immediate motive for prioritization of this group for long-term air monitoring. It was stated however, that additional information, such as expected changes in consumption patterns, or additional knowledge about toxicity may alter this prioritisation. An ambient air quality criterion of 0.01 mg/m^3 has been proposed for the linear siloxane HDMS (MM), a substance which has not been detected in any air samples analysed (d.l 0.004 µg/m^3). The question regarding biotic uptake and potential for bioaccumulation and/or biomagnification needs to be further investigated. Siloxanes have been found in biotic tissues, and high levels were found in particular in cod caught in a contaminated area. In the Nordic screening study, however, it was not possible to state whether observed levels in biota is due to uptake via water, food or a combination of these. The Norwegian study on siloxanes in different aquatic species from the same area suggest that the choice of food and preferred depth may have an influence on the uptake processes of siloxanes in biota. A recent risk assessment performed in the UK (Brooke & Crookes, 2009) reports a high bioconcentration factor of 7060 L/kg for D5. This study identified risks for some freshwater and marine sediments at local source sites and could not fully assess risks to predators feeding on earthworms due to uncertainties associated with biomagnification factors and PNEC. Apart from this, no risks were identified. More studies investigating levels in surface water, sediments and biota from different trophic levels would bring further light into this issue. In brief, the following general conclusions can be drawn from the Nordic studies on siloxanes:

- Methods for sampling and analysis of siloxanes in biota show acceptable agreement between labs, even though minor deviations have been identified. However, as the intercomparison only concerned three labs on the expert level, and only biota, there is still a need for intercomparative studies of siloxanes in other matrices, involving also routine laboratories.
- Siloxanes are widely distributed in the Nordic environment and diffuse sources via the sewage system to the aquatic environment are the dominant emission pathways.
- There are atmospheric sources to siloxanes, but the atmospheric turnover is relatively quick and therefore this matrix is not the most important for monitoring of siloxanes.
- Foodstuff is not likely to be an important exposure route to humans.
- Further studies are needed to clarify the mechanisms and extent of biotic uptake and bioaccumulation, in the Nordic environment. A recent risk evaluation study in the UK reported high BCF for D5 but identified risks only to some freshwater and marine sediments near sources.
- Initial studies have been performed to investigate the toxicity of siloxanes. This is, however, a field that requires more research, as the overall knowledge on siloxane toxicity is still limited.

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Sources, Fate and Exposure to Poly- and Perfluoroalkyl Substances

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Report from a special workshop held at the 12th EuCheMS International Conference on Chemistry and the Environment, 14th June 2009, Stockholm, Sweden.

Poly- and perfluoroalkyl substances (PFAs) represent a diverse group of high production volume chemicals that have been used in industrial and consumer product applications since the 1950s. The applications are numerous and include metal plating, firefighting foams, processing aids in fluoropolymer manufacture, and incorporation into polymeric and surfactant products that are used as oil- and water repellants in leather, paper and textiles. Owing to their persistence and potential to accumulate in living organisms, concerns about the ecological and human health risks associated with environmental contamination of PFAs have been put forward by scientists and regulatory agencies.

A workshop at the 12th EuCheMS International Conference on Chemistry and the Environment was a forum for discussing recent developments in the environmental chemistry of PFAs. Although there were two plenary lectures given by Scott Mabury (University of Toronto) and Robert Buck (E.I. du Pont de Nemours), the special feature of this workshop was that the majority of the time was devoted to discussing the state of the science in (i) Analytical Developments and Monitoring, (ii) Biological Effects and Toxicology and (iii) Sources, Fate and Exposure to PFAs. The workshop attracted more than 120 participants from various research disciplines in academia as well as representatives from industry and regulating agencies. This article reviews some of the interesting discussions and new research presented in the area of "Sources, Fate and Exposure to PFAs", with the aim of drawing attention to important gaps in knowledge and recommendations for further research. Another article in this newsletter reports on the discussion forum on "Analytical Developments and Monitoring".

ABBREVIATIONS AND TERMINOLOGY: THE NEED FOR CONSISTENCY

The amount of published research on fluorinated compounds has increased exponentially over the past five years. Robert Buck highlighted in his plenary lecture that with the rapid development of this field there is a lack of a distinct and consistent terminology which is broadly accepted among active researchers in the field. For example, several acronyms have been adopted in the scientific literature for this large family of substances that have very different chemical, physical and biological properties. The most commonly used acronym is PFCs, usually standing for perfluoroalkyl compounds, although it has also been used to stand for perfluoroalkylcarboxylates (dissociated form of perfluoroalkyl acids) (Armitage et al., 2009a), polyfluoroalkyl compounds or "perfluorocarbons", meaning fully fluorinated alkanes (C_nF_{2n+2}), which are one of the groups of compounds regulated under the Kyoto Protocol on greenhouse gases. There are numerous other examples of confusing acronyms and terminology in the field.

A specific example of a confusing terminology highlighted in the discussion forum was the use of the terms "direct" and "indirect" to characterize two different types of sources. It became obvious that the definitions of "direct" and "indirect" were far from clear to everyone; in fact it was noted that several definitions exist in the literature. Prevedouros et al., (2006), defined direct sources as industrial emissions which occur during intentional manufacturing and use of perfluoroalkyl carboxylic acids (PFCAs), while indirect sources were defined as releases due to the presence of the substance as a residual impurity (i.e. present unintentionally) and through degradation of "precursor" compounds. Similar terminology was used by De Silva and Mabury (2006) who defined emissions of PFCA processing aids as a direct source and biotic or abiotic degradation of precursor compounds as indirect sources of PFCAs to humans. Paul et al., (2009) however, defined direct sources to include only manufacturing emissions and indirect sources as all other sources. Trudel et al., (2008) may have caused further confusion by using the terminology often used in exposure modelling of "direct exposure sources" to describe human exposure to consumer products and "indirect exposure sources" as exposure to environmental media. It was agreed that the direct/indirect source terminology, when used, needs to be carefully and explicitly defined to avoid more confusion in the literature.

In order to improve consistency in the future it would be a useful exercise for experts to agree on a common glossary of acronyms and terms.

SOURCES OF PFAS TO THE ENVIRONMENT

Since perfluorooctane sulfonate (PFOS) was first found to be globally present in wildlife (Giesy and Kannan 2001) there has been a lively scientific debate about the sources of perfluoroalkyl sulfonic acids (PFSAs) and PFCAs in the environment, and this debate continued at the workshop. The early work of Scott Mabury and co-workers established that volatile precursor compounds such as the fluorotelomer alcohols (FTOHs) and perfluoroalkane sulfonamidoethanols (PFASEs) break down to form persistent PFCAs andPFSAs. As these precursor compounds were used in high quantities to synthesize commercially important products they were hypothesized to be a major source of PFSAs and PFCAs in the environment (Ellis et al., 2004). For perfluorooctanoic acid (PFOA), an alternative hypothesis, first proposed in the literature by Prevedouros et al., (2006), suggests that the majority of the PFOA present in the environment stems from the historical manufacture and use of ammonium perfluorooctanoate (A-PFO). A-PFO has historically been primarily manufactured by the Electrochemical Fluorination (ECF) process and used as a processing aid in the manufacture of polytetrafluoroethylene (PTFE) (Prevedouros et al. 2006). Mass balance modelling studies (e.g. Armitage et al., 2006, 2009a,b) have successfully reconciled inventories of PFOA and even perfluorononanoic acid (PFNA) present in the environmental with global historical estimates of source emissions. However, skeptics have questioned the accuracy of the historical global emission estimates published in Prevedouros et al., (2006) and thus the plausibility of the mass balance exercise. It was therefore an exciting development that new experimental results presented at the conference showing PFOA isomer profiles in ocean waters were able to provide an independent test of the different source hypotheses. Isomeric profiles of PFOA in ocean waters from this work were shown to be generally consistent with that of an ECF standard (20–30% branched) (Benskin et al., 2009), with the exception of one sampling site in an industrialized harbour area (Tokyo Bay).

The observed isomer profile is consistent with the hypothesis that historical ECF-derived emissions are the major source of PFOA to the oceans (Prevedouros et al., 2006). However, the authors of the work added a word of caution in over-interpreting their results, as preferential enrichment of branched isomers in surface waters may influence the observed pattern (Benskin et al., 2009).

Although recent mass balance modeling work by Armitage et al., (2006, 2009a,b) suggests that historical source emissions of PFOA (C_8) and PFNA (C_9) are broadly consistent with available monitoring data, the sources of higher chain-length homologues (>C_9) remain unresolved. Armitage et al., (2009a) showed that model estimated concentration ratios of C_{11}:C10 and C_{13}:C_{12} in abiotic compartments are difficult to reconcile with concentration ratios reported in biota. Concentrations of C_{10} and C_{12} in biota are higher than can be explained from "direct" manufacturing/use emissions alone and what is known about the relationship between bioaccumulation potential and chain length. The model results imply that either (i) indirect (volatile precursor) sources are dominant for the C_{10} and C_{12} homologues or (ii) estimates of direct emissions are not accurate for these homologues.

The source debate is further complicated by the fact that the relative importance of different sources depends on the type of environment being studied. Clearly inland environments such as the High Arctic, soils and many lakes will be largely impacted by atmospheric inputs. Armitage et al., (2009b) suggested that direct sources of PFOA to the atmosphere could still make an important contribution to atmospheric deposition of PFOA even in remote environments but definite conclusions cannot be reached until the controversy regarding the acid-dissociation constant (pK_a) is resolved (see next section). Sources of PFOA to the atmosphere resulting from the degradation of volatile precursor compounds may also be underestimated because only a few of the potential precursors have been studied to date. Novel data of fluorotelomer acrylates (FTACs) at concentrations similar to those of FTOHs (Dreyer et al., 2009) underline that atmospheric transport models may have underestimated the deposition of PFCAs from precursor degradation (Butt et al., 2009).

Much of the above discussion focuses only on the sources of PFCAs and excludes discussion of the sources of perfluorooctanesulfonyl fluoride (POSF)-based products (including PFOS). It was noted at the workshop that it has not so far been possible to obtain much official information on the industrial discharges of POSF-based compounds, although some attempts have nevertheless been made at making source inventories for PFOS (Paul et al., 2009; Armitage et al., 2009c).

TRANSPORT, FATE AND BIOACCUMULATION

James Armitage (Stockholm University) suggested in the discussion forum that a major obstacle to pursuing more refined multimedia fate modelling of PFAs is the uncertainty in key physical–chemical properties. In particular, the true value of pKa for long chain PFCAs has major implications for the atmospheric transport potential of these compounds. Hans Peter Arp (Norwegian Geotechnical Institute, Oslo) provided his thoughts on the pKa debate currently going on in the literature. A pK_a of 3.8, as measured by Burns et al., (2008) would imply that the volatilization of neutral PFOA from low pH water surfaces and condensed water droplets in the atmosphere could be an important environmental transport process. On the other hand, if the pKa is <1 as advocated by Goss and Arp (2009) then water is much more likely to be a sink and not a source of atmospheric PFOA. Further, with such a low pK_a, condensed atmospheric water (e.g. clouds, fogs, marine aerosols) would be expected to "taxi" PFOA in the atmosphere, as both adsorption and absorption to water droplets would be substantial. The problem with constraining the pK_a of PFCAs using a titration method primarily lies in the aggregation of both the acid and its conjugate base leading to the formation of dimers and larger aggregates at typical laboratory concentrations, which in turn influences the apparent pK_a. For example, the presence of oligomers of the anion (i.e. An, where n ≥ 2) suppress the apparent pK_a, whereas the presence of oligomers of the acid (i.e. H_nA_n) elevate the apparent pK_a. Cheng et al., (2009) in a study published just weeks after the workshop, concluded dimers of the form $(PFO)_2H$ readily form at low concentrations, and raise the apparent pK_a in laboratory experiments; they, also concluded the pKa of monomeric PFOA is < 1. The possibility of aggregation in the environment may also influence their environmental fate. If it turns out that PFCAs dimerise at environmentally relevant concentrations or under environmentally-relevant conditions, then dehydration of newly formed marine aerosols may add to the transport mechanisms across the water–air interface. To overcome the uncertainty in pK_a, indirect methods including measurement of the Henrys Law constant at varying pHs may present a feasible option to test the previous observations. The experiences during analytical method development among the workshop participants do not seem to support a pK_a of 3.8 of PFOA. For example, it was pointed out that extraction and clean-up procedures in strongly acidified solutions (pH 2) have produced excellent recoveries with no observed volatilization of PFCA analytes.

Amila de Silva (Environment Canada, Burlington) provided an overview of recent research in the field on the underlying mechanisms of uptake, retention and elimination of PFAs in biota. It has been shown that bioconcentration in fish is dependent on PFCA chain length (Martin et al., 2003), indicating that hydrophobicity of the perfluoroalkyl chain is an important predictor of accumulation in biota. Hence, applying the critical micelle concentrations (CMC) as a hydrophobicity predictor may be a feasible approach, but hydrophobicity predictors cannot explain the observed differences in bioconcentration and bioaccumulation potential between perfluoroalkyl carboxylates and sulfonates. As biomagnification in aquatic species appears to give conflicting results in the lab and the field, it is even more difficult to develop a meaningful normalization criterion for PFCAs and PFSAs. In contrast to controlled laboratory studies, the positive relationship between BMF and perfluoroalkyl chain length has been observed to curve off for the higher homologues (C>11) in field studies. Typically, PFA bioaccumulation/biomagnification has been evaluated on a total body wet weight basis. However, the derivation of whole body burdens becomes a challenge for higher trophic levels of a food web. As long-chain PFCAs and PFSAs have a high affinity for plasma proteins and accumulate in blood rich organs such as liver and kidneys, Kelly et al., (2009) recently reported protein normalized trophic magnification factors of PFCAs in an Arctic food web. Although interesting, the total protein normalization may not be appropriate because different proteins can have a varying affinity for PFCAs and PFSAs and the expression of these proteins may display differences between species and sexes. An additional problem with currently calculated BMFs is the exclusion of precursor compounds that are metabolized to PFCAs/PFSAs. Armitage et al., (2009c) explored the possibility that the uptake of POSF-based precursor compounds followed by subsequent metabolism to PFOS was the underlying mechanism for the divergent time trends in Arctic wildlife (Butt et al., 2007; Bossi et al., 2005; Hart et al., 2009). Biotransformation rates for precursors have only been examined for a few laboratory test animals (mice, rats and trout). Thus, uncertainty in extrapolating biotransformation rates for these test animals to other species in food web studies is currently hampering the inclusion of precursors in BCF/BMF calculations.

THE PATHWAYS OF HUMAN EXPOSURE TO PFAS

The discussion forum closed with a lively discussion of the human exposure pathways for PFAs. Despite extensive efforts over recent years to monitor PFAs in human serum, there still remains uncertainty about the major exposure pathways. Factors contributing to the complexity of human exposure are the multitude of media from which exposure may occur and temporal changes in consumer product formulations that complicate the interpretation of historical and ongoing exposure. A key question, surrounded by some controversy, is the extent to which exposure to and metabolism of precursor compounds are responsible for the concentrations of perfluoroalkyl acids in human sera (Vestergren et al., 2008). Retrospective analysis of identified oxidation products of PFASEs (Olsen et al., 2005) is clear evidence of expo-

sure to fluorinated materials used in carpet and textile treatment and food packaging materials in the past. Taken together with a rapid decrease of PFOS in human sera after the year 2000, when the POSF phase-out commenced, it may be concluded that exposure to precursor compounds in consumer products was a substantial source of PFOS. However, the sources of PFOA in human sera are more difficult to elucidate as PFOA may originate from both historical and ongoing production sources. The matching initiation year of decreasing concentrations and a significant correlation between PFOS and PFOA concentrations in human sera indicate that these compounds had a historical exposure source in common. On the other hand, some authors have noticed that the concentrations of PFOS decrease at a faster rate than those of PFOA relative to the total elimination half-life in humans of the respective compounds (Olsen et al. 2008). Therefore the apparent difference in disappearance rates indicate a decoupling of the ongoing exposure sources of PFOS and PFOA after the year 2000-2002.

Current exposure modelling studies suggest that intake of food is a major background exposure source of PFOA compared to other environmental and consumer product based exposure sources after 2002 (Trudel et al., 2008; Vestergren et al., 2008). These estimations of exposure were criticized by Scott Mabury, who suggested that the assumptions in these studies were so constrained that it was impossible to reach such a conclusion. He also emphasized that polyfluoroalkyl phosphoric acid esters (PAPs) were not included in these exposure modelling studies. The recent findings of PAPs in human sera of the North American population illustrate that exposure to PAPs may be an overlooked source of PFCAs to humans (D'eon et al., 2009a). As well as consideration of PAPs, much effort is needed to provide improved analytical data for other PFAs in food to further test the conclusion of Trudel el al., (2008) that food is the major contemporary human exposure pathway.

NEW PFAS AND SIDE-CHAIN-FLUORINATED POLYMERS

Although not discussed at length during the discussion forum, it is worth highlighting that novel results were presented by Scott Mabury's group on the fate, occurrence and persistence of commercially used materials such as PAPs, and on the degradation of side-chain-fluorinated polymers. The findings of PAPs in waste water and paper- and pulp sludge together with refined studies on their degradation imply that reservoirs of these compounds may act as sources of PFCAs (D'eon et al., 2009a). POSF-based PAPs were widely used in basically any paper that needed to be grease-protected, including sweet wrappings, butter wrapping, fast food wrappings and paper plates prior to phase-out in 2002. Scott Mabury suggests that the paper industry also widely uses FTOH-based PAPs. This statement is supported by the finding of PAPs in recently collected popcorn bags from Denmark and Canada (Trier et al., 2009). Interestingly, DuPont representative Robert Buck was of the opinion that FTOH-based PAPs are not currently used much in food contact paper. He described it as "old technology" and was of the opinion that the paper industry uses mainly polymeric products for grease protection these days. Hence, it would be particularly interesting to obtain temporal trend data of PAPs in paper- and pulp sludge to test the intriguingly contradictory statements regarding the contemporary manufacture and use of these compounds.

It was further reported in Scott Mabury's plenary lecture that side chain fluorinated polymers synthesized at laboratory scale in his group degrade to form PFCAs at a much higher rate than previously observed. The findings of polymer degradation are divergent to a previous study demonstrating that perfluoroacrylate side-chain-polymers are recalcitrant to degradation under aerobic conditions (degradation half-lives of 1200–1700 years) (Russell et al., 2008). The polymers synthesized in Mabury's group are not identical to those in commercial use and so the obvious reaction by industry may be to claim that the experiments are not relevant. However, Scott Mabury ensured that in designing their polymer they precisely followed a combination of patents from major polymer manufacturers, functionally equivalent to those in actual use (although purposely not identical). Just a couple of weeks after the workshop, Washington et al., (2009) reported degradation half-lives of side-chain-fluorinated polymers similar to those of Russell et al., (2008). But, assuming surface mediated reaction kinetics, Washington et al. suggested that the degradation half-life of a commercial side-chain-fluorinated polymer may be substantially lower (10–17 years) for more finely grained polymers (Washington et al., 2009). Considering the high production volume of side-chain-fluorinated polymers and their legacy use, even a low degradation rate would have implications for global emission inventories (Prevedouros et al., 2006; Paul et al., 2009) and even human exposure (Trudel et al., 2008). Hence, follow up research on the experimental factors affecting the degradation of polymers and most realistic conditions to mimic an environmental setting is strongly needed.

Another interesting finding presented was the discovery of perfluoroalkyl phosphonic acids (PFPAs) in surface waters and waste water effluents (D'eon et al., 2009b). Although the origin of this "new" class of PFAs has only been briefly investigated, the uses of PFPAs are thought to include use as wetting agents and anti-foaming additives in pesticides. The future study of PFPAs is relevant, as they are likely to have similar bioaccumulation potential and toxicological effects compared to PFCAs and PFSAs. Scott Mabury noted during his plenary presentation that the presumably similar physical–chemical properties to PFCAs and PFSAs and lack of known precursor compounds also makes the continued monitoring of PFPAs valuable to unravel the transport mechanisms of legacy PFAs.

In response to the environmental risks associated with poly- and perfluoroalkyl substances, industry has made a series of voluntary efforts to reduce emissions from manufacturing and use of many PFAs. A commitment to phase out production of eight carbon fluorinated chemicals by 2015 at the latest has also been signed by the major producers in Europe, North America and Japan. Currently, the industry is moving towards shorter perfluoroalkyl chain replacement chemicals in order to reduce the bioaccumulative potential of these compounds (Telomer Research Program 2002). But the reformulation of fluorinated products does not mean that exposure to humans and wildlife will be negligible. In fact, the replacement substances are all persistent and bioavailable, but crucially not likely to accumulate in biota. Robert Buck said that the key difference between the old and the new PFAs is that the new shorter-chain products are non-biopersistent and thus not likely to cause toxic effects. Concerns were, however, expressed by Scott Mabury about the potential for short-chain precursor compounds to form fluorotelomer acids and fluorotelomer aldehydes that may react with biological material (Rand and Mabury, 2009). The question marks regarding replacement chemicals along with continued exposure to legacy PFAs are important issues that warrant continued research about the presence of PFAs in the environment.

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Analytical developments and monitoring of poly-and perfluoroalkyl substances

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Report from a special workshop held at the 12th EuCheMS International Conference on Chemistry and the Environment, 14th June 2009, Stockholm, Sweden

Understanding the reliability of analytical data from environmental measurements of poly- and perfluoroalkyl substances (PFAs) is essential to understanding environmental exposure, fate, and transport. Since the year 2000 over 2400 peer-reviewed papers have been published about these compounds (Scopus, 2009). Initially there were few analytical standards of known purity available and there were no isotopically enriched standards to aid in analysis and quantification of environmental and human levels of PFAs (Martin et al, 2004; de Voogt and Saez, 2006; Larsen and Kaiser, 2007). Over time many of these materials have become commercially available, but questions still remain about the accuracy, precision and environmental meaning of these measurements. The workshop preceding the 12th EuCheMS Conference addressed many of these analytical questions.

CRITICAL CONSIDERATIONS FOR SAMPLING AND ANALYTICAL DETERMINATION OF HIGHLY FLUORINATED SUBSTANCES

Mary Kaiser (DuPont, Wilmington, DE, USA) presented recent studies showing that eleven- and twelve-carbon perfluorocarboxylic acids (PFCAs) in aqueous solution adsorbed to polypropylene (PP) containers (but not onto amber glass or high-density polyethylene). Approximately 25% of the C_{11} PFCA and 50% of the C_{12} PFCA were lost after 28 days at ambient temperature. All the same, EPA drinking water method 537 (EPA, 2008) specifies PP containers to be used in PFA analysis. ISO method 25101 (ISO, 2009), a drinking, ground, and surface water method for perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) also specifies PP containers.

Since PFCAs are hydrophobic in the neutral (protonated) state, care must be taken at low pH levels so that losses do not occur into the headspace. Since both the commonly observed acids and ammonium salts sublime, care must also be taken in bringing solutions to dryness. Good peak symmetry is necessary for reliable integration of analyte peaks. Mary Kaiser pointed out that a hydrofluorocarbon solvent (DuPont Vertrel®) showed peak distortion in liquid chromatography when used to dissolve some fluorotelomer alcohols (FTOHs). When methanol was used instead, peak symmetry returned.

HOW SURE ARE WE ABOUT THE QUALITY OF PFA ANALYSES?

The Institute for Environmental Studies, Free University, Amsterdam, The Netherlands, and the Man-Technology-Environment Research Centre at Örebro University, Sweden, carried out worldwide interlaboratory studies of PFAs in human and environmental matrices (van Leeuwen et al., 2006 and 2009). Interlaboratory comparisons are important in helping regulators set exposure levels and make decisions on assessing risk. Stefan van Leeuwen (Institute for Environmental Studies, VU University, Amsterdam, The Netherlands) reported that performance improved tremendously for analysis of fish and water between the first and second comparison studies. The key difference between the two was that, in the second, many isotopically enriched standards and improved quality native standards were provided. Van Leeuwen suggested that this high performance level in the second comparison study may not be able to be retained when each laboratory returns to using standards from diverse sources, the laboratories attempt to go to lower concentrations, and the matrices become more complicated. Additional interlaboratory comparisons need to be initiated in other matrices such as air, sediment, soil and food. When these interlaboratory comparisons are accomplished, we will better understand the quality of the data.

CHALLENGES IN THE ANALYSIS OF FOODS FOR PFAS

Dietary intake probably accounts for about 60% of human exposure to PFAs. Many of the reports about food levels in the peer-reviewed literature to date use liquid chromatography with tandem mass spectrometry (LC/MS/MS), but often the chromatographic resolution is not sufficient to differentiate among branched isomers. Using gas chromatography mass spectrometry (GC/MS) may be a better alternative for neutral PFAs. Sheryl Tittlemier (Health Canada, Ottawa, Ontario, Canada) further reported that controlling and understanding potential sample contamination from within the laboratory or from packaging is essential. She reported that nylon filters sorb PFOS but polytetrafluoroethylene-lined lids did not introduce PFOA contamination into a sample. With LC/MS the matrix can either suppress or enhance the signal. This effect is usually due to co-eluting matrix constituents, so that improved sample clean-up can help eliminate this problem. For determination of PFAs in food, isotopically enriched internal standards are essential.

ANALYSIS AND MONITORING HUMAN EXPOSURE OF PFAS

PFAs are globally distributed in human beings (Kannan et al., 2004; Kärrman, 2006). Levels appear to be declining in the United Sates and Norway for some lower chain lengths. Anna Karrman (Man-Technology-Environment Research Centre, Örebro University, Sweden) showed that Swedish human blood levels declined for PFOS and PFOA between the periods 1997–2000 and 2007–2008, while at the same time concentrations of longer chain PFCAs increased. A future challenge is the separation and accurate quantification of branched PFA isomers. Better isomer separation can occur with a longer, slower LC gradient. Anna Kärrman reported that isomers can have significantly different detector response factors in different MS/MS transitions. She found that it is important to monitor several transitions to assure the identity of the individual peaks.

OBSERVATIONS ON THE DETERMINATION OF PFAS IN AIR

In recent years attention has expanded from environmental monitoring of acidic PFAs to include neutral compounds such as fluorotelomers (olefins, alcohols, acrylates), fluoroalkyl sulfonamides, and fluoroalkyl sulfonamidoethanols. For these volatile or semi-volatile compounds, adsorbents such as XAD resin and glass fibre filters are employed for sampling. These media are extracted and the solutions analyzed via GC/MS. Jon Barber (Centre for Environment, Fisheries and Aquaculture Science, Lowestoft, UK) reported that significant deterioration of chromatographic performance occurred over time for analyses involving analytes with an alcohol group. Loss of peak resolution was not readily observed for the other functional groups. Typical instrument maintenance such as changing the liner or removing a few centimeters from the column helped, but it did not achieve optimum signal

output. Deactivating the column with a "dirty" sample seemed to affect the best peak shape and signal strength. Often matrix effects are not constant across the whole chromatogram. These effects are usually due to co-extractants and can be mitigated somewhat by using multiple internal standards (Jahnke et al., 2009).

Fluorotelomer olefins were especially difficult to capture on media, and to measure, due to their high volatility and tendency to elute from the GC column before the injection solvent. Often there is breakthrough on the sampling media and losses due to evaporation during the concentration steps. In general the lack of isotopically enriched standards and the lack of multiple ions for confirmation make these determinations highly challenging.

Using monitoring studies to investigate PFA dynamics and pathways
In order to understand what is happening to PFAs in the environment over time, it is necessary to perform time trend studies. Good time trend studies require a long time course and the examination of multiple wildlife species. Craig Butt (University of Toronto, Ontario, Canada) discussed how time trends and monitoring studies in general might help us to understand the sources (direct/indirect) and fate of PFAs in the environment. Inherent challenges in time trend studies include obtaining appropriate archived samples, having samples that allow sufficient temporal resolution (inter-year variability), and getting samples from a sufficiently long time course.

DISCUSSION

In the discussion period following the formal presentations, several additional topics were considered.

- How are surfactants dissolved?

Using a strong solvent to dissolve the surfactant then diluting appropriately for introduction onto the chromatographic column has worked for some systems. Shaking or ultrasonification often causes foam formation. Cooling the ultrasonic bath will help avoid sample degradation or evaporation of the analyte and solvent.

- Should blanks be subtracted?

Blanks should never be subtracted if the blank levels are high. One should determine what is causing the high blanks and eliminate the problem. If the blanks are small, be consistent and blank subtraction should not be a problem.

- Are the collection media causing problems with blood samples?

Some studies have examined the collection and storage media and have not found them to have background levels for some analytes. Some polypropylene containers apparently have background levels of PFCAs of multiple chain lengths. These acids may have come from slip agents used in the manufacturing of the tubes or caps. Exposure of the tubes to the background in the laboratory might also bring about background contamination. Experience suggests that these media should be checked before use, especially if they come from a different manufacturing lot. Some laboratories routinely solvent rinse their labware, but this adds to additional time and solvent waste.

- Should manufacturers put Chemical Abstract Service Numbers on their internet sites to help scientists?

When CAS numbers are available, they should be used since they are unique identifiers of molecules. Structural information would also be useful. However, since marketing groups usually design the web site content, such specific "chemical" information may be lacking. Company scientists and customers need to intercede to make this information available.

- The second interlaboratory comparison got better results, but are they the "right" answer? Linear standards were used. Do we need to match isomer patterns in our standards?

Quantifying isomer mixtures on the basis of linear standards can indeed lead to a bias in accuracy. However, matching isomer patterns poses analytical challenges and may be too laborious for screening studies. For complex biological media, the isomer pattern would have to be known in advance. The pattern could be different in the same matrix but from a different location. In toxicity studies, it may be beneficial to have isomer information since the toxicity of one isomer may be quite different from another and the bioaccumulation potential may also differ.

- Are food samples difficult to analyze?

Yes. Each sample is a different matrix for food. Concentrations of analytes are often very low.

- Are more sensitive instruments going to make it easier to perform analyses, since concentration steps may not be required and dilutionmay become a part of the method?

Matrix effects would be reduced upon dilution. The effect of dilutions would have to be examined to see the effect on the accuracy of the measurement. However, more sensitive instruments and diluted samples may lead to larger relative importance of blank contamination.

OVERALL CONCLUSIONS

- Isotopically enriched internal standards are vital for accurate determination of PFAs; the more the better.
- Lab contamination and matrix effects are still important issues and have to be controlled.
- Isomer specific analysis is important for exposure/toxicity studies, bioaccumulation and source apportionment, but not necessary for screening and monitoring studies.
- Certified reference materials are needed and are under development.
- Interlaboratory comparison studies show a promising improvement but only if common native and isotopically enriched standards are used.

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Interlaboratory Comparison on Sucralose

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INTRODUCTION

The substance sucralose (CAS No 56038-13-2) has a strong sweet taste and is one of several artificial sweeteners used in food and beverages. It was recently reported as being present in treated sewage effluents in µg/l concentrations and also in surface waters in Norway and Sweden [1-3]. This is not surprising, as it is known that sucralose passes through the human body essentially unchanged, thus contains no metabolic calories, and is excreted in the urine [4]. The analytical results from the outdoor environment were questioned.

To strengthen the findings, the Swedish Environmental Protection Agency gave an assignment to IVL Swedish Environmental Research Institute to conduct an interlaboratory study on analysis of sucralose in relevant concentrations in environmental waters. The idea was to invite laboratories internationally to analyse a few samples with methods of their own choice. This was done in the autumn of 2008. The results were reported back to the participants in November 2008 and are also reported in some detail here. Since then, sucralose concentrations in a large number of European river waters have been reported [5].

Sucralose has also been measured together with other artificial sweeteners in German waste waters and surface waters [6]. The environmental concern is not about acute toxicity, but about a slowly degraded substance potentially building up higher concentrations and, for example, entering drinking water systems or having an undesirable influence on sensitive organisms.

PARTICIPATING LABORATORIES

Participants in the interlaboratory comparison were invited using the Norman network website [7] and also at a meeting held in Copenhagen on 18 June 2008 on the initiative of the European Environment Agency. Nine institutions, all in different countries, registered (Table 1).

Table 1 Institutions that registered and received samples. The institutions in bold text reported results.

Institution	Country
Center for Environmental Biotechnology, Arizona State University, Tempe, Arizona	**USA**
Department of Applied Environmental Science, ITM, Stockholm University, Stockholm	**Sweden**
Department of Environmental Chemistry, IIQAB-CSIC, Barcelona	Spain
Environmental Chemistry, Eawag, Swiss Federal Institute of Aquatic Science and Technology, Dübendorf	**Switzerland**
Institute for Environment and Sustainability at JRC, Ispra	**Italy**
Institute of Food Chemistry, University of Hohenheim, Stuttgart	Germany
National Water Reference Laboratory for Slovakia, Bratislava	**Slovakia**
Norwegian Institute for Air Research, NILU, Kjeller	**Norway**
School of Studies in Chemistry, Raipur	India

SAMPLES FOR ANALYSIS

Effluent water from a large municipal sewage treatment plant (Henriksdal) in Stockholm, Sweden was collected on 29 May 2008. The water, 45 L, was acidified to pH 3, filtered (glass fibre filter GF/C, Whatman) and divided into two equal parts. One part was further divided into 20 one-litre polyethylene bottles labelled A and a consecutive number. The other part, labelled B, was spiked with 5 ml of a 10 µg/ml aqueous solution of sucralose and mixed by extensive swirling. As a result the sucralose concentration was increased by 2.2 µg/l. Sample B was then divided into 20 numbered one-litre polyethylene bottles. Surface water from the inner archipelago of Stockholm was sampled at Nacka Strand, approximately 2 km in the main direction of flow from the discharge point of the Henriksdal treatment plant. The water was acidified (pH 3) and filtered as described above. The water was distributed into 40 one-litre polyethylene bottles which were randomly labelled C or D followed by a consecutive number. A summary of the samples is given in Table 2.

Table 2 Summary of samples used in the interlaboratory study

Sample	Content
A	Effluent water
B	Effluent water spiked with sucralose
C, D	Surface water, C and D identical

To check for homogeneity, two bottles of sample A were analysed as single determinations, and three bottles from the beginning, middle and end of the sample B series were analysed in duplicate at IVL on the day of preparation. The results are given in Table 3. The average coefficient of variation (CV) estimated from the three duplicate determinations was 2.5%. The CV for all six determinations is 4.5%. This indicates that a CV of 3.7% ($2.5^2 + 3.7^2 = 4.5^2$) could be attributable to inhomogeneity between the sample bottles. No action was taken to further homogenize the samples as it was anticipated that this would not have a significant impact on the overall results.

Table 3 Analytical results to check for homogeneity of samples

Bottle	Conc 1 ug/l	Conc 2 ug/l	CV %
A3	6.6		
A20	6.5		
B1	8.9	8.5	4.1
B12	8.0	7.9	1.1
B20	8.2	8.1	1.1

One set of samples A–D was stored at room temperature and another at +8°C for stability studies. All other sample bottles were frozen (-18°). Samples stored at +21°C, +6°C and -18°C were analysed after 0, 22, 89 and 146 days of storage. Results are given in Table 4. No significant change in concentration with storage time or temperature was found.

Table 4 Analytical results to check for temporal sample stability

Days	Sample B +21 °C µg/l	Sample B +6°C µg/l	Sample B -18°C µg/l	Sample C/D +21 °C µg/l	Sample C/D +6°C µg/l	Sample C/D -18°C µg/l
0 8.2	8.2	8.2	0.18	0.18	0.18	
22	8.4	7.9	8.4	0.19	0.19	0.18
89	7.9	8.0	8.7	0.17	0.17	0.17
146	8.5	8.0	7.6	0.19	0.16	0.17

DISTRIBUTION OF SAMPLES

An insulated box containing one bottle each of samples A to D was sent frozen to each of the nine participating laboratories in the middle of June 2008. The participants were informed that samples A and B contained effluent water with a concentration of sucralose above 1000 ng/l and that samples C and D were surface waters with a concentration of sucralose below 1000 ng/l. They were asked to analyse the four samples with the method of their choice together with a short description of the method used. Results were due by 31 October 2008.

RESULTS

Six laboratories contributed with results (Table 1, bold text). The laboratories were assigned arbitrary numbers. Results from the organizing laboratory were also included, making a total of seven sets of results. A preliminary compilation was sent out to the participants on 5 November 2008. One laboratory responded that they had mistakenly omitted a multiplication of the results by a factor of 10. This was corrected and new preliminary results were sent out on 11 November 2008. All results for samples A and B are presented in Table 5, leftmost columns, and Figure 1.

Table 5 Results for Samples A and B

	All results		After rejection of outliers		
Lab ID	Sample A ng/l	Sample B ng/l	Sample A ng/l	Sample B ng/l	B-A ng/l
1	7100	9900	7100	9900	2800
2	4490	5597	4490	5597	1107
3	5113	5264	5113	5264	151
4	500	350			
5	6500	7900	6500	7900	1400
6	5513	6950	5513	6950	1438
7	6500	8200	6500	8200	1700
mean	5102	6309	5869	7302	1433
s	2222	3069	991	1738	859
CV,%	44	49	17	24	60
n	7	7	6	6	6

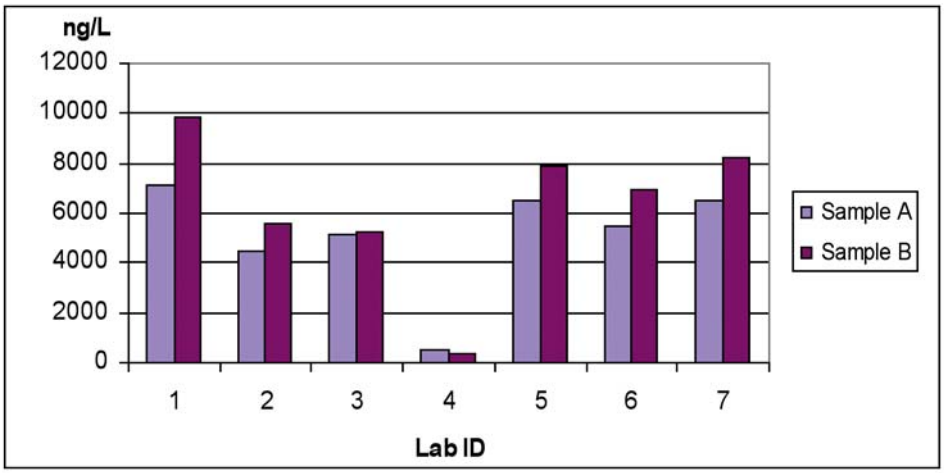

Figure 1 Samples A and B, all results

The results from laboratory 4 are significantly lower than the others and considered outlying. The remaining results and the differences between samples A and B are presented in Table 5, rightmost columns. The differences between samples A and B are also illustrated in Figure 2 together with a line representing the nominal value 2 200 ng/l. Individual results ranged from 150 to 2 800 ng/l. The average recovery of the spike was 1 400 ng/l, 64% of the nominal value. The spike constituted a 37% increase for sample B from the average sucralose concentration obtained for sample A. Five laboratories reported a result for sample B that was 22–39% higher than for sample A. One laboratory reported only a 3% increase.

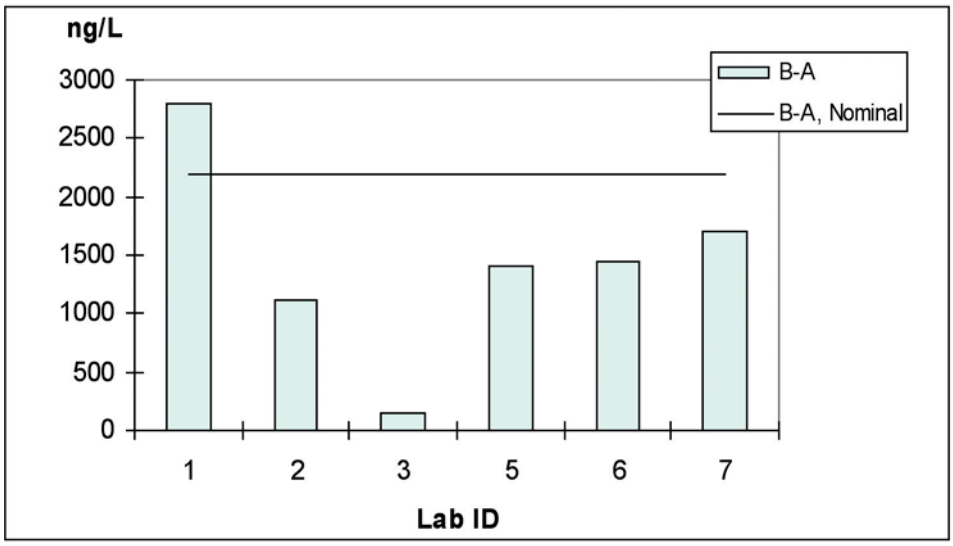

Figure 2 Difference between Sample B and Sample A

All results for samples C and D are presented in Table 6, leftmost columns, and Figure 3. The result for sample D from lab 4 deviates and is considered outlying. Statistics for the remaining results are given in Table 6, rightmost columns.

Table 6 Results for Samples C and D

	All results		After rejection of outliers		
Lab ID	Sample C ng/l	Sample D ng/l	Sample C ng/l	Sample D ng/l	D-C ng/l
1	230	270	230	270	40
2	188	190	188	190	2
3	121	138	121	138	17
4	200	600	200		
5	230	230	230	230	0
6	155	193	155	193	38
7	180	180	180	180	0
mean	186	257	186	200	16
s	38	172	39	45	
CV %	20	67	21	23	
n	7	7	7	6	

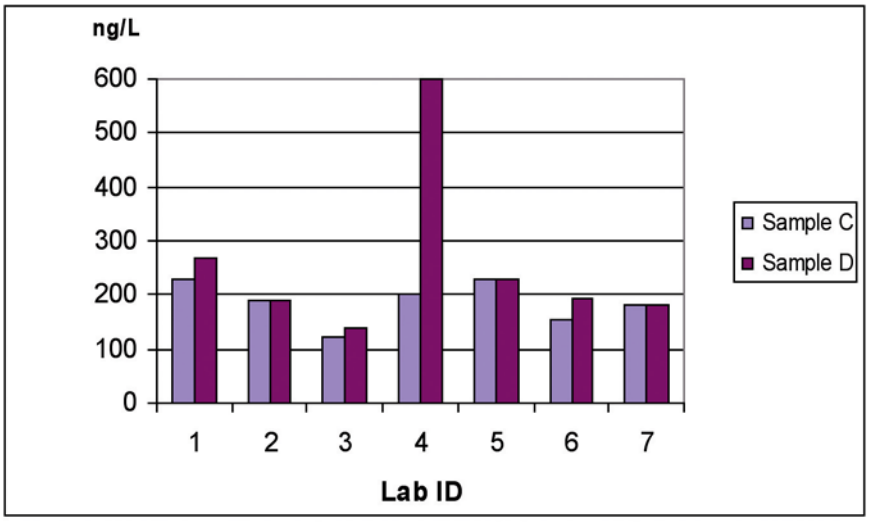

Figure 3 Samples C and D, all results

The difference between samples D and C is illustrated in Figure 4. The samples were identical so ideally there should be no difference. Three laboratories reported a difference of less than 2%, three laboratories a difference of 13–22%.

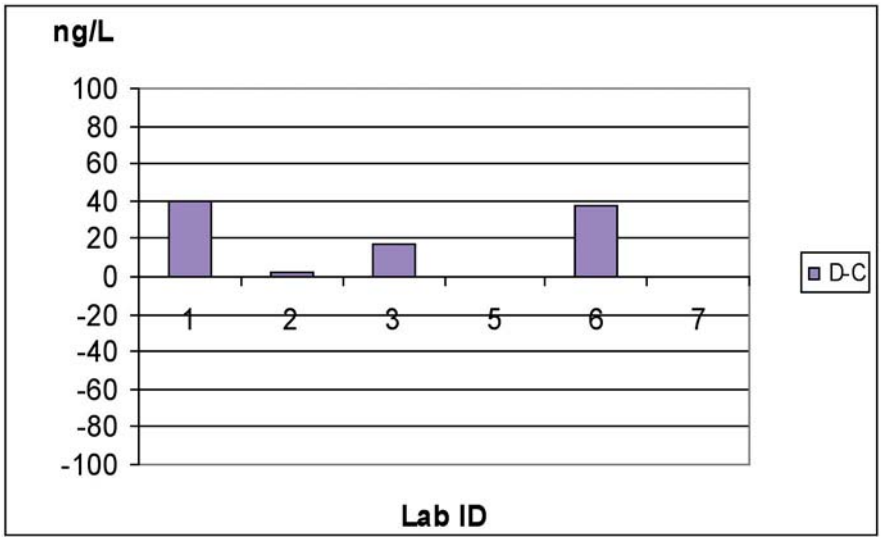

Figure 4 Difference between samples C and D, after rejection of outliers

As samples C and D were identical, the results could be treated as one dataset, Table 7. The total coefficient of variation is 21%. The paired results for samples C and D from each laboratory could be used to estimate the intralaboratory coefficient of variation. This varies from 0% to 19% with a mean of 11%.

Table 7 Results for samples C and D combined

Lab id	3	3	6	7	7	2	2	6	4	1	5	5	1	mean ng/l	S ng/l	CV %	n
Conc, ng/l	121	138	155	180	180	188	190	193	200	230	230	230	270	193	41	21	13

METHODS

All laboratories extracted the samples using solid phase extraction (SPE). Four laboratories used Oasis HLB (Waters) columns; Strata X (Phenomenex) and a mixed layer SPE-cartridge were also used. Two laboratories indicated a change of sample pH to 6.5 or 7. Isotopically labelled surrogate standard (D6-sucralose) was added by five laboratories. Different sample volumes, 2–1000 ml, were extracted. After extraction one laboratory washed the column with 0.5 M ammonium hydroxide. Elution was done with methanol, acetone+methanol 1+1, or (in the case of the mixed mode SPE-column) with a basic and an acidic mixture of ethyl acetate + methanol 1+1.

Two laboratories cleaned up the extracts using Isolute M-M (IST) and Oasis MAX (Waters) columns.

All laboratories used RP-HPLC separation. Five laboratories used C18 separation columns, one a C12 column and one a C8 column. Gradient elution, with increasing relative concentration of the organic solvent with time, was performed using water/acetonitrile, in one case with 0.05% acetic acid added, or water/methanol with 0.1% formic acid, 25 mM ammonium acetate or without additives.

Laboratory 4 used precolumn chemical derivatisation (DNBC benzoylation). This laboratory used UV/DAD 230 nm for detection.

All other laboratories used some type of mass spectrometric detection following electrospray ionisation (ESI). Laboratory 1 used ESI in positive mode, all others in negative mode. Laboratories 1, 3, 6 and 7 used triple quadrupole instruments with unit mass resolution, laboratory 2 used high resolution TOF (time of flight)-MS and laboratory 5 used high resolution LTQ-Orbitrap-MS.

The most abundant monoisotopic mass for sucralose ($C_{12}H_{19}Cl_3O_8$) is 396.0. This corresponds to the isotopic composition $^{35}Cl_3$. The composition $^{35}Cl_2{}^{37}Cl$ is almost as abundant (98%) and gives a mass of 398.0.

Laboratories 3, 6 and 7 recorded the MRM (multiple reaction monitoring) transitions 395>359 for sucralose and 401>365 for D6-sucralose. This corresponds to [M - H]- > [M - ^{35}Cl]-, for the $^{35}Cl_3$ isotopic composition.

Laboratory 1, using positive ionisation, recorded the signals for masses 419, 421 and 427 with both first and third quadrupole transmitting the same ion. The masses correspond to the sodium adduct of $^{35}Cl_3$-sucralose, $^{35}Cl_2{}^{37}Cl$-sucralose and D6$^{35}Cl_2{}^{37}Cl$-sucralose. This was done as it gave a more intense signal than [M - H]- when using negative ionisation, but no stable product ion was found.

Laboratory 2 used masses 397.0040 and 403.0040 for sucralose and D6-sucralose respectively.

Laboratory 5 performed full scan high resolution mass analysis from 115 to 1000 m/z with data-dependent MS–MS analyses triggered by the parent ion mass of sucralose and D6-sucralose. Deprotonated formic acid adduct ion [M+FA-H]- and deprotonated molecule ion [M-H]- of sucralose and D6-sucralose were extracted from the full scan with a mass tolerance of 5ppm.

DISCUSSION

The six laboratories that used a variety of LC-MS and LC-MSMS methods and instruments to analyse a real effluent water from a municipal sewage treatment plant (sample A) for sucralose produced results with a total coefficient of variation as low as 17%. This must be considered impressive, as common experience is that repeated analysis of organic substances with the same method and instrument often produces variation of this magnitude. The results for sample B, which was the same sample spiked with sucralose, showed a somewhat higher variation, CV 24%.

It cannot be ruled out that this could at least in part be due to inhomogeneity between sample bottles. It is a lesson for the organizer that this should have been checked more thoroughly.

The spike added to sample B (2 200 ng/l) constituted a 37% increase of the concentration relative to sample A (analysed mean value). It was interesting to see if this relatively low spiking level could be recovered. Five laboratories reported results in the range 22–39%. As an average, 66% of the nominal spiked amount was recovered. An explanation for the deviation from 100% could, perhaps speculatively, be a matrix effect, ion suppression, that would in that case also have lowered the results for sample A. Analysts could only be encouraged to check for such effects. A linear response when serially diluting a sample is usually a good indicator that a matrix effect is not present. If method sensitivity puts a limit on dilution, extract clean-up can be necessary.

One laboratory used LC-UV. Their results were considerably lower than the rest.

The results for the surface water sample C/D were also very consistent with a total CV of 21% at a mean concentration of 193 ng/l after the rejection of one outlier (LC-UV data). The ratio of the average concentrations of samples A and C/D equals a dilution factor of 30.

These results show that many LC-MS approaches to analysis of sucralose can be successful but give no basis to recommend one method or instrument over another.

According to a European Commission Decision [8] a reliable identification by LC–MS–MS requires one precursor and two product ions or two precursors, each with one product ion. None of the laboratories have reported results that live up to this. This could be met by using both transitions 395>359 and 397>361 (ESI-).

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The debate on environmental and human health risks

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This note reports on the latest developments in the discussion of the risks to human health and the environment of the substance Bisphenol A (BPA) (4,4'-Isopropylidenediphenol CAS No: 80-05-7 EINECS No: 201-245-8).

PRODUCTION AND USE

BPA is one of the most highly produced chemicals worldwide. It is used in the production of polycarbonate plastics and epoxy resins, which are used in many consumer products, such as baby-feeding bottles, plastic food containers and tableware, recycled cardboard and paper used for food packaging, toys, eyeglass lenses, dental monomers, medical equipment and tubing, and electronics, as well as in lining food and beverage cans and water pipes.

The annual production volume of BPA in the EU increased from the 1996–1999 average of 700,000 metric tons to 1,150,000 metric tons in 2005 and 2006.

BPA has been shown to leach from food and beverage containers and some dental sealants and composites, under normal conditions of use. The main route of environmental exposure is from use in the thermal paper and PVC industries.

DEBATE ON HUMAN HEALTH RISKS

The debate on whether or not BPA causes effects of concern for human health at current exposure levels has lately escalated as a result of several recent evaluations of its toxicity.

BPA is one of a number of chemicals that may have the potential to interact with hormone systems in the body. It has been known since the 1930s that BPA can mimic the female sex hormone, oestrogen. The effects on fertility and reproduction and the endocrine (hormonal) system have been subject to much scientific debate, linked to reports of low-dose effects of BPA in rodents.

In Canada, health authorities recently banned the use of BPA in baby-feeding bottles; the evaluations made in Canada raise concern, especially about developmental effects in foetuses and infants.

Proposals to ban the use of BPA in certain products used by and/or for infants and children are also being considered in several states in the US.

The FDA (Food and Drug Administration–USA) stated that there is a large body of evidence that indicates that FDA-regulated products containing BPA currently on the market are safe and that exposure levels to BPA from food contact materials, including for infants and children, are below those that may cause health effects. But FDA will continue to consider new research results and information as they become available.

In Europe, EFSA (European Food Safety Authority) is the keystone of European Union (EU) risk assessment regarding food and feed safety; in close collaboration with national authorities, and in open consultation with its stakeholders, EFSA provides independent scientific advice and clear communication on existing and emerging risks.

In 2006 and 2008, EFSA provided two opinions in which the conclusion is that there are no health concerns for any part of the European population at current exposure levels of BPA.

EFSA took account of the recent concerns assessing the differences between infants and adults in the elimination of BPA from the body and has collected all the most recent information and data available.

The EFSA Panel's conclusions are based on the currently available, extensive database on repeated dose toxicity, reproductive and developmental toxicity of BPA in rodents and on the comparison of toxicokinetics in primates, including humans, and rodents.

EFSA concluded that there is sufficient capacity for biotransformation of BPA to hormonally inactive conjugates in neonatal humans at exposures to BPA that were considered in the EFSA opinion of 2006 and the European Union Risk Assessment Report. EFSA therefore considers that its risk assessment based on the overall NOAEL for effects in rats, and using a default uncertainty factor of 100, can be considered as conservative for humans and established a full TDI (estimate of the amount of a substance, expressed on a body weight basis that can be ingested daily over a lifetime without appreciable risk) of 0.05 mg BPA/kg bw.

Following the EFSA Opinion other studies have been published on the possible effects of BPA, in particular very recent results, from the study in press of Bondesson M. et al, describe additional effects of BPA on hormone signalling, developmental effects, exposure biomarkers and metabolism; in this study the results from different in vitro and in vivo models collectively indicate that the mechanisms by which BPA interferes with hormone signalling are both diverse and complex. The range of pathways with which BPA potentially interferes may be much wider than expected, and may therefore be overlooked if toxicity is measured by the classical testing paradigm only.

ENVIRONMENTAL RISK (WATER COMPARTMENT)

BPA is included in Annex IIII of the Directive 2008/105/EU that set Environmental Quality Standards for the priority substances in water bodies; the European Commission is currently carrying out a review to evaluate the possibility of including BPA on the list of substances that have to be reduced (priority substances) or eliminated (priority hazardous substances) from all sources, emissions and losses in European water bodies.

The review is based on a methodology, foreseen by the Water Framework Directive 2000/60/EC, that takes into account monitoring and modelling data; it is clear that possible inclusion on the final list of priority substances of BPA will depend on the defined PEC value (predicted environmental concentration), based on monitoring and modelling data, but also on the selection of the PNEC (predicted no effect concentration).

To assess the potential for BPA to reach drinking water, samples from sewage treatment works effluents, rivers, creeks and drinking water reservoirs were collected in Germany (Kusch and Ballschmiter). BPA levels in drinking water ranged from 300 pg/l to 2 ng/l. BPA was also detected (Belfroid et al) in surface water in 96 samples collected from 38 different locations distributed equally throughout the Netherlands in which nine locations reported levels over 100 ng/l and up to 330 ng/l and one occasional observation was of 21 µg/l. In the River Elbe (Germany), BPA was detected at concentrations from 9 to 776 ng/L in water and from 66 to 343 µg/kg in sediments (Heemken et al).

The EU Risk Assessment Report (RAR) of 2003 stated that there is a need to limit the risks for water and sediment compartments only for the following uses: thermal paper recycling, use as an inhibitor in PVC production, preparation of additive packages for PVC processing, and use as an anti-oxidant in the production of plasticizers for use in PVC processing. For other uses, the RAR indicates that there is no risk when the PNEC based on the standard endpoint of egg hatchability of 16 µg/l is used. As there are long-term NOEC values available for fish, invertebrates and algae, a factor of 10 can be used on the NOEC in accordance with the usual TGD method to give a PNEC of 1.6 µg/l.
In 2008 an updated RAR was produced. This report brings together the revised exposure information and an updated review of ecotoxicity data, as an addendum to the original RAR.

In the updated RAR of 2008, no risks are indicated using the freshwater and marine PNEC respectively of 1,5 and 0,15 µg/l for any scenario. Some authors, however, challenge this conclusion on the basis of the results of test studies on the effects of BPA on fish and molluscs. In particular, there are still uncertainties over the potential effects of BPA on snails, despite the thorough testing undertaken as part of the "conclusion (i) programme" of the RAR.

For example, in the study by Oehlmann et al, is stated that the lack of risks for the aquatic environment at current exposure levels in European ecosystems was not conclusively shown.

Oehlmann et al reported that exposure of ramshorn snails (M. cornuarietis) induces a superfeminization syndrome at BPA concentrations as low as 1 µg/L; in the experiments the complete set of superfemale effects occurred: additional female organs, enlarged accessory sex glands, gross malformations of the pallial oviduct, stimulation of egg and clutch production, resulting in increased female mortality.

A further exposure series demonstrated that the effect of BPA on reproductive output and oviduct malformations in the snail M. cornuarietis is also temperature-dependent: snails exposed to BPA at 20°C produced significantly more clutches and eggs compared to controls. The calculated EC10 value was 14.8 ng/L for egg production, which would lead to a possible $PNEC_{water}$ of 1,48 ng/L, which is much lower than the value currently defined in the RAR.

CONCLUSIONS

The toxicity of BPA has been quite widely investigated in recent years. The risk assessment reports and opinions of the European Union represent a milestone on this issue, although there is still no scientific consensus regarding the exposure levels at which BPA poses a health and environmental risk. The debate is caused by the potential endocrine disrupting effects caused by BPA on humans and on aquatic organisms. More research is therefore needed to evaluate the effects of endocrine disrupting compounds. Such research should include the use of new toxicological and ecotoxicological tests, and should also take into account the fact that we are exposed to a mixture of endocrine modulating compounds. The monitoring of levels of BPA in environmental compartments, in food, human tissues and fluids should also be improved in order to present a clear picture of the level of exposure.

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

Milestones and achievements in 2009

2009 saw the first milestone in the life of NORMAN – the establishment of the NORMAN association in February 2009. After three years of life as an EC-funded project (6th Framework Programme – Priority 6.3 - Contract N° 018486), the NORMAN network was established in February 2009 as a non-profit association under French Law 1901 with its own Statutes and Internal Regulations.

The NORMAN association - network of reference laboratories, research centres and related organisations for the monitoring and biomonitoring of emerging environmental substances - now has 43 members (as at 23 October 2009), plus JRC, which has a permanent invitation to the Steering Committee in a consultative role, and collaborates with NORMAN under a specific Collaboration Agreement (CA) which will be probably signed by NORMAN and JRC by the end of the year 2009.

NORMAN is financed by the contributions of its wide membership of interested stakeholders dealing with emerging substances. The synergies between research teams from different countries in the field of emerging substances help to make that financing possible and contribute to the harmonisation of common measurement methods and monitoring tools.

AMONG THE ACHIEVEMENTS OF THE NETWORK IN 2009:

- Databases

In 2009 the databases have been regularly updated with new data from monitoring campaigns and projects. Moreover, the databases have been completely reprogrammed to improve their performance in terms of speed and functions. The new versions of the databases are now available on the NORMAN website (except for EMPOMASS which will be available by January 2010).

In 2010 the focus will be on extraction of data from the projects listed in EMPOMAP, population of EMPODAT with bioassay and biomarkers data and continuous updating of interlinking between the three databases. It is also proposed to develop a module for upload and visualisation of (eco)toxicity and other REACh-related data from UBA and other national databases. To this end, UBA has proposed organising a workshop on "Data exchange" in 2010, stressing the fact that this workshop should be specifically addressed to IT experts to discuss the setting up of protocols for automatic data exchange / sharing between national databases.

- Workshop on "Mixtures and metabolites of chemicals of emerging concern"

This workshop was organised by RIVM - National Institute for Public Health and the Environment and IVM - Institute for Environmental Studies - VU University (The Netherlands) and took place in Amsterdam on 18-19 November 2009. The programme covered various aspects related to the formation of metabolites and degradation products of emerging substances and mixture effects – a topic of crucial importance for the assessment of the toxicity of emerging pollutants and treatment techniques.

- Working Group on prioritisation of emerging substances

The objective is the identification of those emerging substances that warrant priority attention (including priority needs in terms of improvement of existing data), based on common criteria such as their (eco)toxicity, persistence, bioaccumulation potential, spatial and temporal distribution, occurrence in the environment, usage pattern, level of consumption, etc. A questionnaire for the update of the list of emerging substances and preparation of the prioritization work was developed and circulated to the members of the WG and all NORMAN. The activities of this working group with the definition of the prioritisation criteria and methodology will continue in 2010.

- Expert Group N°2 meeting "Use of passive sampling for emerging substances" with publication of Position Paper (VUVH)

The meeting of the EG took place in Prague on 26 May 2009 - jointly with the "3rd International Passive Sampling Workshop and Symposium - IPSW 2009". The minutes of the meeting and the presentation are available on the website and the publication of the Position Paper is planned for the beginning of 2010. As a follow-up to this EG meeting, the organisation of an intercalibration study on passive sampling of emerging pollutants is among the proposals for NORMAN activities for 2010 or 2011. There are already on-going activities, for example, in the Czech Republic and France for the organization of intercalibration exercises using passive samplers, but they are all focused on the WFD Priority Substances.

- Working group N°2 "The value of bioassays and biomarkers in water and sediment quality monitoring programmes: strategies for the interpretation of results" (RIVM / IVM / INERIS) and Expert Group N°1 meeting "Toxicity profiling" with publication of Position Paper (IVM)

The Working Group (10 Member States represented by 12 leading organizations), met for the first time on 8 October in Amsterdam. One of the first objectives of the Working Group is the preparation of an inventory of available biological tools, including strategies for the interpretation of results, and evaluation of those strategies.

Moreover, an Expert Group meeting was held on 9 October in order to discuss in detail the current state of the art and perspectives on the use of toxicity profiling approaches (in vivo, in vitro and omics) and their combination with chemical analytical techniques, to provide information on the mode of action of emerging substances and the assessment of their impact. The conclusions of these thematic groups, regarding the concrete possibilities and limitations for the application of biological effect tools in the assessment of the impact of environmental contaminants in the aquatic environment, will be published and disseminated in the form of position papers in the course of 2010.

- Organisation of an interlaboratory study on "Perfluorinated Co pounds in Water, Fish and Sludge" (IVM / QUASIMEME)

Work is under way – data are being evaluated and the final report will be published by the end of 2009.

- Implementation of NORMAN protocol for methods validation in European standardisation

There is on-going activity at the European Standardisation body (CEN) to start with the drafting of a new working document for method validation (future CEN Technical Specification) which will be entirely based on the NORMAN validation framework produced during the NORMAN project. As a conclusion of the 5th meeting of the experts of the CEN/TC 230 / WG 1 AHG on "Water analysis" (28 May 2009, Lelystad, The Netherlands), the NORMAN validation protocol should be considered as a basis for a future New Work Item Proposal, which would lead to a future CEN Technical Specification. This work is lead by IWW and the setting-up of a new NORMAN Working Group is proposed for 2010 for the drafting of the Working Document which will precede the New Work Item Proposal. This Working Document building on the NORMAN Validation Protocols will be finished in April 2010.

NORMAN events

FOCUS on the Workshop on "Mixtures and metabolites of chemicals of emerging concern" – Amsterdam, 18-19 November 2009

Releases of chemicals in the environment often cause the formation of transformation products which may be more toxic than the parent compound. This possibility of increased toxicity over time has been afforded insufficient attention in chemical regulation. There is, moreover, limited awareness of the analytical implications of this phenomenon. With this in mind, a workshop on mixtures and metabolites of chemicals was organised by RIVM (National Institute for Public Health and the Environment) and IVM (Institute for Environmental Studies – VU University, The Netherlands) and took place in Amsterdam on 18–19 November 2009.

About 70 participants attended the workshop, with 16 presentations (available as pdf files on the NORMAN website) and 11 posters. The conclusions of this two-day workshop will be presented in a specific report. However, it was already clear from the discussion that the co-occurrence of chemicals in the environment plays an important role in the overall environmental impact of chemicals. The ecotoxicological assessment of mixtures is complex and there are still many knowledge gaps. But checking compliance with environmental quality standards alone is obviously not sufficient: a number of modelling tools for prediction of mixtures effects exist already and they need to be integrated in future routine risk assessment protocols.

The second day was focused on the tools for identification and analysis of the metabolites and transformation products of chemicals of emerging concern. Here again, the main tools available (in silico methods, analytical techniques, bioreactors, field studies) to study the chemicals' transformation products were presented. But knowledge gaps still exist in the analysis of transformation products, fate and transport, and toxicity of these compounds. Moreover, most of the current studies addressed two main classes of compounds: pesticides and pharmaceuticals. Is this the tip of the iceberg? How many transformation products should also be covered?

NORMAN General Assembly, Amsterdam 20 November 2009

The first NORMAN General Assembly took place this year on 20 November 2009. The progress of the work and the proposed activities for 2010 were discussed with all members and the results of the discussion will be the basis for the finalisation and approval of the NORMAN Joint Programme of Activities for 2010 by the Steering Committee.

Forthcoming events

20 YEARS OF RESEARCH IN THE FIELD OF ENDOCRINE DISRUPTORS & PHARMACEUTICAL COMPOUNDS: CHALLENGES AND SOLUTIONS IN THE WATER SECTOR
10 February 2010, Berlin, Germany

Awareness of the potential hazards posed by endocrine disrupting and pharmaceuticals compounds has led to intensive research programmes over the past 20 years. The performance of current water supply systems, urban drainage and wastewater treatment systems is suitable to solve conventional problems only. This one-day workshop organised by Kompetenzzentrum Wasser Berlin and sponsored by VEOLIA Environment intends to review and discuss with leading international scientists the status of knowledge regarding the risks, impacts and available or future technical solutions for the water sector. The deadline for registration is on 31 January 2010.
For any further information on programme and registration go to:
http://www.kompetenz-wasser.de/Kompetenzzentrum-Wasser-Berlin.1.0.html?&L=1&type=title%3DContact

6TH ANNUAL LC/MS/MS WORKSHOP ON ENVIRONMENTAL APPLICATIONS AND FOOD SAFETY - FOCUS ON EMERGING SUBSTANCES

25 ⇢ 26 February 2010, Barcelona, Spain

Following the success of previous 5 international workshops on Liquid Chromatography-tandem mass spectrometry for screening and trace level quantitation in environmental and food samples, this annual workshop will address practical aspects of the usefulness of tandem mass spectrometric techniques for screening and quantitation of organic contaminants in the environmental and food samples. The following practical aspects will be discussed:

- Advantages, comparison and complementarities of advanced tandem and hybrid MS instruments, such as QqLIT, QqTOF, Orbitrap in the quantitative and qualitative determination of complex environmental and food samples
- Advanced sample preparation technologies for food and environmental analysis like the use of molecularly imprinted polymers and other selective SPE cartridges, including on-line pre-column technology coupled to LC/tandem MS
- Large number of applications in environmental analysis, basically water and soil/sediment, and food, like fruits and vegetables, juices and meat
- Broad range of contaminants and their degradation products.

Deadline for registration and abstract submission: 15 January 2010. For more information go to **http://www.cid.csic.es/barcelona2010/home.htm**

INTEGRATED RIVER BASIN MANAGEMENT UNDER THE WATER FRAMEWORK DIRECTIVE (WFD) CONFERENCE: ACTION PROGRAMMES AND ADAPTATION TO CLIMATE CHANGES

26 ⇢ 28 April 2010, Lille, France

The conference will review technical challenges faced by Member States, stakeholder organisations and scientists, while developing the first River Basin Management Plan under the Water Framework Directive (WFD). It will focus on aspects of integration, looking at the way cross-sectoral and multidisciplinary co-operation has developed, and how emerging issues such as adaptation to climate changes will be considered in the future.
This event aims to be a forum of exchanges between policy-makers, stakeholders, and scientists on issues that are closely related to the implementation of EU water policies.
Discussions will hence not be limited to the WFD, but will open up to related policies concerning, for example, priority substances, groundwater, floods, climate change adaptation, etc. For further information go to **http://www.WFDLille2010.org**

TRANSCON2010 - INTERNATIONAL CONFERENCE ON ENVIRONMENTAL TRANSFORMATION OF ORGANIC COMPOUNDS: TOWARDS A JOINT PERSPECTIVE ON THE IMPORTANCE OF TRANSFORMATION PRODUCTS AS ENVIRONMENTAL CONTAMINANTS

⇢ 12-17 September 2010, Monte Verità, Ascona, Switzerland

TransCon2010 will address the possible formation of stable, environmentally relevant transformation products. Sessions will cover experimental and model-based scientific methods to investigate and predict transformation processes, and to assess the environmental fate and toxicity of transformation products. The conference's aim is to develop a better scientific understanding of how much transformation products contribute to the overall chemical risk in the environment and of how to integrate this knowledge into chemical risk assessment procedures.
Abstracts: The deadline for submission of abstracts for poster and platform presentations is 16th April 2010.
Detailed information on the conference website:
http://www.eawag.ch/medien/veranstaltungen/events/transcon2010/index_EN

>>>>>>>>>>>>>>> *Contributing to the Newsletter*

If you like to contribute to a future issue of this Bulletin or announce an upcoming event, you can contact: valeria.dulio@ineris.fr