Network of reference laboratories, research centres and related organisations for monitoring of emerging environmental substances

BULLETIN

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WELCOME TO ISSUE N°4
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

NORMAN Network: almost 10 years of commitment

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It is with great pleasure that we bring you this 4th issue of the NORMAN network Bulletin. We apologise for our two “silent springs” since the 3rd issue, but we – by which I mean the secretariat and the membership – have been immersed in the implementation of a good number of collaborative projects, both national and international.

The NORMAN network exists to enhance the exchange of information on emerging environmental substances, and encourage the validation and harmonisation of common measurement methods and monitoring tools. Decision-makers at the level of the EU Commission and Member States are now fully aware of the need to look beyond conventional regulated contaminants and they expect clear answers by the scientific community to improve future environmental monitoring. Various examples (EMPODAT as a reference database on emerging contaminants, the use of effect-based tools in monitoring programmes, the development of innovative prioritisation methodologies, etc.) prove the strong commitment of NORMAN here. NORMAN is part of major EU projects for the improvement of environmental monitoring, and results show that there is a concrete benefit from the synergies that the network can promote among research initiatives at national and international level to make more efficient progress in emerging substances science and bring the messages of the scientific community closer to decision-makers.

This 4th issue of the Bulletin reflects the great contributions many of our network members make towards the achievement of our objectives. Some of the contributors are ‘veteran’ members contributing since the creation of the network: others are new partners in our venture. We are particularly pleased to note that we also have contributors from outside of Europe, which enhances our international reputation.

The aim of the Bulletin is to update our members in EU Member States – and our wider readership – on what is happening in ‘emerging pollutants’ science and to provide a quick focus on ongoing projects. You will find, for example, interesting contributions about nanopesticides, illicit drugs, microplastics and more…We also aim here to update the readership on the work done by our working groups towards improving the overall communication and involvement of our members.

Many NORMAN network working groups have been extremely active in the past few months, with significant involvement by many institutes, on many fronts. While it is difficult to capture in great detail all the work that is being done, you will find some of the details in this issue of the bulletin, such as the collaborative trial on non-target screening techniques, the first time it has been done worldwide in environmental samples, the interlaboratory study organised by the Bioassays Working Group, or the screening campaign of selected antibiotic resistant bacteria and resistance genes in treated effluents from wastewater treatment plants organised by the Wastewater Reuse Working Group.

We hope that you find this issue both interesting and informative and, as always, we hope that you will contribute to the Bulletin, and share with us your expertise,

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research and anything else that you feel it would be worthwhile for the scientific community to know.

I would also like to thank Fabrizio Botta at INERIS who has now taken on the role of Contributing Editor, for the time and energy he has contributed towards getting this Bulletin published.

The NORMAN network is almost 10 years old. It is no surprise, then, that the scientific impact of the NORMAN network is growing and it is my sincere hope that the Bulletin will continue to assist in promoting studies on emerging contaminants worldwide.

Issue N°4 - March 2015

SCIENTIFIC WATCH

PROJECTS

LIFE OF THE NETWORK

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How to substitute hazardous chemicals? The search for environmentally compatible flame retardants

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In modern society many thousands of chemicals are used in everyday products, such as paints, personal care products, petrol, medicine, electronics, cleaning products etc. Products can contain toxic chemicals and if they are inappropriately used can cause adverse effects for humans or the environment. Chemicals can be emitted or leached from products to the indoor and outdoor environment, and people, animals or plants are exposed via various pathways.

One type of large volume chemicals used in our everyday life are flame retardants (FR), with an annual consumption of more than 1 million tonnes. They are used in thermoplastics, thermosets, textiles and coatings and used in different applications such as printed circuit boards, electronic components, telephones, wires, carpets, curtains etc. They have an inhibitory effect on the ignition of combustible organic materials and are highly effective in plastics and textile applications such as electronics, clothes and furniture, and are commonly used to reduce the flammability of a product. However, some brominated flame retardants (BFRs) have unintended negative effects on the environment and human health. Some of them show a strong bioaccumulation in aquatic and terrestrial food chains, some are very persistent, and some show serious toxicological effects such as endocrine disruption. During the last decade, an increasing number of reports have presented evidence of these negative effects caused by some BFRs. A number of BFRs (in particular polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane (HBCD) and tetrabromobisphenol-A (TBBP-A)) can be found indoors and outdoors in places ranging from the human food chain, human tissues and breast milk to polar bears [1-6].

Less toxic alternatives appear to be available but comprehensive information on their possible toxicological effects is lacking. For three years, the European Commission-funded project ENFIRO (www.enfiro.eu) investigated the substitution options for some BFRs and compared the hazard, exposure, fire performance and application of the alternatives with those of the BFRs. In addition, a risk assessment and comparative life cycle assessment were carried out.

In a chemical alternative assessment project the central question is, how can we distinguish and search for safer and technologically feasible compounds? ENFIRO developed an approach that was based on the chemical substitution cycle [7, 8] consisting of four major elements (Fig. 1), i) prioritisation and selection of alternatives, ii) technical, toxicological, and exposure assessment, iii) risk assessment, and iv) impact assessment.

Figure 1: ENFIRO approach: Chemical substitution cycle

ENFIRO showed that it is important to follow the full substitution chain based on these four elements, in contrast to many substitution programmes which focus on the first two elements only. ENFIRO developed a unique assessment scheme for the evaluation of the data that was based on three levels, i) the flame retardant (hazard, exposure, risk), ii) the material (fire performance, technical applicability, leaching and air emissions), and iii) the product (impact assessment including life cycle assessment (LCA) (Fig. 2).

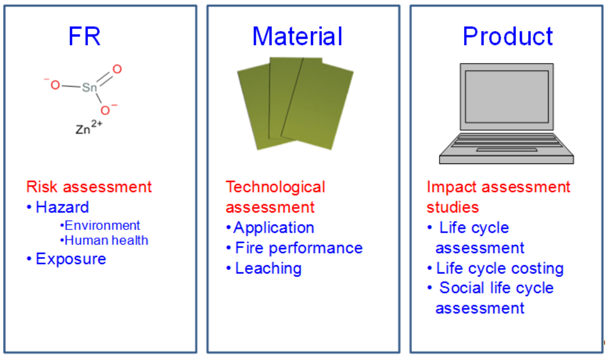

Figure 2: ENFIRO assessment approach at three levels: Flame retardant, material and product.

The substitution options for three BFRs were investigated by comparing the hazard, exposure, fire, and application performances. Risk and impact assessments were carried out based on these results. In total, 14 halogen-free flame retardants (HFFRs) as alternatives for decaBDE, TBBP-A, and brominated polystyrenes were selected. These were phosphorous, metal, and nano-based flame retardants. The flame retardants were studied in five applications – printed circuit boards (PCBs), electronic components, injection moulded products, textile coatings and intumescent paint.

The results showed that all of the selected alternative flame retardants do fulfil the regulatory fire test. An important finding was that halogen-free systems have clear benefits as demonstrated, e.g. less visible smoke, in some cases lower peak heat release rate with halogen-free products, and less toxic components in smoke.

A comprehensive overview of the persistency, bioaccumulation, toxicity, and physical-chemical properties of the 14 HFFRs was made at the start of the project and showed that large data gaps and contradictory information exist for these compounds [9]. ENFIRO filled some of the gaps, and some data became available via the ECHA database and other projects during the project. The combination of polymers with HFFR that were selected and considered to be commercially viable alternatives to specific commercial BFRs (TBBP-A, decaBDE, brominated polystyrene (BPS)) contained phosphorus FRs, inorganic tin-based FRs, nanoclays and combination of nanoclays with phosphinates, full details can be found in the final report of ENFIRO. Selection criteria were that the FRs should be halogen-free, commercially available, and some information on the compatibility behaviour in polymer materials should be available.

The ENFIRO hazard characterisation studies, the data from literature and databases showed that, from the initial selection of 14 alternative flame retardants, the following seven were found to have fewer issues of toxicity concern: ammonium polyphosphate (APP), aluminium diethylphosphinate (Alpi), aluminium hydroxide (ATH), magnesium hydroxide (MDH), dihydrooxaphosphaphenanthrene (DOPO), zinc stannate (ZS) and zinc hydroxstannate (ZHS). These assessments were based on the US EPA Design for the Environment (DfE) programme alternatives assessment criteria for hazard evaluation [10], which has the advantage that a wider range of hazard characterisation categories are used than in the REACH classification. Two organic HFFRs, resorcinol bis(diphenylphosphate) (PBDPP) and bisphenol A bis(diphenylphosphate) (BPA-BDPP), are of some concern as they show varying results between aquatic toxicity studies in the literature (moderate-low and high-low toxicity, respectively). This variation may be due to the amount of triphenyl phosphate (TPP) present in the technical products; TPP is a by-product and known to be very toxic for aquatic organisms. In addition, BPA-BDPP is a persistent compound. Another compound that is of concern and needs further study is the nanoclay (nano-MMT) that showed a strong *in vitro* neurotoxicity effect. Also the fate (leaching) of nanoclay from polymers needs further study.

Environmental fate models predicted that the organic HFFRs would be found primarily in soils, sediments and dust and to a lesser extent in water and air. Controlled air emission experiments showed that all organic HFFRs emitted from polymers at elevated temperature but not at lower temperatures. Leaching experiments showed that both HFFRs and BFRs can leach to water. Both a worst case (TLCP[1]) and a conservative (DIN[2]) leaching method were used to study the leaching of FRs from the prepared polymer/FR materials. For some polymers no differences in leaching behaviour were found between BFRs and HFFRs, but some HFFR systems had higher leaching properties than polymeric based BFRs. In general, it was found that the polymer type is the main parameter determining leaching behaviour, and the more porous the more FRs can be released. The porosity of the materials has a high influence on the leaching behaviour of the flame retardants.

Analysis of organic HFFRs in dust from microenvironments and environmental samples showed highest concentrations on and around electronic equipment, in sediment and sewage sludge. The environmental and human risk assessments showed that the predicted environmental and human exposure concentrations were below the toxicity thresholds for the selected HFFRs. However, the lower risk of HFFRs compared to BFRs is mainly due to the lower hazards of the HFFRs, and not due to a lower exposure. Reducing the leaching of HFFRs from polymer materials is one of the immediate challenges for the development of new FRs.

The comparative life cycle assessment (LCA) of BFR vs HFFRs, using a laptop as a case study showed that the waste phase was the most relevant. In particular, the formation of brominated dioxins out of BFRs during improper electronics waste treatment had a strong negative impact on the LCA-scores. Overall, the LCA performance of the HFFR scenario was better than that of the BFR scenario. The same life cycles were also evaluated on social criteria, using a Social Life Cycle Assessment. Several hotspots were found in the raw material mining phase. In conclusion, ENFIRO showed that viable alternative flame retardants are available. Some HFFRs showed less risk for the environment and human health, and show similar fire performance and technical application capabilities to BFRs.

LESSONS LEARNED

We found that for the substitution of chemicals, a complete substitution cycle is needed: technical/application performances, hazard, exposure and impact assessments. Such an assessment can only be performed with a group of experts from different disciplines (material experts, fire safety researchers, toxicologist, chemist, social scientist, lifecycle experts etc). The use of a stakeholder forum, as used in ENFIRO, with members from the FR users (e.g. formulators and users of FRs, waste(processing) plants and other bodies, such as NGOs and policy-related ones), was of great help for the project as they could provide technical and market based information.

Overall it can be said that the approach adopted by ENFIRO was very successful and can be used for similar substitution studies, e.g. REACH. There is a short film of the main outcomes on the ENFIRO website. More details of the outcomes of the ENFIRO project have recently been published on the European Cordis website: http://cordis.europa.eu/publication/rcn/15697_en.html.

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[2] German standard DIN leaching method

Investigating the occurrence of C8-based perfluorinated substitutes in Italian waters

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ALTERNATIVES TO LONG CHAIN PERFLUOROALKYL ACIDS

In the last decade there has been increasing concern in the scientific community over perfluoroalkyl and polyfluoroalkyl substances (PFASs), because of their worldwide distribution in the different environmental compartments. This class of chemicals has been used in a wide range of industrial and consumer products for the past six decades mainly to repel dirt, water and oil. PFASs include thousands of chemicals but the environmental studies have been concentrated mainly on perfluorosulfonic acids (PFSA), perfluorosulfonamides and perfluorocarboxylic acids (PFCA). C8-based perfluoroalkylacids (PFAA) such as perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) have been demonstrated to be persistent in the environment and bioaccumulative in the trophic chain, giving concern about the risks for the end consumers, including humans. In 2000, 3M started a global phase-out of its products based on C6, C8 and C10 chemistry and replaced them with products based on C4 chemistry such as perfluorobutanesulphonic acid (PFBS). In January 2006, under USEPA pressure, the eight major companies producing or using PFOA launched the 2010/2015 PFOA Stewardship Program to formally stop the environmental release of PFOA and its related compounds. The companies also committed to working toward fully eliminating PFOA emissions and product content by 2015. In 2006 the European Commission published the Directive 2006/122/EC, which restricts the marketing and use of PFOS. Regulatory restrictions on the use of PFOS and PFOA have led the major fluorochemical producers to seek substitutes for these compounds, especially among homologues with shorter chain lengths (Wang et al., 2013). Nowadays all companies are replacing C8-based PFAAs, and their associated compounds with shorter perfluoroalkyl chain compounds that have the same functional properties as the longer chain compounds. Although the alternatives are just as persistent, they should be less bioaccumulative and toxic – which is still being confirmed by testing – and are thus considered sound replacements (Ritter, 2010). A recent review by Wang et al. (2013) of the fluorinated alternatives to long chain PFAAs and their potential precursors highlights the major gaps that must be filled for a reliable assessment of the risks for human and the environment.

In this note we provide a summary of the results of a recent survey investigating the distribution of short chain PFAA in Italian rivers and hotspots correlated with specific industrial sources and discharges. By this twofold approach, on one hand we try to highlight the PFAA pattern in surface waters released by the use of everyday products, while on the other hand we fingerprint the discharges of specific industrial sites such as fluorochemical and fluoropolymer plants and tannery and textile industrial districts. In the same basins drinking waters and groundwaters were also analysed. The complete results have already been discussed in two recently published papers (Castiglioni et al., 2015; Valsecchi et al., 2014). Finally we present preliminary data on retrospective analysis carried out by high resolution mass spectrometry on selected water samples to verify the occurrence of fluorinated substitutes which do not belong to the PFAA class.

TREND AND SOURCES OF PERFLUOROALKYLACIDS IN ITALY

In 2010–2013 we sampled about 35 rivers, belonging to the basins of rivers Po, Adige, Brenta, Arno and Tevere, which cover more than 40% of the national surface area. The aim of the project, funded by the Italian Ministry of the Environment (http://www.irsa.cnr.it/ShPage.php?lang=it&pag=PFAS), was to map the occurrence and emissions of PFAA in the main Italian rivers, highlighting hotspots correlated with specific sources and industrial emissions. A statistical summary of the data, divided into two-year periods, is shown in Table 1.

As a general result, it can be concluded that PFOA is the compound with the highest concentration and detection frequency in all kinds of waters. Though the dataset is biased by the fact that several samples were collected downstream of a fluoropolymer plant, monitoring data show that PFOA is still largely used in the manufacturing processes and present in everyday products. No evidence of a substitution of PFOA in industrial processes is observed from monitoring data, though the main producers signed up to the PFOA Stewardship Program. Other PFCAs frequently found in surface waters are PFHxA, PFHpA and PFNA. PFBA seems to be significantly increasing in the last couple of years. The pattern of PFCA in drinking- and groundwaters is similar even if at a reduced detection frequency, while substantial differences are evident in the PFSA pattern among the different water typologies. In surface waters, concentrations and detection frequencies of PFBS and PFOS are similar while PFHxS has been very rarely detected. On the contrary in drinking- and

RIVERS		PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFBS	PFHxS	PFOS
		LOD 5 ng/L	LOD 2 ng/L	LOD 0.2 ng/L	LOD 0.2 ng/L	LOD 0.5 ng/L	LOD 0.5 ng/L	LOD 0.5 ng/L	LOD 0.5 ng/L	LOD 1 ng/L	LOD 1 ng/L	LOD 5 ng/L	LOD 2.5 ng/L
2010/2011 (N=102, 17 rivers)	**Median (ng/L)**	<5	2	4	2	42	1	<0.5	<0.5	<1	3	<5	<2.5
	90°percentile (ng/L)	15	30	70	40	895	7	4	1	<1	16	<5	16
	detection frequency (%)	10	52	79	72	87	62	35	12	10	44	0	43
2012/2013 (N=138, 35 rivers)	**Median (ng/L)**	<5	<2	4	2	22	<0.5	<0.5	<0.5	<1	3	<5	6
	90°percentile (ng/L)	110	72	82	48	974	13	11	4	3	75	<5	38
	detection frequency (%)	43	43	70	59	87	39	49	34	20	61	6	70
DRINKING WATER		**PFBA**	**PFPeA**	**PFHxA**	**PFHpA**	**PFOA**	**PFNA**	**PFDA**	**PFUnDA**	**PFDoDA**	**PFBS**	**PFHxS**	**PFOS**
2008/2011 (N=34, 22 sites)	**Median (ng/L)**	<5	<2	3	1	8	<0.5	<0.5	<0.5	<1	<1	<5	<2.5
	90°percentile (ng/L)	<5	18	13	5	25	1	1	<0.5	<1	4	<5	14
	detection frequency (%)	0	47	68	53	65	15	21	6	9	24	3	41
2012/2013 (N=181, 152 sites)	**Median (ng/L)**	<5	<2	<0.2	<0.2	2	<0.5	<0.5	<0.5	<1	<1	<5	<2.5
	90°percentile (ng/L)	55	14	20	15	171	1	1	<0.5	2	50	31	86
	detection frequency (%)	41	23	43	30	51	10	13	5	14	28	20	44
GROUNDWATER		**PFBA**	**PFPeA**	**PFHxA**	**PFHpA**	**PFOA**	**PFNA**	**PFDA**	**PFUnDA**	**PFDoDA**	**PFBS**	**PFHxS**	**PFOS**
2012/2013 (N=68, 65 sites)	**Median (ng/L)**	<5	<2	2	<0.2	8	<0.5	<0.5	<0.5	<1	<1	<5	<2.5
	90°percentile (ng/L)	24	6	26	63	1936	<0.5	<0.5	<0.5	<1	2	5	16
	detection frequency (%)	28	25	62	40	71	4	4	4	4	28	12	44

Table 1: Summary of the PFAA monitoring in Italian rivers, drinking and groundwaters

groundwaters PFHxS was detected with frequency and concentrations similar to PFBS, while PFOS prevailed among PFSA, suggesting that groundwater pollution reflects past use of longer chain PFSA. Furthermore, the results of the survey regarding PFAA emissions from different anthropic activities enable us to reach the following conclusions.

Urban emissions. PFAA are present in many consumer products of daily use and thereby the urban conglomerations can be considered point and diffuse (by run-off) sources of these compounds for the receiving water bodies. Domestic emission factors (EF) of 10 μg/day per capita for total PFAA and 5 μg/day per capita for PFOA were calculated, averaging outputs of three different WWTPs of Milano, characterised by low industrial component (< 4%) (Castiglioni et al., 2015). These EF are lower than those estimated from river concentrations in industrialised countries (Pistocchi and Loos, 2009), but very close to EF (3.5 μg/day per capita for PFOA) measured in domestic Korean WWTPs (Kim, 2012).

Fluorochemical and fluoropolymer plants. In the studied basins we identified two plants which produce fluorochemical intermediates and fluoropolymers. The fluoropolymer plant, sited in Piedmont on the river Bormida, a tributary of the river Tanaro in the Po basin, is still the most significant source of PFOA and short chain PFCAs (PFPeA and PFHxA) as already identified (Loos et al., 2008). Maximum PFOA concentrations of 6.5 μg/L were measured in the river Bormida from July 2008 to July 2013. No trend of reduction of PFOA use in fluoropolymer production was detected from 2008 to 2013. The second important plant is located in Trissino, Vicenza province, Veneto region and produces fluorinated molecules, such as PFOA and PFBS. The plant discharges into the municipal WWTP whose output is then mixed with the outputs of four other WWTPs and carried by a single sewer pipeline (called Collettore ARICA) to the river Fratta-Gorzone. PFAA composition of the river water and the WWTP effluents are very similar to the composition of the effluent discharged by the fluorochemical plant, with the main fluorocompounds being PFBS (68%), PFHxA (11%), PFOA (10%) and PFPeA (8%).

Use of PFAA in industrial applications. A very favourable situation for distinguishing the emissions of textile and tannery activities is present in the river Arno basin (Tuscany, Italy). Along the river course there are two specific districts, well spaced from each other and close to the principal course of the river. The textile district of Prato, whose WWTPs discharge into the tributaries Bisenzio and Ombrone, is a significant source of PFOA and short and long chain PFCAs (especially PFHxA and PFDA), while the contribution of PFSAs is more limited (Figure 1). In contrast, a significant input of PFSAs, mainly PFBS, comes from the tannery district in the province of Pisa, a few kilometers from the mouth (Figure 1).

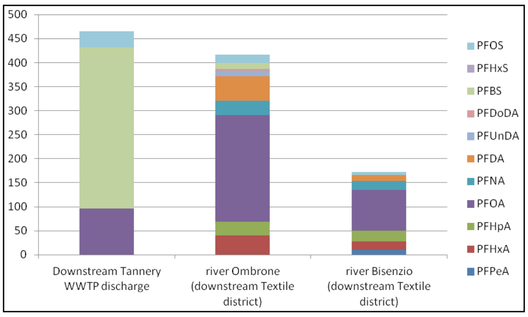

Figure 1: PFAA distribution in textile and tannery districts in the river Arno basin (Tuscany, Italy)

RETROSPECTIVE ANALYSIS FOR NEW FLUORINATED SUBSTANCES

As part of the survey, some water samples, collected in sites polluted by specific activities as identified by target PFAA analysis, were subjected to retrospective analysis by high resolution mass spectrometry. Samples were on-line extracted and separated with the same method used for HPLC-MS with a triple quadrupole analyser (Valsecchi et al., 2014). HRMS analysis was carried out using a Thermo Scientific Q-Exactive by selecting accurate masses of 62 PFAS selected from the available literature (see e.g.Wang et al., 2013). Three case studies which exemplify the information obtained by this HRMS retrospective analysis are presented below.

1) Groundwater impacted by PFSA used as drinking waters (Figure 2a): This sample, collected from a well at Lodi (Lombardy, Northern Italy), presented the maximum concentrations of PFHxS and PFOS among all the analysed waters in our dataset. By retrospective analysis perfluorohexanesulfonamide (FHxSA) was also identified. This pattern has not been found in any other well of the same town, suggesting that the pollution was very local, probably linked to a past activity or dumping site. A similar PFAS pattern has been detected in sites used as a training area by the US Military and thereby impacted by Aqueous Film Forming Foams (AFFF) (Houtz et al., 2013). Since 3M ceased production of their PFOS-based AFFF in 2002, and the rest of the AFFF manufacturers agreed to the voluntary regulations of the PFOA Stewardship Program, which calls for the complete phase-out of C8-based products from materials, it can be argued that the pollution identified in this well has not been a recent source.

2) River Bormida downstream of a fluoropolymer plant (Figure 2b): The fluoropolymer plant, sited in Spinetta Marengo (Piedmont, Northern Italy) where PTFE is produced by suspension polymerisation, discharges PFHxA, PFHpA and PFOA as main compounds. In the polymerisation

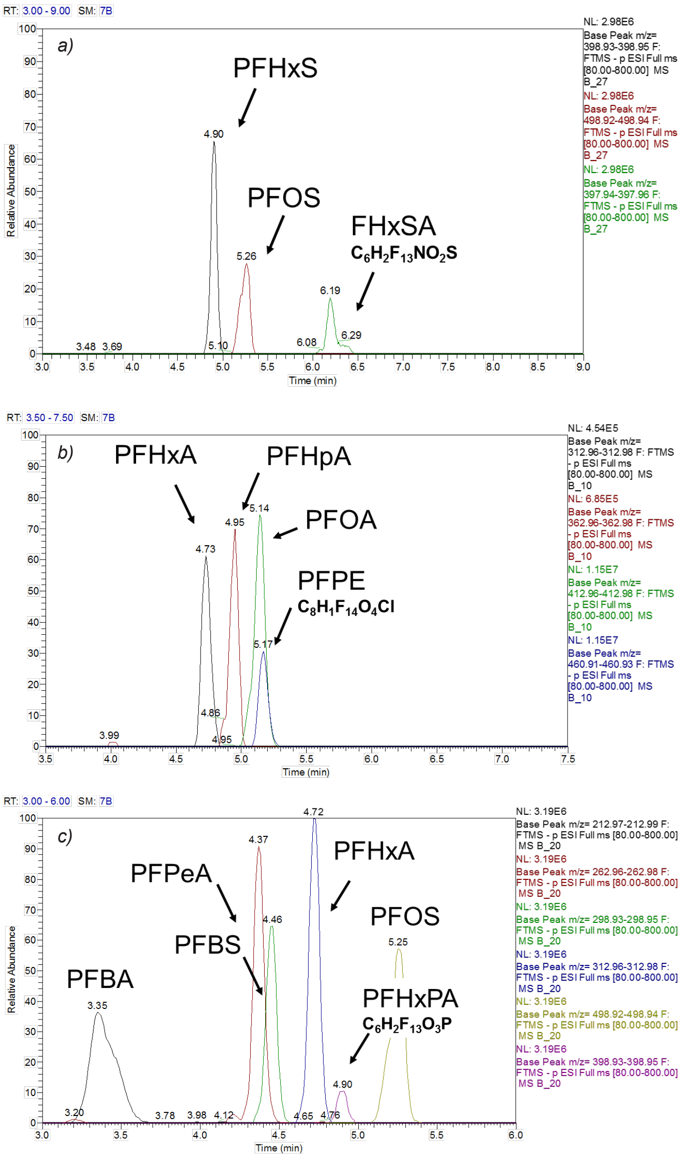

Figure 2: Retrospective analysis of:
a) Groundwater in Lodi (Lombardy, Italy);
b) River Bormida (Piedmont, Italy);
c) River Serio (Lombardy, Italy)

process, PFOA is partially substituted by a proprietary fluorinated surfactant which is a functionalised PFPE already reported (Wang et al., 2013)(CAS 329238-24-6). This compound has actually been identified by retrospective analysis and the fact that it coelutes with PFOA on a reverse phase column confirms that these two compounds have similar physico-chemical characteristics.

3) River Serio: unidentified pollution source (Figure 2c):
River Adda, an important tributary of river Po, showed significant concentrations (up to 300 ng/L) of short chain PFCA, but unfortunately their source was not identified because its basin is mainly agricultural without specific manufacturing activities. Most of this pollution came from an Adda tributary, the river Serio, which drains a small basin characterised by a cluster of small and medium enterprises (SME) operating in different industrial sectors The identification of perfluorohexyl phosphonic acid (PFHxPA) by HRMS may be allocated to emissions from industries using perfluorinated organic compounds in soil-resistant coatings, antireflective glass coatings, and release coatings.

ON-GOING ACTIVITIES WITH A REGULATORY PERSPECTIVE

In conclusion, the data collected in this survey make it possible to highlight the diffuse presence of PFOA as the compound with the highest concentration and detection frequency in all kinds of waters in Italy, in spite of the substitution measures and phase-out programmes launched by PFAS manufacturers and users. The increasing presence of short-chain PFAAs (PFHxA and PFBS in particular) as a result of the replacement of longer-chain homologues (C8-based PFAAs) by fluorochemical producers was also confirmed by this survey. Moreover, less investigated fluorinated compounds were identified thanks to retrospective analysis, showing the need for further monitoring programmes addressing new compounds used as substitutes for PFAAs (and not belonging to the PFAA class).

With datasets collected in the present survey we developed a geo-referenced national database which will be linked to IPCheM - the Information Platform for Chemical Monitoring (http://ipchem.jrc.ec.europa.eu/) managed by the JRC of the European Commission. The same datasets have been uploaded in the NORMAN EMPODAT database. These datasets will be used in the new prioritisation process for the revision of the priority list under the Water Framework Directive (WFD). We also submitted to NORMAN a revised list of perfluorinated compounds to be included in the NORMAN list of emerging substances.

As Italian delegates in the WG Chemicals of the WFD Common Implementation Strategy we proposed a revision of the definition of “Perfluorooctane sulfonic acid and its derivatives”, which has been introduced as a new Priority Substance by the Directive 2013/39/EU, in order to clarify to which compounds the definition “its derivatives” applies. We have also developed and published EQS for a selected number of PFAAs (PFBA, PFPeA, PFHxA, PFOA and PFBS) on behalf of the Italian Ministry of the Environment in order to add them to the list of Specific Pollutants, defined at national level (revision of the Italian Decree DM 260/2010 on the classification of surface water bodies).

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New automated extraction method to analyse synthetic musk compounds in environmental water samples

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Synthetic musks are organic compounds known by their fixative properties and strong odour. These compounds are used as fragrance ingredients in personal care products (PCPs) such as cosmetics, detergents and cleaning agents [1]. Nitro and polycyclic musks (Table 1) were investigated in this study. Nitro musks are identified as very persistent and very bioccumulative (vPvB) compounds (e.g. musk xylene is identified as a vPvB substance under REACH regulations) and are therefore already phased out, while polycyclic musks are still produced and used in high quantities, particularly galaxolide (HHCB) and tonalide (AHTN) (1,000 – 10,000 tonnes per year, according to the European Chemicals Agency–ECHA Portal), the two polycyclic musks most commonly found in environmental samples [3].

Although musks are not included in the list of priority substances of the Water Framework Directive (WFD 2013/39/EU), their high concentrations, persistence and worldwide use make these emerging compounds serious candidates for monitoring and regulation [4], which highlights the need for reliable analytical methods able to detect and quantify these compounds.

Microextraction by packed sorbent (MEPS) is a miniaturisation of solid phase extraction (SPE) techniques and was used to extract simultaneously nine musk compounds from environmental water samples (estuarine and wastewater samples) collected in the Adour estuary in France, and in the Urdaibai estuary, in the Basque Country (northern Spain). This recent technique allows in-line sample preparation and requires small sample and solvent volumes, as well as short extraction times. When combined with a gas chromatograph inlet system as a programmed temperature vaporiser (PTV), which allows large volume injection (LVI), method sensitivity can be highly improved.

WHY PRE-CONCENTRATE?

Additionally, environmental water samples may sometimes carry a high load of suspended particulate matter and organic carbon, which hinders the analytical process. To achieve good analytical performances, i.e. low limits of quantification, accuracy and precision, new analytical methods are being developed and adapted to new and more demanding matrices in order to measure lower amounts of the target compounds. Recent micro-extraction and pre-concentration techniques based on new solid phase extraction have shown great potential, as they allow: miniaturised sample extraction, using little to no solvent; the elimination of some matrix compounds that could interfere with the analytical process; and even the purification of extracts.

MICROEXTRACTION BY PACKED SORBENT (MEPS) TECHNIQUE

MEPS was first introduced by Abdel-Rehim in 2004. It is a miniaturisation of SPE techniques as it uses only 2–4 mg of sorbent while classical SPE uses 60–200 mg. The techniques are based on similar principles: the extraction is based on the analyte retention from an aqueous sample that flows through the solid sorbent and the following desorption of those

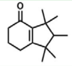
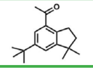
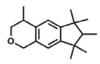
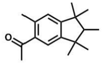
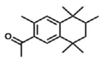
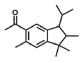
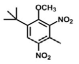
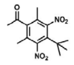
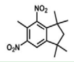
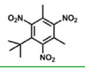
Analyte	CAS number	Structure	Target Ion quantifier (qualifiers)	Log K_{ow}
Cashmeran (DPMI) 6,7-dihydro-1,1,2,3,3-pentamethyl-4(5H)-indanone	33704-61-9		191 (206, 192)	4.9
Celestolide (ADBI) 4-acetyl-1,1-dimethyl-6-tert-butylindane	13171-00-1		229 (244, 173)	6.6
Galaxolide (HHCB) 1,3,4,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta-(γ)-2-benzopyran	1222-05-5		243 (258, 213)	5.9
Phantolide (AHMI) 6-acetyl-1,1,2,3,3,5-hexamethylindane	15323-35-0		229 (244, 187)	6.7
Tonalide (AHTN) 7-acetyl-1,1,3,4,4,6-hexamethyl-1,2,3,4-tetrahydronaphthalene	1506-02-1		243 (258, 159)	5.7
Traseolide (ATII) 5-acetyl-1,1,2,6-tetramethyl-3-isopropylindane	68140-48-7		215 (258, 173)	6.3
Musk Ambrette (MA) 1-tert-butyl-2-methoxy-4-methyl-3,5-dinitrobenzene	83-66-9		253 (268, 254)	3.7
Musk Ketone (MK) 4-aceto-3,5-dimethyl-2,6-dinitrotert-butylbenzene	81-14-1		279 (294, 280)	4.3
Musk Mosken (MM) 1,1,3,3,5-pentamethyl-4,6-dinitroindane	116-66-5		263 (278, 264)	5.8
Musk Xylene (MX) 5-tert-butyl-2,4,6-trinitro-m-xylene	81-15-2		282 (283)	4.5

Table 1. Target synthetic musk compounds (polycyclic and nitro musks), their abbreviations and IUPAC names, CAS number, chemical structure, target ions used in MS detection and their octanol-water partition coefficient (Kow) data.

analytes by elution.Other solid phase extraction techniques could also be used, such as the classic solid-phase microextraction (SPME) or the recent stir-bar sorptive extraction (SBSE), but MEPS provides the lowest sample and elution volumes and also enables in-line sample preparation.

In this study, the extraction procedure was carried out according to Cavalheiro et al. 2013 [5], as well as all the parameters settled for the analysis by large volume injection GC-MS. The figures of merit of the method are represented in Table 2 and show excellent analytical performances in terms of linearity, precision, detection limits and recoveries, allowing the possible monitoring of synthetic musk compounds in various complex water matrices such as wastewater treatment plant influent and effluent and estuarine water samples.

Analytes	Linearity. R^2	Precision (%. n=4))		MDLs* ng/L			Recovery (% at 200 ng/L)		
	(MDL – 2500 ng/L)	20 ng/L	200 ng/L	WWTP influent	WWTP effluent	Estuarine water	WWTP influent	WWTP effluent	Estuarine water
DPMI	0.9635	8.6	13.2	10	7	22	108	76	102
ADBI	0.9958	12.1	5.8	8	14	11	135	86	85
HHCB	0.9705	9.3	8.8	23	39	84	89	133	96
AHMI	0.9948	11.2	6.2	7	14	9	123	86	81
AHTN	0.9850	11.8	8.4	25	31	32	76	108	96
ATII	0.9948	8.1	7.3	6	7	8	106	84	85
MA	0.9970	1.1	5.3	5	9	8	105	75	88
MK	0.9927	11.9	6.0	9	10	10	118	87	87
MM	0.9899	14.9	13.2	degradation			85	75	93

Table 2. Figures of merit of the analytical method used to quantify synthetic musk compounds.

** MDL – method detection limit*

OCCURRENCE OF SYNTHETIC MUSK COMPOUNDS IN WASTEWATER TREATMENT PLANTS (WWTPS)

This methodology was applied to 3 wastewater treatment plants (influents and effluents) discharging in the Adour estuary (France), as well as 1 influent and effluent sample from the Urdaibai estuary (Spain). The average (n=3) analyte concentrations were determined in those samples and their associated uncertainties. Figure 1 shows the results obtained for DPMI, HHCB and AHTN; as for the other musk compounds, results were below the method detection limits.

The results show that A3 is the WWTP with the systematically highest musk concentrations, while U1 is the one with the lowest concentrations. It is known that the studied WWTP have different capacities, types of treatment and daily flow rates (described in Table 3) which could explain the differences found in the results, but that would mean that the results obtained in U1 should be between the ones in A1 and A3 (as it has intermediate capacity and flow rate), which is not the case. Additionally, musk concentrations found in the Urdaibai WWTP using MEPS technique are similar to ones found while using another microextraction technique [6]. Another important indication given by these results is the low removal percentages the WWTP are able to achieve. This means that these molecules, widely used in everyday personal care products and fed constantly into the WWTP, are barely removed from the effluents, representing a high input into the estuarine ecosystem, no matter what type of treatment is applied.

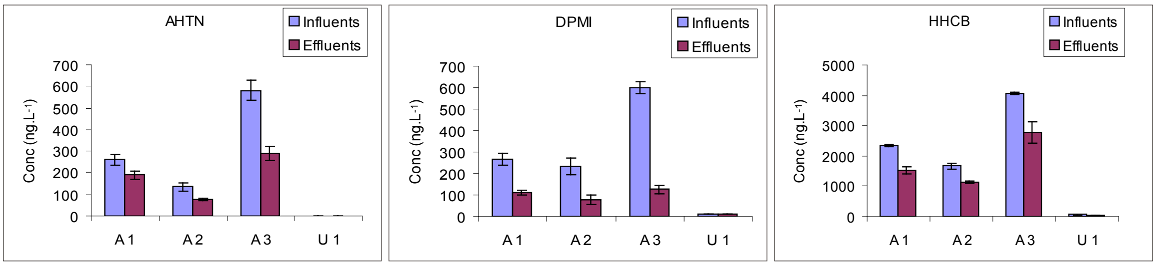


Figure 1. Concentrations (ng/L) determined in influents and effluents of 3 wastewater treatment plants in the Adour estuary (labelled as A1, A2 and A3) and 1 WWTP from the Urdaibai estuary (U1).

WWTP	Capacity	Treatment	Flow rate dry / wet
A1	55,000	Pretreatment; primary; activated sludge+biofilter	11,000 / 21,000
A2	110,000	Pretreatment; primary; activated sludge odour chemical removal	20,000 / 46,300
A3	5,000	Pretreatment; primary; activated sludge	1,000 / n.a.
U1	18,000	Pretreatment, primary, activated sludge + UV	4,500 / n.a.

Table 3. Description of the studied WWTPs: capacity (inhabitant equivalent, IE), type of treatment, average flow rate (m^3/d) in dry and wet weather

CONCLUSION

Although DPMI, HHCB and AHTN concentrations appear to be extremely high in the WWTP of the Adour estuary (45–2347 ng/L) when compared to the concentrations obtained in the WWTP of the Urdaibai estuary (<MDL-62 ng/L), similar or higher concentration values have been reported in several studies from Europe, U.S. and Canada [7-11]. These differences, however, have inspired further studies, in the wastewater treatment plants in the Adour estuary, of the impact and fate of these emerging contaminants. Additionally, different types of wastewater treatment should be studied and developed in order to improve the removal efficiency of the WWTP. Finally, the MEPS technique revealed itself as a useful tool in the monitoring of musk compounds in wastewater treatment plants due to its automation, speed and low sample and solvent volumes.

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Pharmaceuticals and other contaminants of emerging concern in landfill leachate of the United States

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INTRODUCTION

Landfills are commonly the final respository for a heterogeneous mixture of waste from residential, commercial, and industrial sources. The use of landfills as a means of waste disposal will likely increase as the global population increases and nations develop. Thus, landfills receiving such waste have the potential to produce leachate containing numerous organic chemicals including contaminants of emerging concern (CECs) such as pharmaceuticals, personal care products, and hormones. This leachate is often discharged to pathways that lead directly (e.g. groundwater, streams) or indirectly (e.g. wastewater treament plants) to the environment. Limited research, however, has been conducted regarding the characterisation of landfill leachate for CECs.

To provide the first national-scale assessment of CECs in landfill leachate across the United States, fresh leachate samples (i.e. prior to onsite treatment) from 19 landfills in 16 states were collected in 2011 and analysed for 202 CECs [1]. The targeted CECs were selected for analysis because they were expected to be persistent in the environment; are used, excreted, or disposed of in substantial quantities; may have human or environmental health effects; or are potential indicators of environmentally relevant classes of chemicals or source materials.

MATERIALS AND METHODS

The sampling network for this study included 12 municipal and 7 private landfills across the United States with varying landfill waste compositions, geographic and climatic settings, ages of waste, waste loads, and leachate production. Landfills were selected based on the following criteria: (1) active, (2) permitted to accept municipal solid waste, (3) receivers of non-hazordous commercial and industrial waste, and (4) equipped with leachate-collection and recovery systems. Fresh leachate samples were collected from 13 landfills equipped with sump pumps that were part of the leachate-collections systems and 6 landfills equipped with gravity-fed leachate-collection systems with access to the leachate stream by a manhole (Figure 1). All samples were analyzed for 202 CECs using the following methods: 1) LC/MS/MS for pharmaceuticals [2], 2) GC/MS for pharmaceuticals [3], 3) GC/MS/MS for hormones [4], and 4) GC/MS for household/industrial chemicals [5]. Field quality-control protocols for this study consisted of field blanks and field replicates.

Figure 1. Example sample collection for this national landfill leachate study. (A) Manhole access to leachate stream, (B) Leachate sample collection using filter, and (C) Leachate filled bottles for sample analysis. Photographs by Dana W. Kolpin (U.S. Geological Survey).

RESULTS

A total of 129 out of 202 CECs were detected during this study, including 62 pharmaceuticals, 23 industrial chemicals, 18 non-prescription pharmaceuticals, 16 household chemicals, 6 hormones, and 4 plant/animal sterols. CECs were detected in every leachate sample, with a total number of detected CECs in samples ranging from 6 to 82 (median = 31). Bisphenol A, cotinine, and DEET were the most frequently detected CECs, with each being found in 95% of the leachate samples. Other frequently detected CECs included lidocaine (89%), camphor (84%), benzophenone (79%), naphthalene (79%), and amphetamine (79%). A total of 21 CECs were measured in 50% or more of the leachate samples (Figure 2).

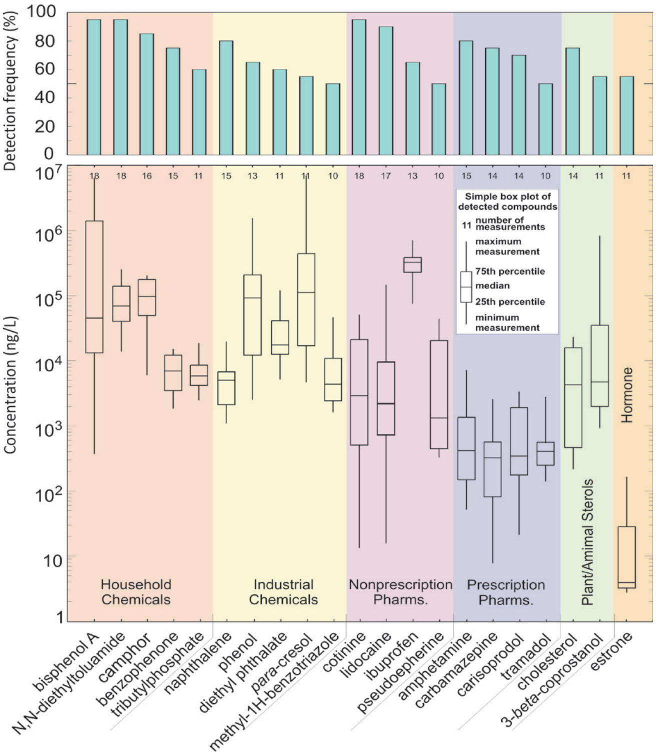

Table 1. Select maximum concentrations and frequencies of detection observed for this study[1].

CEC concentrations spanned six orders of magnitude from 1 ng/L to over 1,000,000 ng/L. Maximum concentrations for three chemicals exceeded 1,000,000 ng/L for this study: para-cresol (7,020,000 ng/L), bisphenol A (6,380,000 ng/L), and phenol (1,550,000 ng/L). Select maximum concentrations and frequencies of detection are provided in Table 1. Industrial and household chemicals were generally measured in the greatest concentration, composing 82% of the total measured CEC concentrations, followed by non-prescription pharmaceuticals (12%), plant/animal sterols (4%), prescription pharmaceuticals (1%), and hormones (<1%). Leachate from landfills in areas receiving greater amounts of precipitation had greater frequencies of CEC detections and concentrations in leachate than landfills receiving less precipitation. The primary leachate disposal mechanism for landfills in wet environments was discharge to wastewater treatment plants. In contrast, landfills in dry environments recycled or retained leachate on-site. A complete summary of the CEC results for this study and potential relations between CECs and select landfill characteristics is provided elsewhere [1].

Maximum Concentration (ng/L)	Frequency of Detection (%)	Chemical (primary use)
7,020,000	55	para-cresol (plasticizer and flame-retardant, antioxidant in oils, rubber, polymers, and wood preservative)
6,380,000	95	bisphenol A (used in plastics, thermal paper, and epoxy resins)
834,000	55	3-beta-coprostanol (fecal indicator)
705,000	65	ibuprofen (analgesic, antipyretic)
254,000	95	DEET (insect repellent)
205,000	84	camphor (natural compound with medicinal uses and embalming)
147,000	89	lidocaine (local anesthetic, topical anti-itch treatment)
51,200	95	cotinine (transformation product of nicotine)
46,900	50	methyl-1H-benzotriazole (corrosion inhibitor)
44,100	50	pseudophedrine (appetite suppressant, decongestant, stimulant)
18,800	60	tributylphosphate (antifoaming agent, flame retardant)
3,400	70	carisoprodol (muscle relaxant)
2,590	75	carbamazepine (anticonvulsant and mood stabiliser)
168	55	estrone (natural estrogenic hormone)

Figure 2. Frequency of detection and detected concentrations for CECs found in 50% or more leachate samples from the 19 landfills for this study.

CONCLUSION

Fresh landfill leachate was found to contain complex mixtures of CECs that include household and industrial chemicals, prescription and non-prescription pharmaceuticals, plant/animal sterols, and hormones. Levels of select CECs can be quite large, with concentrations as high as 7,020,000 ng/L measured for this study. Landfills in wet environments produced greater quantities of leachate and contained greater frequencies of CEC detections and concentrations than landfills in dry environments. Analysis of fresh leachate is an important first step in understanding landfills as a source of CECs, but may not necessarily be representative of CEC concentrations in leachate ultimately being discharged to environmental pathways. Follow-up research is currently being conducted regarding CEC occurrence and concentration in final leachate in landfills across the United States.

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Fate of phthalates and bisphenol A in the environment: the Seine River basin as an experimental field

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USES AND REGULATION

Phthalates and bisphenol A (BPA) are commonly used as plasticisers in a large number of consumer products. Phthalates have numerous applications in everyday life, such as automotive manufacturing, coatings for floors and walls, medical equipment, medicines, food packaging and cosmetics. For example, PVC may contain up to 50% DEHP. As it is not chemically bound to the polymer, it can easily be released into the environment during PVC production, end-product use, storage, disposal or even recycling activities. BPA is an essential ingredient in polycarbonate production and, unlike phthalates, it is chemically bound to polymers. However, after hydrolysis, BPA may be released into the environment during the production of polycarbonate and during the use of consumer products containing this substance.

Phthalates and BPA are known to compete with endogenous hormones through binding to their specific receptors or interfering in their synthesis and metabolism (Akingbémi, 2004). Exposure to these compounds was associated with altered hormone levels, reproductive adverse effects (particularly male fertility), precocious puberty, increased incidence of chronic diseases and a possible role in cancer development (Moore et al., 2002). The European Food Safety Authority (EFSA) has set Tolerable Daily Intake (TDI) values for BPA, DEHP and other phthalates. The TDI for both BPA (EFSA, 2007) and DEHP (EFSA, 2005) is 0.05 mg/kg body weight but improvements are still needed for the determination of DEHP exposure from all sources along with their relative importance, in order to decide what proportion of the TDI can be allocated to food contact materials alone (EFSA, 2005). Moreover, DBP, BBP and DEHP are listed among hazardous substances of very high concern for humans and the environment under the REACH Regulation. As a result, the use of phthalates in children's toys has been restricted by the European Union. DEHP, BBP, and DBP are banned for all toys; DiNP, DiDP, and DnOP are restricted only in toys that can be placed into the mouth (Directive 2005/84/CE). Furthermore, DBP and DEHP (Directive 2004/93/CE) are banned for use in cosmetics as well as MnPP, DnPP, MiPP, DiPP, BBP (Directive 2005/80/CE).

There are some restrictions on the use of phthalates in food contact materials in the European Union (Directive 2007/19/CE). DBP and DEHP are not permitted for single-use applications such as cap seals or gaskets but can be legally used in disposable packaging in contact with non-fatty foods, provided the migration of the plasticisers does not exceed the Substance Migration Limit (SML) of 0.3 mg/kg food (DBP) and 1.5 mg/kg food (DEHP). Meanwhile, BBP is allowed for use in disposable packaging and is also permitted for use in food contact with fatty food single-use applications, except for infant formulae and follow-on formulae for young children (Directive 91/321/EC) and processed cereal-based foods and baby foods for infants and young children (Directive 96/5/EC). The corresponding SML for BBP for these uses is 30 mg/kg food. For drinking water, a DEHP limit value of 8 µg/L is recommended by the World Health Organisation (WHO, 2011) and of 6 µg/L by the US Environmental Protection Agency (USEPA, 1991) but no regulation has yet been proposed in Europe. BPA is permitted for use in food contact plastics in the European Union with a specific migration limit of 0.6 mg/kg food and is prohibited in baby bottles (Directive 2011/8/CE). In France, further to Law n° 2012-1442, the manufacture, import, export and marketing of any packaging in food distribution containing BPA ceased on 1 January 2015.

Finally, DEHP is on the list of Priority Hazardous Substances under the Water Framework Directive and its concentration in water monitored as an annual average should not exceed 1.3 µg/L (Environmental Quality Standard – EQS).

EMISSION SOURCES AND FATE OF PHTHALATES AND BPA AT RIVER BASIN SCALE: RESULTS OF THE PIREN SEINE PROGRAMME

Phthalates and BPA can be regarded today as well studied chemicals: they are already part of regulatory frameworks and they can be considered as "former emerging contaminants". The focus is now on the definition and implementation of appropriate management measures. In that context, it is crucial to get a complete overview of the main emission sources and the fate of these contaminants in the environment at the river basin scale. To this end, BPA and phthalates have been studied for more than 10 years within the PIREN-Seine programme (http://www.sisyphe.upmc.fr/piren/), an interdisciplinary programme designed to explore the biogeochemical and ecological functioning of the Seine River system at the scale of its whole drainage network in relation to land use and environmental management in the watershed. The Seine river basin is dominated by the megalopolis of Paris (10 million inhabitants), surrounded by intensive agricultural areas: it is a prime example of a regional territory strongly affected by anthropogenic activities. Micropollutant contamination studies have been conducted at different water basin scales on urbanised (Orge) and rural (Charmoise) rivers.

ATMOSPHERIC COMPARTMENT

Phthalates and BPA were first investigated in the atmospheric compartment. Except for DMP, which is a VOC (Volatile Organic Compound), phthalates are classified as semi-volatile organic compounds. BPA has low volatility.

The fate of six phthalates in the ambient air was investigated in the Paris area. Total atmospheric levels as ng/m^3 were as follows: DMP, 0.5; DEP, 10.7; DnBP, 22.2; BBP, 4.6; DEHP, 18.9; and DnOP, 0.5, showing a prevalence of DnBP, DEHP. Phthalates were mainly present in the vapour phase, from 94% to 65%, particularly the esters with alkyl chain lengths of less than 6 carbons. An inverse correlation was found between the vapour phase concentrations and the molecular weight, along with a direct correlation between the vapour phase concentrations and the logarithm of vapour pressure (P) of the compounds. Seasonal variations of phthalate concentrations were correlated with air temperature.

Rain water concentrations as ng/L, followed the same sequence as air ones: DMP, 116; DEP, 333; DnBP, 592; BBP, 81; DEHP, 423 and DnOP, 10. Yearly balances for rainwater and bulk deposition allowed the estimation of dry deposits that represented about half of total contamination, highlighting the important role played by particles in atmospheric deposition processes (Teil et al., 2006).

BPA was also measured in ambient air and was quantified in 75% of the collected samples, but at lower concentrations than phthalates (< 1 ng/m^3).

The indoor air contribution to the overall balance was also studied in the Paris area. Indoor air measurements in three different types of representative indoor environment (an office, a flat and a nursery) displayed concentrations in the range of 28 to 70 ng/m^3 (DEHP) and 0.7 to 1.2 ng/m^3 (BPA). In general in urban areas, higher levels are observed for phthalates and BPA in indoor than in outdoor air. Population density is a major factor affecting semi-volatile organic compounds' emissions in urban areas, and indoor sources might even be considered as a factor influencing outdoor ambient air concentrations in densely populated areas (Alliot et al., 2014).

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WASTEWATER TREATMENT PLANT (WWTP) EMISSIONS

The PIREN-Seine studies confirm the occurrence of phthalates (with the exception of DnOP) and BPA at high concentrations at WWTP inlets. DEHP and DiNP are in general the most abundant compounds (30% and 25%, respectively), followed by DiDP (21%) and DiBP (9%). Average raw water concentrations are in the range of about 4 µg/L for BPA and 0.7 - 33.3 µg/L for phthalates. Phthalates and BPA are found at far lower concentrations in WWTP effluents, with removal ratios from 90% to 98%. The contaminant load was well abated during the combined treatment (decantation + biodegradation) leading to the elimination of 95% of the particles from the WWTP inputs (Tran et al., 2015). DMP and DEP were primarily distributed in the dissolved phase and thus, decantation processes played a minor role. These phthalates undergo volatilisation and biodegradation, which represent the main elimination pathways. BPA poorly adsorbed (6%) as compared to DEHP (78%), was only partially removed by decantation. Meanwhile, in the dissolved phase, BPA's mean concentrations dropped from 5 µg/L at the inlet to 0.4 µg/L at the outlet of the treatment plant. For BPA, Samaras et al (2013) reported that accumulation on sludge was of minor importance and that its removal was due to biodegradation/biotransformation.

DEHP removal efficiency varied little throughout the year, the temperature playing a minor long-term role on its sorption to particles. BPA removal efficiency varied with temperature.

SURFACE WATER

Phthalates and BPA are ubiquitous in both urban and rural areas of the river Seine basin, with DEHP always the most prevalent. According to PIREN-Seine investigations, the phthalate concentrations in the Seine were 4 times higher in urban than rural areas: 846 against 226 ng/L (Dargnat et al., 2007). BPA concentrations observed in the Seine in Paris city ranged from < 11 (LQ) to 154 ng/L (Cladière et al., 2013).

Phase distributions are notably different for these compounds and they depend on their physico-chemical properties controlling the affinity for particles. Marked seasonal variations in the river water were found: in summer, for instance, increased degradation processes produced the lowest BPA contamination, whereas low flow conditions caused phthalate concentrations to increase (Tran et al., 2015). Seasonal variations of the phthalate concentrations in Paris appear to be closely associated with the rainfall pattern and with the hydrological regime of the river, with concentration peaks preceding flow peaks (Teil et al., 2007). That reflects the local origin of contaminants (i.e., runoff from urban surfaces and inputs from storm sewers at the beginning of rain episodes).

The phthalate pattern in a rural basin (Charmoise, a sub-catchment of the Orge River, a Seine River affluent) showed that all the compounds except DnOP were detected at 3 sites (upstream, downstream and far downstream of WWTP). DEHP remained the major compound but it never exceeded the EQS of 1.3 µg/L, with a mean concentration downstream of the WWTP discharge of 1.0 µg/L. Nevertheless, in summertime, high DEHP concentrations up to 1.7 µg/L were temporarily detected, indicating poor water quality (Figure 1).

Annual variations of BPA at the same 3 sites displayed a seasonal cycle, with high concentrations during winter when the river flow was maximal. Because the river is narrow and shallow, two parameters might interfere with the pollutant fate: (i) an increase of biodegradation activities by microorganisms in the WWTP and in the river during summer (ii) higher BPA photo-degradation in summer (as previously reported by Nakatani et al. (2004) in rivers in Japan). A low-flow dilution of WWTP outputs might be hypothesised to explain the higher levels of DEHP during summer, since, contrary to BPA, the WWTP discharge is the main input source of DEHP to the river.

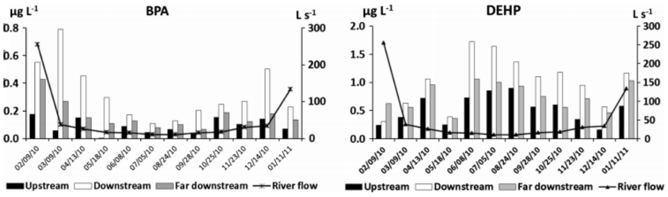

Figure 1: BPA and DEHP raw water concentrations (µg/L) and river flow (L/s) of the Charmoise River.

BIOTA CONTAMINATION

Phthalates were investigated in muscle tissue in three fish species from the Seine River and the Orge River, upstream and downstream of urban areas (Teil et al., 2014): two Cyprinidae (Roach and Chub) and one Percidae (Perch) (Teil et al., 2012). Muscle tissue contents ranged from 2.25 to 5.12 µg/g dry weight as the sum of 7 phthalates. The highest contents were found in the perch. In addition, the distribution of these lipophilic chemicals between different target organs in roach gives evidence of a preferential accumulation gradient, i.e., first in gonad, then liver and then muscle. Phthalate contents in roach from the Orge River were low at the upstream part of the Orge basin and remained lower than in roach from the Seine River at the basin outlet. Results were consistent with those reported in the Netherlands for phthalates commonly found in bream (Abramis brama; Vethaak et al.. 2005). Variations of roach concentrations gave an indication of their habitat contamination increase observed downstream of the densely urbanised areas. The Piren-Seine programme has not yet collected data on exposure of biota fish to BPA.

CONTRIBUTION TO THE RIVER MASS LOAD

The measurements carried out in different compartments allowed the establishment of a first input/output balance for plasticisers at the scale of a rural catchment (Charmoise basin). For phthalates, the major input to surface water was atmospheric deposition (90%) whereas for BPA, the highest contribution was the WWTP discharge (Figure 2).

However, it appears that at the river outlet, the BPA balance was higher than the input. That result would suggest an underestimation of runoff mass load even in the rural area. Storm water was not taken into account in this sub-basin, leading to an underestimation of plasticiser inputs to the river. These aspects are currently being further investigated.

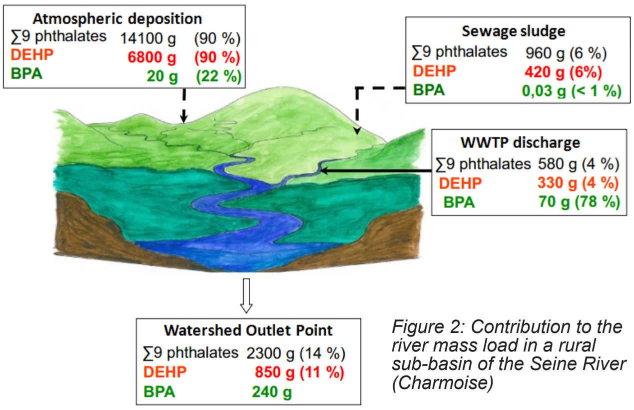

Figure 2: Contribution to the river mass load in a rural sub-basin of the Seine River (Charmoise)

CONCLUSIONS

PIREN-Seine studies confirm that phthalates and BPA are ubiquitous in the environment, even in the rural upstream section. The role of atmospheric compartments in the balance of phthalates in the drainage system of the Seine River is proved. The phase distribution of these two families of plasticisers appears significantly different and related to their molecular physico-chemical properties, which control their affinity for particles. Phthalates and BPA were efficiently removed by the WWTP, probably with distinct mechanisms: degradation processes controlled by the temperature for BPA, and decantation mechanisms – mainly by particle sorption – for phthalates. Moreover, marked seasonal variations in concentrations in rivers were shown, with the lowest BPA contamination in summer linked to enhanced degradation whereas there was a phthalate concentration increase related to low-flow dilution.

The study of the Charmoise River sub-basin provides for the first time in an elementary river basin in France a comprehensive overview of the fate of BPA and phthalates and an estimate of the contribution of the different emissions of these compounds to the river mass load.

The mass load of phthalates in the drainage network system is balanced by the sum of contributions by industrial waste and municipal sewage treatment plants. For BPA, however, inputs from storm sewers must be documented to improve the mass balance estimation.

These findings might contribute to develop modelling approaches for the management of surface water quality at the scale of elementary river basins and the evaluation of the substitution scenarios for these still widely used industrial chemicals.

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GLOSSARY

- bisphenol A: BPA
- butylbenzyl phthalate: BBP
- di-(2-ethylhexyl) phthalate: DEHP
- di-iso-decyl phthalate: DiDP
- di-iso-nonyl phthalate: DiNP
- di-iso-pentyl phthalate: DiPP
- di-methyl phthalate: DMP
- di-n-butyl phthalate: DnBP
- di-n-octyl phthalate: DnOP
- di-n-pentyl phthalate: DnPP
- mono-iso-pentyl phthalate: MiPP
- mono-n-pentyl phthalate: MnPP

Emerging risks and benefits of nanopesticides from an environmental perspective

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INTRODUCTION

More than 40 years of research have now provided the EU with one of the most advanced regulatory frameworks to assess the risk associated with the release into the environment of bioactive organic substances such as pesticides, biocides or pharmaceuticals. Environmental risk assessment is based on the solute approach (based on coefficients and the equilibrium paradigm), which considers the soluble portion of organic substances to be of importance (European Commission, 2009).

Following the development of nanotechnologies, investigations into the fate of nanoparticles have demonstrated that the traditional solute approach is not adequate, and that other factors and processes should be considered to assess environmental risk (Figure 1). This prompted the development of a nano approach, which is progressively being implemented in existing frameworks (European Commission, 2012).

Besides hard/rigid particles such as TiO2, nano silver or carbon nanotubes, nanotechnologies have also demonstrated their potential as an enabling technology for the delivery of bioactive organic substances, based on "soft" organic nanoparticles. Both the private and public sector are currently making significant investments to further develop those products (e.g. EU Horizon 2020 call H2020-NMP-2014-2015 for the development of "Novel nanomatrices and nanocapsules" containing active ingredients, € 3–5 million expected budget). The list of novel organic nanoparticles used in the pharmaceutical and agrochemical sectors is thus expected to grow rapidly in the future. Pesticide and pharmaceutical active substances are contaminants of high concern for all environmental compartments. It is therefore essential that the potential impacts of organic nanoparticles are adequately assessed to ensure the protection of human and environmental health. It is not yet known whether the currently applied Solute or Nano approaches are adequate for this purpose.

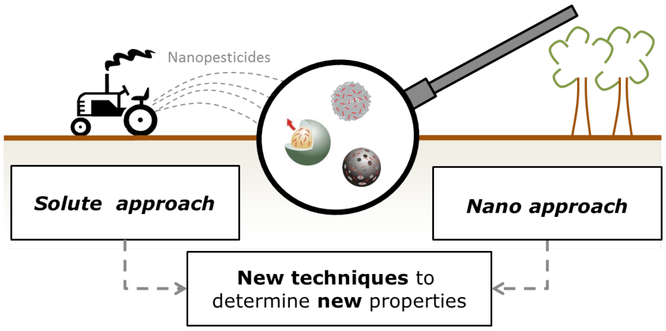

Figure 1. The current level of knowledge is insufficient for a reliable assessment of the impact associated with the use of nanopesticides. The validity of current approaches i.e., the Solute and Nano approaches, should be verified and possibly refined to adequately account for the behaviour of the novel type of contaminants.

WHAT ARE NANOPESTICIDES AND THEIR POSSIBLE BENEFITS?

In the context of environmental research, the most remarkable example of organic nanoparticles is that of nanopesticides, which we here define as nanoformulated plant protection products, intentionally applied into the environment for agricultural purposes. A comprehensive review of the available knowledge of nanopesticides was initiated in 2011, with the objectives: (i) to explore potential applications of nanotechnology within the pesticide formulation sector; (ii) to identify possible impacts on environmental fate; and (iii) to analyse the suitability of current exposure assessment procedures to account for their novel properties within the EU regulatory context (Kah et al., 2013; Kah and Hofmann, 2014).

Based on more than 3000 patents and 250 peer-reviewed publications and reports, nanopesticides represent a wide range of products. With a clear inspiration coming from the pharmaceutical sector, nanopesticides often consist of nanocarriers loaded with active ingredients, and allowing a wide range of objectives to be achieved and possibly combined (e.g., slow/targeted release, increase in apparent water solubility or uptake). Over the last two years, incentives to use nanotechnology to develop formulations that are less harmful to the environment have clearly emerged (Kah and Hofmann, 2014). This is apparent from an increased number of nanopesticides consisting of (i) nano-carriers made of biodegradable polymers of natural origins, as well as (ii) alternative active ingredients of natural origin e.g., essential oils or pheromones that are less harmful to non-target organisms and may potentially reduce the development of resistances. Nanopesticides could thus offer a range of benefits relative to conventional pesticides, including increased efficacy, durability, and a reduction in the amounts of active ingredients that need to be used.

CAN WE ASSESS THE POSSIBLE RISKS ASSOCIATED WITH THE USE OF NANOPESTICIDES?

Whilst some nanopesticides may be a safer alternative to existing products, they may also entail new risks. Nanoformulations are expected to (i) have significant impacts on the fate of active ingredients and/or (ii) introduce new ingredients whose environmental fate is mostly unknown (Kah et al., 2013). Investigations into the environmental fate of nanopesticides remain scarce, and have generally only focused on the particular processes targeted by the nanoformulation, without considering possible unintended changes (Kah and Hofmann, 2014). For instance, a nanoformulation may be designed to protect an active ingredient from premature degradation, thus allowing the active ingredient to remain biologically active for longer, and reduce both the quantities applied and the number of applications. The longer persistence of a pesticide could, however, become a disadvantage if, for example, the release of the active ingredient from the carrier continues or even increases into wetter periods of the year. Transport properties of the nanoformulated active ingredient are also expected to significantly differ from those of the pure active ingredient. Current analytical methods, test protocols and fate modelling procedures that are based on the solute approach cannot account for those novel "nano" properties, as recently demonstrated for a nanoformulation of atrazine (Kah et al., 2014). The current level of knowledge therefore appears to be insufficient for a reliable assessment of the benefits and risks associated with the use of nanopesticides.

A number of international organisations have recently discussed potential issues that will result from the use of nanopesticides (e.g., FAO/WHO, 2013). The International Union for Pure and Applied Chemistry, IUPAC, organised the first international workshop on nanopesticides in 2013, followed by a special symposium as part of the ACS-IUPAC 2014 Congress of Pesticide Chemistry. International experts from academia, industry and regulatory bodies discussed the inadequacy of current approaches based on the solute and nano paradigms. A number of recommendations and guiding principles for ecological risk assessment were developed and were summarised in Kookana et al. (2014).

CONCLUSION

Nanotechnologies have demonstrated their potential as an enabling technology for the delivery of bioactive organic substances. From an environmental perspective, nanoformulations are expected (i) to have significant impacts on the fate of active ingredients and/or (ii) to introduce new ingredients whose fate is still poorly understood. The current level of knowledge does not appear to allow a fair assessment of the advantages and disadvantages that will result from the use of nanoformulations.

Nanopesticides are the priority for environmental research as they would be intentionally applied in large quantities into the environment. Research is urgently required in order to (i) identify the assumptions currently applied that may not be valid in the case of nanopesticides, (ii) evaluate the points or situations in which differences may impact significantly on the risk assessment outcomes, and (iii) refine or adapt approaches as required. The aim should be not only to ensure the protection of human and environmental health, but also to allow the emergence of innovative solutions to plant protection. Research on the environmental impacts of nanopesticides certainly comes with great challenges, but it also represents a great opportunity to better integrate knowledge and approaches from several fields of environmental sciences, and to combine experiences gained from the development of regulatory frameworks currently in place. Success will require collaborative initiatives on all aspects of risk assessment science, including analytical, experimental and modelling fields.

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Fate of silver nanoparticles in urban water systems

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Silver nanoparticles (Ag-NP) are amongst the most intensively investigated nanomaterials, and are already used in numerous consumer products. Current production volumes of Ag-NP are substantially lower than those of other nanoparticles such as nano-TiO2 (Hendren, Mesnard, et al., 2011), but the well-known antimicrobial properties of Ag+ require a thorough investigation of possible environmental effects of Ag-NP, especially if the Ag-NP is released in an uncontrolled manner. There seems to be a general consensus that the dissolved Ag+ is responsible for the observed toxicity of Ag-NP (Xiu, Zhang, et al., 2012) and the considerable (eco)toxic response of particle-bound Ag may be explained by the strongly localised effects resulting from the particles that serve as an ‘infinite’ reservoir of Ag+ ions (Yin, Cheng, et al., 2011). It is expected that Ag-NP will mainly be released to the wastewater stream and results from Choi, Deng, et al. (2008) suggest that the activated sludge process in wastewater treatment plants (WWTP) may be compromised at higher input levels of Ag-NP. On the other hand, in an experimental study conducted on a pilot scale WWTP, we did not observe any complications related to the dosing of Ag-NP (Kaegi, Voegelin, et al., 2011).

The extraordinary reactivity of Ag-NP, which dramatically influences the (eco)toxicity of Ag, requires the transformation processes of Ag-NP to be assessed throughout their transport and in various compartments of urban wastewater systems, including sewer systems and WWTP, as well as in urban surface waters.

To assess the transport and transformations of Ag-NP in sewer systems, we spiked Ag-NP directly into a 5 km-long main trunk sewer and collected grab samples at 500 m, 2500 m and 5000 m downstream of the dosing locality (Kaegi, Voegelin, et al., 2013). We found an excellent mass closure of close to 100 %, which indicated that losses of Ag-NP to the sewer biofilm were negligible. Analytical electron microscopy analysis revealed that the Ag-NP were at least partially sulphidised (Figure 1) and were dominantly attached to other colloids in the wastewater.

X-ray absorption spectroscopy measurements from time-resolved wastewater batch experiments revealed that the degree of sulphidation was about 30% after 24h.

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These results demonstrate that it is very unlikely that pristine Ag-NP reach the WWTP. The dramatic reduction of toxicity, even of only partially sulphidised Ag-NP compared to pristine AgNP as shown by Reinsch, Levard, et al. (2012), suggest that the activated sludge process in a WWTP will not be compromised at the predicted mass loads of Ag-NP.

A small fraction of Ag-NP will pass the WWTP and will reach urban surface waters as possibly incompletely sulphidised Ag-NP. In addition, direct inputs of Ag-NP to urban surface waters are conceivable. Although bisulphide (HS-) is not stable under oxic conditions (surface waters), metal sulphides have been detected in oxic surface waters (Rozan, Benoit, et al., 1999) from urban areas. In batch experiments, we have recently shown that metallic Ag-NP will turn into Ag_2S under oxic conditions through the reactions with metal sulphides, such as ZnS or CuS (Thalmann, Voegelin, et al., 2014). Thus, it is expected that metallic Ag-NP that reach urban surface waters will be completely sulphidised within a few days (Figure 2).

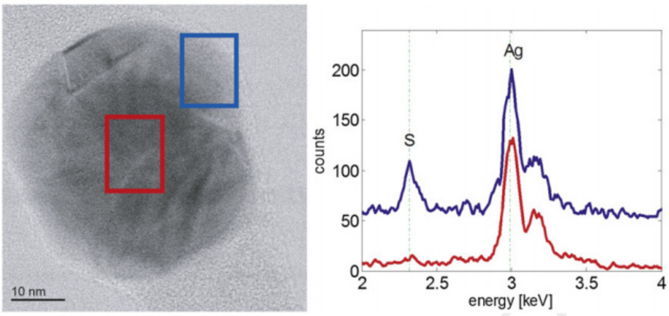

Figure 1: left: Transmission electron microscope (TEM) image of an Ag-NP reacted with wastewater. Energy dispersive X-ray (EDX) spectra of the red and the blue rectangles revealing different Ag/S ratios and thus different degrees of sulphidation are given on the right.

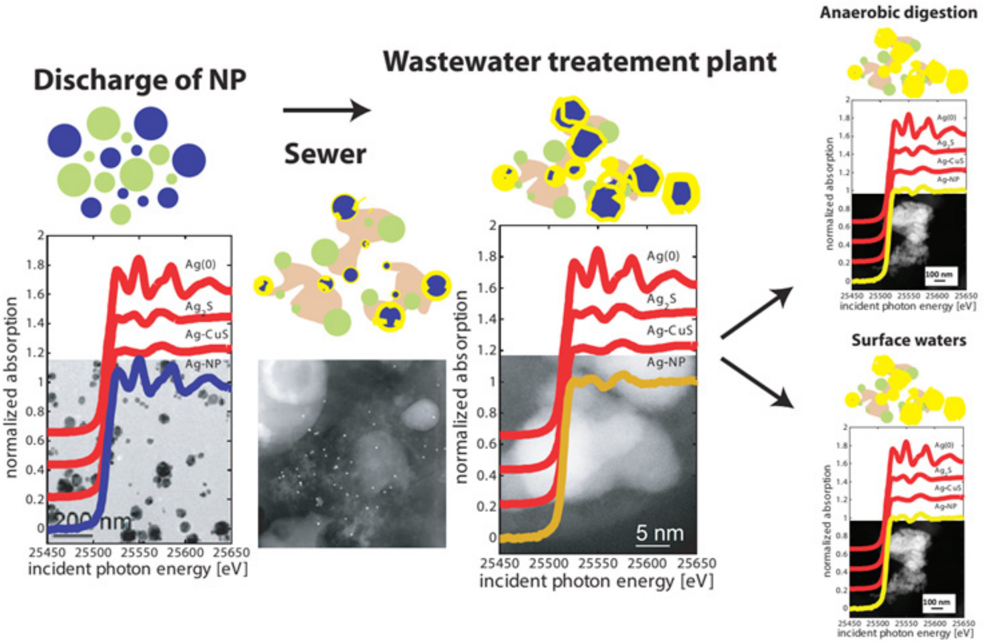

*Figure 2:
Schematic representation of the fate of (Ag)-NP in urban wastewater systems:
left: Release of pristine Ag (blue dots),
and Au (green dots)
to the sewer system.
Middle: transport of the NP attached to the biomass and partial sulphidation.
Right: complete sulphidation of Ag-NP either during anaerobic digestion or in urban surface waters.*

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Microplastics in the continental area: an emerging challenge

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MICROPLASTICS ISSUE

World plastic production has increased rapidly from 1.7 to 288 million tons annually within the last 60 years (PlasticsEurope, 2013). In the early 70s, the presence of plastic debris in the marine environment within the order of the millimeter size was highlighted (Carpenter et al., 1972) and since 2008, plastic particles < 5 mm have been defined as microplastics (Arthur et al., 2009). These microplastics cover a large and continuous spectrum of sizes and shapes including 1D-fibres, 2D-fragments and 3D-spherules. Microplastics are either primary ones, manufactured for various applications, or secondary ones, resulting from the fragmentation of larger plastic debris, mainly as a result of ultraviolet rays or mechanical abrasion. Synthetic clothes also release millimetric/sub-millimetric fibers.

Two environmental issues concerning the plastics are raised: i) the ingestion of microplastics by various species and ii) the interaction between microplastics and micropollutants. Microplastics ingestion may have various effects, including intestinal obstructions (Carpenter et al., 1972) and false indication of satiation, causing less food intake (Derraik, 2002). Browne et al. (2009) mentioned a possible translocation of small microplastics (< 10 µm). Microplastics can also act as passive samplers and adsorb hydrophobic organic pollutants (Teuten et al., 2007).

MICROPLASTICS IN THE CONTINENTAL AREA

While marine plastic pollution is beginning to be well documented, there is a limited focus on the continental area. Some preliminary studies show widespread contamination of continental aquatic environments by plastics in lakes (Eriksen et al., 2013; Faure et al., 2012; Free et al., 2014; Imhof et al., 2013) and in rivers (Gasperi et al., 2014; Lechner et al., 2014; Moore et al., 2011; Morritt et al., 2013; Rech et al., 2014). These field works deliver initial conclusions on the abundance of plastics and microplastics in lakes or in surface water but, to date, knowledge of the sources, fate and transfer of microplastics in continental environments is extremely limited. The research project launched in 2013 (PhD student 2013–2016 and ANR research proposal in 2015) by the LEESU (Laboratory of Water, Environment and Urban Systems) aims to investigate the sources, fates and fluxes of microplastics in urban areas and the subsequent impact of urban areas on surface water. Greater Paris is a relevant site since the Seine River basin combines strong anthropogenic pressures (12 million inhabitants) with a very limited dilution factor (Seine River median flow at Paris: 350 m^3/s). This project is investigating microplastic contamination of total atmospheric fallout, wastewater, wastewater treatment plant (WWTP) effluents and stormwater. Monitoring of surface water up- and down-stream of Paris has also started.

MICROPLASTICS IN URBAN AREAS AND IN SURFACE WATER

Total atmospheric fallout

Total atmospheric fallout was collected through a funnel in a 20 L glass bottle on the rooftop of the university, located in a dense urban environment (Figure 1). Monitoring started on 26 February 2014. For the first time, microplastics were observed in atmospheric fallout. More than 90 % of the microplastics observed have a fibrous shape, while 2D-fragments are occasionally observed. Approximately 50 % of the fibres are longer than 1 000 µm. Microplastic atmospheric fallout ranged from 29 to 280 particles/m^2/day. Free et al. (2014) reveal the presence of fibres in remote lakes and assume that some of them may originate from atmospheric fallout.

Urban raw wastewater, settled and treated water

Wastewater was collected at the Seine-Centre WWTP (240,000 m^3/d). The water treatment includes pretreatment, a primary treatment (physical-chemical lamellar settling) and a trickling biological treatment. Raw wastewater, settled wastewater and treated water were considered. First results underlined high concentrations of microplastics in raw wastewater (260–320 x 103 particles/m^3). All microplastics observed are fibrous. In the final effluent, the contamination decreases to 14–50 x10^3 particles/m^3, suggesting that the WWTP removes a great amount of the microplastics, probably transferred to sludge. Moreover, the size distribution of the particles shifts toward smaller sizes.

Surface water

For surface water, two different but complementary sampling approaches were used: i) sampling with a plankton net up- and down-stream of Paris (mesh size of 80 µm) and ii) sampling with a manta trawl (mesh size of 330 µm) (Figure 1). The net is immersed for 1 minute in the flow direction within the superficial layer (0.10–0.35 m) sampling about 400–2 000 L. The manta trawl is towed by a motor-boat (about 2 m/s) in the upstream direction for 15 minutes allowing the sampling of volumes ranging from 182 to 200 m^3 of the 0–0.30 m surface layer. Both sampling approaches highlighted the contamination of rivers by microplastics but they produced complementary results about their size. Campaigns performed with a plankton net showed that most of the microplastics are fibres. Their concentrations are site-dependent and lie in the 4–108 particles/m^3 range. In manta trawl samples, fibres, 2D-fragments and 3D-spherules were observed. Macroplastics (> 5 mm) were also trapped in the trawl. Concentrations of plastic items varied from 0.28 to 0.47 particles/m^3. About 40–50% of them are fibres. A direct comparison of results between manta trawl and net results is not relevant, since the size range of trapped particles is not similar (as a result of the manta trawl's larger mesh size and larger sample volumes). Using a 500 µm net, Lechner et al. (2014) also reported the presence of microplastics on the Danube at levels about 0.32 particles/m^3 and observed that fragments and spherules are the most frequent shapes of microplastics encountered.

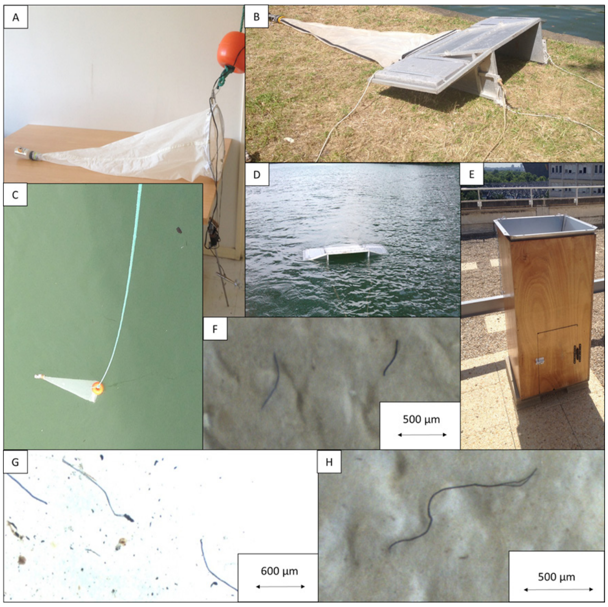

Figure 1: A/ Plankton net with a current meter that serves also as a ballast and a float that can be moved along the rope to fix the depth sampling. B/ Manta trawl. C/Plankton net in deployment. D/ Manta trawl in deployment. E/ Atmospheric fallout collector. F, G and H/ Fibres encountered on different samples

DISCUSSION

This project delivers initial data on the sources and fate of microplastics in an urban area and its subsequent impact on surface water. These first investigations confirm the presence of microplastics in sewage, freshwater and total atmospheric fallout and provide knowledge of the type and size distribution of microplastics. Investigating microplastics in urban areas and in surface water needs an updated methodology, since the presence of organic matter and clay matter adversely affect the observation and counting of microplastics. Thus, enzymatic digestion is required. Moreover, from an ecotoxicological point of view, the literature reports that risks of ingestion and ecotoxicological impacts are higher with smaller microplastics (Wright et al., 2013). In this context, manta trawl sampling campaigns alone cannot characterise this risk but investigations of smaller microplastics are also required. Therefore, both different but complementary sampling approaches developed in this study could be implemented in future studies. While analysing fibres needs the use of the plankton net due to its small mesh size, sampling higher volumes is mandatory to collect other shapes of microplastics.

This work may also contribute to the debate on microplastics sampling and analysis strategies in freshwater. Future research as a part of the LEESU project will also soon be performed on the interaction between microplastics and micropolluants within the receiving water.

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The NORMAN interlaboratory study on biotesting of spiked water extracts

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BACKGROUND

The NORMAN network maintains five Working Groups focusing on specific issues related to emerging substances. The NORMAN working group on Bioassays and Biomarkers (Bio WG) has its focus on the application of biotools for environmental quality monitoring. A main objective is to provide recommendations for the implementation of effect-based tools in regulatory frameworks.

During the re-launch meeting of the Bio WG in November 2012 (IVM, VU University Amsterdam, the Netherlands), a blind interlaboratory study (ILS) applying biotests to evaluate complex surface water extracts was proposed as a main activity for 2013–2014. The ILS objective was to verify whether a battery of bioassays conducted in different laboratories following their own methods and protocols would produce comparable results when applied to evaluate spiked water extracts. Another important expected outcome of the ILS was the promotion of the use of biotests for water quality monitoring at the level of European policy-makers.

The lead in planning and organising the ILS was taken by the Department of Ecosystem Analysis (ESA) of the Institute for Environmental Research, RWTH Aachen University, Germany. In parallel, activities towards the validation of a common battery of bioassays were developed within ongoing European monitoring projects, such as the demonstration programme of the Marie Curie ITN EDA-EMERGE (www.eda-emerge.eu), the SOLUTIONS project (www.solutions-project.eu), and the Joint Danube Survey 3 (www.danubesurvey.org). In all these projects, there is close cooperation between the Bio WG and the NORMAN activity on large-volume active sampling for effect-based monitoring, chemical screening and Effect-Directed Analysis (EDA). Such NORMAN activity is organised by the EDA Working Group (EDA WG), led by the Department for Effect-Directed Analysis of the UFZ Helmholtz Centre for Environmental Research, Leipzig, Germany [1].

THE INTERLABORATORY STUDY

During the re-launch meeting of the Bio WG, all participants contributed to the discussion and selection of the biotests that would make up the ILS bioassay battery. The final bioassay selection was done after considering the relevance of different test systems and endpoints, as well as logistic limitations. The selected bioassay battery includes three acute-toxicity assays with organisms representing different trophic levels (Algae assay, Daphnia assay, Fish embryo toxicity test); and mechanism-specific bioassays for estrogenicity (YES assays, ER-Luc cell-based assays) and mutagenicity (Ames fluctuation test) assessment.

To identify which partners could perform which bioassays, a query was sent around to the Bio WG participants. Since a limited volume of the water extract was available for the ILS as described below, a number of institutes were selected to perform each bioassay. In making that selection, an important decision criterion was the inclusion of all interested partners in the ILS. Finally, there was the selection of three to four participants to perform each bioassay (Table 1).

	RWTH (DE)	BfG (DE)	Ifremer (FR)	IVM (NL)	Recetox (CZ)	INERIS (FR)	Entox (AU)	ITM (SE)	Ecotox Centre (CH)	ISSeP (BE)	Waternet (NL)
Algae					X		X		X		X
FET	X		X		X						
Daphnia						X		X		X	X
YES		X			X					X	
ER-Luc	X			X		X	X				
Ames		X		X			X				

Table 1: Bioassays performed by each participant institute

The preparation of the clean water extract was done by the EDA department of UFZ. 180 litres of clean water were collected at a previously studied reference site, followed by concentration using large-volume solid-phase extraction (LVSPE) to a final volume of 18 mL, resulting in a 10 000 times concentrated extract.

There was the decision by RWTH and UFZ on four emerging pollutants, i.e. triclosan [2] (CAS 3380-34-5), acridine [3-5] (CAS 260-94-6), 3-nitrobezanthrone [6] (CAS 17117-34-9) and 17-alpha-ethinylestradiol [7] (CAS 57-63-6), to be used for the spiking of the water extract. The selection of the chemicals considered their relevance as environmental pollutants and their capacity to cause effects on the different bioassays.

Preliminary tests were done by RWTH to evaluate the water extract with the bioassay battery. In addition, the selected chemicals were also tested as single chemical exposure in some of the bioassays whenever previous results were not available.

For the composition of the spiked water extracts, there was decision on spiking with single chemicals and as well with a final chemical mixture (Table 2). The selected concentrations were aimed at producing full dose-response curves in the bioassays. That was done considering own results and literature data. The composition of chemical spiking of the water extract was designed for each bioassay, resulting in one or two simple mixtures plus a final mixture for each bioassay. The spiked water extracts were prepared, separated in aliquots for the different biotesters, identified with codes, and sent to the biotesting partners. The institutes were therefore not informed of the composition of the spiked extracts throughout the testing procedure.

Bioassay	Code	Chemicals for spiking	Water extract
Algae	A	TCS	10,000 x
	B	ACR	10,000 x
	C	TCS, EE2, ACR	10,000 x
FET	A	TCS	10,000 x
	B	ACR	10,000 x
	C	TCS, EE2, ACR, 3-NBA	10,000 x
Daphnia	A	TCS	10,000 x
	B	ACR	10,000 x
	C	TCS, EE2, ACR, 3-NBA	10,000 x
YES	A	EE2	10,000 x
	B	TCS, EE2, ACR	10,000 x
ER-Luc	A	EE2	10,000 x
	B	TCS, EE2, ACR	10,000 x
Ames	A	3-NBA	10,000 x
	B	TCS, EE2, ACR, 3-NBA	10,000 x

Table 2: Composition of spiked water samples, which consisted of one or two single chemical spiking and a chemical mixture for each bioassay

TCS: triclosan
ACR: acridine
EE2: 17-alpha-ethinylestradiol
3-NBA: 3-nitrobenzanthrone

Regarding biotesting protocols, standardised methods such as OECD or ISO guidelines were recommended, but were not mandatory, so biotesters were free to use their own methods. The only restriction was the limited volume of extract for biotesting. Also, specific dilution series were recommended to the biotesters, but were not mandatory either. During the biotesting period, the RWTH group provided assistance to all participants regarding biotesting.

NORMAN ILS WORKSHOP

The results from the different bioassays were sent to RWTH. When necessary, the participants were requested to provide additional or missing data or information. Finally, the RWTH team grouped the results and prepared a summary of the full ILS, which was provided to the ILS participants. On the 22–23 October 2014, the participants of the ILS and of the Bio WG, as well as external experts, were invited to join a workshop at RWTH Aachen University. The event had participants from the following institutes and countries: BfG (Germany), Waternet (the Netherlands), Waterproef (the Netherlands), INERIS (France), RECETOX (Czech Republic), ISSeP (Belgium), IVM-VU (the Netherlands), Ecotox Centre (Switzerland), LANUV- NRW (Germany), IWW Zentrum Wasser (Germany), and Bio5-RWTH (Germany).

During the workshop, a summary of the ILS and respective results was presented, followed by discussion in small groups of the outcomes from the different bioassays. Additionally, outreach actions and the planning of the 2015 activities of the Bio WG were proposed and discussed.

Bioassays produced mostly highly comparable results, even when protocols differed strongly. For statistical evaluation with respect to a scientific publication of the results, data are currently collected by the RWTH group in a uniform format. This exercise is also the most important next step towards the implementation of bioanalytical monitoring tools, where harmonised methods for data analysis and results evaluation are crucial. Experiences from sampling, bioassay, data analysis and evaluation will then be integrated into a testing strategy outlined by the forthcoming final public report of the ILS, showing the capabilities and advantages – but also the limitations – of bioanalytical water quality monitoring and management.

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NORMAN WG-5: Wastewater reuse and contaminants of emerging concern

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INTRODUCTION – CURRENT STATE OF KNOWLEDGE

In response to the escalating problem of water shortage, treated wastewater is nowadays widely reused and is generally considered as a reliable alternative water source for irrigation and replenishment among other applications. Water demands already exceed supplies in regions with more than 40% of the world's population and it's expected that in the coming years as much as 60% of the world's people may confront water scarcity [1].

Although the reuse practice is accompanied by various benefits relating to the enhancement of water balance and soil nutrition, a number of questions are still unanswered, rising concerns within the scientific community. Besides the lack of knowledge in respect of possible elemental interactions that may influence the accumulation of metals/elements in the soil and the subsequent uptake by plants and crops, organic microcontaminants and antibiotic resistant bacteria and antibiotic resistance genes (ARB&ARG) in treated wastewater require much attention. After conventional treatment, the organic matter remaining in the effluents consists of a number of recalcitrant organic compounds including potential endocrine disrupting compounds and pharmaceutical residues such as antibiotics, since the treatment processes currently applied fail to completely remove such microcontaminants, including ARB&ARG. This leads to their subsequent release in terrestrial and aquatic environments, with major consequences as far as human and environmental health is concerned.

Current open challenges associated with wastewater reuse include (i) the reduction of the emission from urban wastewater treatment plants (UWTPs) of a wide range of microcontaminants including ARB&ARG, as well as their transformation products formed during treatment and while being in the environment after wastewater is discharged or reused, (through biotic/abiotic processes), and (ii) the control of their potential uptake by plants/crops, and the potential transfer of ARG to the indigenous environmental microbiota, which in turn can be transmitted through the food and water network. It is therefore imperative to assess the impacts that these microcontaminants may have in the environment. In particular, the examination of the evolution of antibiotic resistance after treated wastewater is discharged in the environment or reused is urgently required. To identify the technologies that are most suitable to remove such microcontaminants from wastewater, taking into account their cost-effectiveness is of utmost importance [2-5].

To avoid negative environmental and human impacts, and considering the EU precautionary principle [6], regulatory frameworks are required, based on validated scientific information. The NORMAN Network, through its WG-5, aims to increase the scientific understanding of these crucial issues and to potentially boost technological developments to reduce the emission of microcontaminants from wastewater.

OBJECTIVES

WG-5 addresses critical questions related to the issues discussed above, associated with the release of microcontaminants from wastewater in order to provide deeper insight into the effects of long-term environmental and biota exposure even to sub-lethal levels of microcontaminants, to consolidate data on crop uptake, to propose criteria/specs on technologies/ assessment methods, to suggest advanced effluent quality criteria to mitigate the risks associated with wastewater reuse, and therefore to contribute to and encourage the sustainable reuse of reclaimed wastewater.

More specifically, WG-5 focuses its efforts on: (i) evaluating the risks associated with wastewater reuse in respect of the evolution and spread of antibiotic resistance in the environment and water resources, (ii) evaluating, based on research studies and information available, the risks associated with microcontaminant uptake by crops, (iii) revealing and counteracting weaknesses/knowledge gaps in environmental chemistry and microbiology/toxicology required for the above-mentioned activities,

(iv) delivering best-practice advice to practitioners and dissemination of unbiased perspectives of scientific knowledge to decision-makers and the public and, (v) assessing which of the information is valid and reliable for use in regulatory frameworks (i.e. Water Framework and Urban Wastewater Treatment Directive).

For the efficient implementation of its goals, WG-5 formulated four sub-working group activities (SWGs) as follows:

- SWG-1 Microbiome and mobile resistome in combined treatment and reuse systems
- SWG-2 Uptake, transmission and persistence of microcontaminants / ARB&ARG in crops and water resources
- SWG-3 Technologies efficient and economically viable against the current urban wastewater reuse challenges
- SWG-4 Risk assessment and policy development

More details on the main activities of each SWG are provided in the White Paper (Mandate) that is available on the NORMAN website (http://www.norman-network.net/).

ACTIVITIES AND MAIN OUTCOMES SO FAR

2013 - The kick-off meeting of WG5 was held in Vienna, Austria in June 2013 and a White Paper (Mandate) on the objectives and planned activities of WG-5 was prepared, based on the decisions taken during the meeting.

2014 - Screening campaign of selected antibiotic-resistant determinants and mobile genetic elements (ARG/MGE) in WWTP effluents in Europe. Antibiotic residues and bacteria with acquired resistance are able, at the levels commonly found in treated wastewater, to produce alterations in the microbial community, with still unknown consequences [5]. Certain ARB are highly resilient and can thus be transferred from treated wastewater to humans via water-soil-food products or surface and groundwater. Furthermore, ARG (antibiotic resistance genes) associated with broad host range mobile genetic elements can be horizontally transferred and thereby be transmitted to a diverse array of microorganisms across environmental barriers [7]. Recently the WHO [8] re-emphasised the need for coordinated analyses of antibiotics and resistance determinants to combat the current rise and evolution of antibiotic resistance.

To this purpose a campaign was organised by NORMAN in June 2014, in order to assess differences in the abundance and diversity of antibiotic resistance genes over distinct UWTP effluents, and geographic areas, thereby offering a reliable and up-to-date support for future risk assessment studies. The campaign took place in a representative set of WWTPs around Europe (i.e. Austria, Cyprus, Finland, France, Germany, Israel, Italy, Netherlands, Norway, Portugal, Romania, Spain, Turkey and UK). Eighteen universities/institutes were responsible for collecting wastewater samples for analysis: (1) Nireas-IWRC, University of Cyprus (CY), (2) Technical University of Dresden (DE), (3) CBQF-ESB, Universidade Católica Portuguesa (PT), (4) Volcani Agriculture Research Cente (IL), (5) Vienna University of Technology (AT), (6) University of Salerno (IT), (7) Karlsruhe Institute of Technology (DE), (8) Université de Lorraine (FR), (9) Middlesex University (UK), (10) Universidad de Almería (ES), (11) Catalan Institute for Water Research-ICRA (ES), (12) Namik Kemal University (TR), (13) Finnish Environment Institute Laboratory (FI), (14) AD eco advice (NL), (15) Foundation for Applied Water Management Research (STOWA) (NL), (16) National Institute for Public Health and the Environment (RIVM) (NL), (17) Norwegian Institute for Water research (NIVA) (NO), (18) "Al. I. Cuza" University of Iasi (RO).

24h-composite wastewater samples were collected in triplicate (in total 60 samples) with a harmonised and validated protocol, and analysis of selected antibiotic resistance determinants and mobile genetic elements was performed on the collected samples.

Five laboratories were assigned the task of performing the molecular analysis of resistance genes: (1) TU Dresden, Institute for Hydrobiology (Prof. Thomas Berendonk), (2) Karlsruhe Institute of Technology, Institute of Functional Interfaces, Microbiology of Natural and Technical Interfaces Department (Dr. Thomas Schwartz), (3) Université de Lorraine, LCPME - Pôle de l'Eau (Dr. Christophe Merlin), (4) ARO, Volcani Agriculture Research Center (Dr. Eddie Cytryn) and (5) CBQF-ESB, Universidade Católica Portuguesa, (Dr. Celia Manaia). Evaluation of the results is still on going. However, the fist results seem to show quite good correlation in different European countries between the presence of highly prevalent resistance genes detected in hospitals according to EARSS data (European Antibiotic Resistance Surveillance System) and the resistance detected in the environment. This could provide supporting evidence of the possible role of the environment, in particular wastewater treatment plants, for the ever-increasing occurrence of antibiotic resistance in clinical relevant bacteria.

RELATED PROJECTS RECENTLY APPROVED

WG-5 members have secured funding through the following research projects and networks addressing the current challenges associated with wastewater reuse and microcontaminants of emerging concern:

- The NEREUS "New and emerging challenges and opportunities in wastewater reuse" COST Action was approved in May 2014 and it is now operational (ESSEM COST Action ES1403, coordinator: Dr. D. Fatta-Kassinos, Nireas-IWRC, UCY). The main objective of this Action is to develop a multi-disciplinary network to provide insight into which of the current challenges related to wastewater reuse practice give the most concern from both public health and environmental perspectives (e.g. chemical and biological hazards, crop uptake, etc.), and how these can be overcome. The following 29 COST countries have actively participated in the preparation of this Action (i.e. Austria, Belgium, Bosnia and Herzegovina, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Ireland, Israel, Italy, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Serbia, Slovakia, Slovenia, Spain, Sweden, Switzerland and the United Kingdom), while scientists from 4 non-COST countries (i.e. Australia, Korea, Singapore and the USA) are already included in this COST Action. The kick-off meeting of NEREUS took place on the 7th of November 2014 in Brussels. It actually served as a coordination meeting, in order to assign roles and responsibilities to the participants (http://www.cost.eu/domains_actions/essem /Actions/ES1403).
- StARE "Stopping Antibiotic Resistance Evolution" project (EU JPI on Water Challenges, coordinator Dr. C. Manaia, Universidade Católica Portuguesa) aims at investigating a large number of European WWTPs to evaluate ARB&ARG abundance versus chemical contamination and regional backgrounds. Through this project, guidelines for ARB&ARG monitoring in wastewater will be developed, while the efficiency, impact and cost effectiveness of advanced wastewater technologies will be evaluated, based on an innovative biological risk control strategy. StARE was approved in June 2014. The kick-off meeting of this project took place on 28th January 2015 in Girona, Spain.
- INNOVAT "Sustainable wastewater reuse in irrigation: Innovative tools and technologies to reduce the risks associated with microcontaminants" project (CYPRUS-ISRAEL Bilateral Cooperation Programme, Cypriot coordinator Dr. D. Fatta-Kassinos and Israeli coordinator Mr. Y. Rozenberg) was approved in October 2014 and is expected to launch its activities in Spring 2015. Dr. Benny Chefetz from the Hebrew University of Jerusalem, member of NEREUS COST Action, and Dr. Eddie Cytryn from ARO, Volcani Agriculture Research Center, member of the NORMAN network, are also beneficiaries of the INNOVAT project. The main objective of INNOVAT is to design, develop, test and validate safe wastewater reuse in agricultural irrigation through scaled-up treatment processes for the alleviation of licit/illicit drugs and mobile resistant elements (MREs), and the development of a risk prioritisation and data management software tool for antibiotics, to be a useful tool for public authorities, decision-makers and plant operators.

ACKNOWLEDGEMENTS

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NORMAN goes Non-target

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It is increasingly recognised that the number of compounds measured today via target chemical analysis is not sufficient to provide an exhaustive overview of the status of our water bodies and that the application of non-target screening techniques is needed in order to detect the presence of potentially overlooked harmful substances (including degradation by-products and metabolites).

The identification of emerging organic compounds and their transformation products in the environment is of great interest for NORMAN members. Consequently, non-target screening was on the agenda in a series of NORMAN workshops in September 2014. From September 15 to 18, three workshops on the topic of non-target screening with between 40 and 90 participants from 16 different countries were hosted at Eawag in Switzerland. In the first workshop, the results of a collaborative trial that commenced in 2013 were discussed. The samples for the trial were collected within the International Joint Danube Survey 3 organised by the International Commission for the Protection of the Danube River (ICPDR; August/September 2013). The water samples were extracted and prepared by UFZ (Germany) and sent by Environmental Institute (Slovakia) to laboratories to perform GC-MS and/or LC-MS(MS) screening as comprehensively as possible and to enable a comparison of the various analytical approaches to non-target screening. The evaluation workshop enabled in-depth discussions of the results with the 19 participating laboratories. A report on the results is provided on the NORMAN website (http://www.norman-network.net/?q=node/27) and a joint paper is intended to be published in a peer-reviewed journal. The participants agreed on some parts of a harmonised workflow but at the same time saw a clear need for further research and developments on several aspects such as retention time index for LC-MS and data evaluation software. While the dream of a “fully-automated identification workflow” remains elusive in the short-term, members agreed to exchange “suspect lists” and this, along with the contribution of target substances to open databases such as the NORMAN MassBank (www.massbank.eu), will help bring the automated identification workflow several steps closer to reality.

During the second workshop, organised jointly with the EU project Solutions (http://solutions-project.eu/), current trends in non-target screening were discussed with the goal of achieving a certain harmonisation of the procedure and reaching a common understanding of non-target screening. Beside the practical experiences from the collaborative trial results, current analytical trends such as chemical ionisation in GC-MS, retention time prediction approaches, in silico fragmentation for structure elucidation through to advanced spectral data management and statistical tools for time series analysis were discussed. How to link exposure and toxicity data with the non-target analysis results in order to identify relevant pollutants was another important topic. Lee Ferguson from Duke University gave a keynote presentation with his insights into non-target screening approaches in North America. The outcomes of the workshop will be the basis for the preparation of further NORMAN action and a guidance paper on the harmonisation of methods for non-target screening of environmental samples. In the future, non-target screening is intended to be used to find and subsequently prioritise new emerging contaminants.

In the third workshop in this series, the processing and uploading of mass spectra onto the open-access NORMAN MassBank and other libraries was discussed. At the moment NORMAN MassBank contains 42 739 spectra in total, of which 9060 have been added by UFZ and Eawag within recent years. Masanori Arita from NIG, Japan, presented the latest developments and new ideas from the creators of the Japanese MassBank, including a relauch of the current website. Other topics including processing methods for uploading spectra, new trends in other spectral libraries, a possible collaboration with Steve Stein from NIST and ideas for big data storage, including perspectives from metabolomics by Steffen Neumann, IPB were presented and discussed (see http://www.

norman-network.net/?q=node/163 for more). During the hands-on session on the last day, the first user interface for RMassBank (RMassBankGUI) was premiered, before participants worked on preparing MassBank records of their own data, with rewards on offer as an added incentive. Finally, first place was tied by three parties (University of Athens, RWS from the Netherlands and Duke University) and in the end the spectra of six participants were processed for upload to MassBank (http://massbank.eu/). Several vendors are now interested in providing functionality to export spectra to MassBank format from within their software, while valuable feedback from participants has already been included in newer versions of RMassBank and RMassBankGUI.

This workshop summary has been written on behalf of the organisers of the three workshops: Peter Haglund (Umea University), Peter Oswald, Ildi Ipolyi (EI), Martin Krauss (UFZ Leipzig), Manfred Sengl (Bayerisches Landesamt für Umwelt), Steffen Neumann (IPB, Halle) and Heinz Singer (Eawag).

COST Action ES1205 (ENTER) and NORMAN WG-4: The status quo and future needs

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The COST Action ES1205 ENTER was launched in June 2013 (http://www.es1205.eu and http://www.cost.eu/domains_ actions/essem/Actions/ES1205). In close cooperation with the NORMAN network working group 4 (http://www.norman-network.net/?q=node/54) the Action aims to create and maintain a lasting pan-European network among scientists to gain a better understanding of the role of urban water systems in controlling the release of engineered nanomaterials (ENMs) to the aquatic and related environments (e.g., sewage sludge or wetland soils, and sediments).

Based on the current literature, the members of the COST Action identified the following key questions, which were briefly discussed in a perspective paper (Duester et al., 2014):

- Which and what amounts of ENMs are released to surface waters, soils and sediments?
- How persistent are the ENMs in the environment?
- To what extent do ENMs cause in situ toxicity?

Several source sink scenarios are conceivable for ENMs (Figure 1), and the COST action ENTER will focus on the following pathways:

- Wastewater →wastewater treatment →surface water, sediments;
- Wastewater →sewage sludge →(incineration plant) ash disposal, soil conditioner, fertiliser→soil;
- Wastewater →stormwater →surface water, sediments, stormwater treatment systems (e.g., constructed wetlands),
- Landfill leachate→treatment→surface water, sediments.

For a sound risk analysis of ENMs, a thorough understanding of potential pathways and a linkage between transformation and retention processes of ENMs in different compartments is urgently needed. Analytical tools allowing reliable detection and quantification of ENMs in complex matrices are pivotal for both: i) establishing a mechanistic understanding of ENM behaviour in the environment and ii) conducting reliable ecotoxicity studies. A linkage between fate and toxicity studies eventually enables a comprehensive and realistic risk evaluation of ENMs in urban waters.

Based on an evaluation of the current state of research, the members of the COST Action ES1205 (ENTER) recommend considering the following points to structure future scientific endeavours on ENM risk analysis:

- ENMs are efficiently removed (>95%) during the activated sludge process in wastewater treatment plants.
- ENMs undergo different transformation reactions in urban water systems.
- Studies on remobilisation/speciation of ENMs from/in ashes, sediments, landfills, and soils are mostly lacking, and this gap has to be addressed within the next few years.
- Basic quality criteria for studies with ENMs should be defined to distinguish between good ecotoxicity studies with, e.g., sufficient analytical verification and a high informative value, and those that lack quality as well as environmental relevance.
- Analytical tools should be developed to selectively detect and quantify ENMs in complex (environmental) matrices.
- For a proper method validation, there is a great need for “nano” certified reference materials (certified in size and content).
- Access to data on production volumes and applications of ENMs should be enhanced, possibly by a establishing reliable contacts with industry. This is a major missing link for the prioritisation of ENMs in environmental risk analysis.

Although surface waters represent one of the most important receiving compartments for ENMs, based on the available scientific knowledge the authors representing the COST Action ES1205 ENTER do not see, at the moment, a general need for establishing nano-specific monitoring programmes for surface waters. However, surface waters in the vicinity of production facilities may require increased attention.

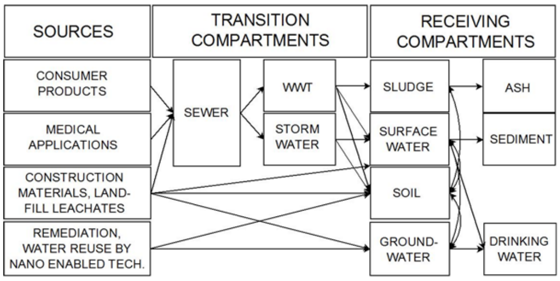

Figure 1: Schematic overview of diffent potential pathways on ENMs focusing on urban systems

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Joint Danube Survey 3
Results of the world's biggest river expedition

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BACKGROUND

The Third Joint Danube Survey (JDS3), organised by the International Commission for the Protection of the Danube River (ICPDR), was the world's biggest river research expedition of its kind in 2013. The JDS is carried out every six years – JDS1 was in 2001 and JDS2 in 2007. The JDS3 catalysed international cooperation from all 14 of the main Danube Basin countries and the European Commission and it was also addressed in the Action Plan of the EU Strategy for the Danube River Basin under the Priority Area 4 "To restore & maintain the quality of waters". The survey took six weeks between 13 August and 25 September, during which period 68 sites were sampled along a 2581 km stretch of the Danube from Germany to the Black Sea; 15 of the sites were located in the mouths of tributaries or side arms. An international Core Team of 31 scientists was responsible for sampling, sample processing and analyses on board the three survey ships. Sampling at the JDS3 stations included different sample types – surface water and connected ground water, sediment, suspended particulate matter (SPM) and biota (fish and mussels) – each with a different determinand list. The hydromorphological survey included collection of background hydromorphological data for each station to support the interpretation of biological results obtained from analyses of benthic invertebrates, phytobenthos, phytoplankton, macrophytes and fish. Altogether more than 800 individual parameters were investigated, including those determined on board during the survey and also the chemical, microbiological, ecotoxicological, radiological, isotope analyses and biological parameters analysed after the voyage. More than 36 leading laboratories from around Europe carried out analyses of samples provided from the survey. All activities and results of the JDS3 are presented in the JDS3 Final Scientific Report (Liska et al., 2015).

NORMAN ACTIVITIES

A specific focus in the JDS3 was given to the identification and prioritisation of Danube River Basin Specific Pollutants (RBSPs) in support of the revision of the Danube River Basin District Management Plan by 2015. NORMAN members recognised the potential of the JDS3 for mapping of the occurrence and toxic effects of a large number of emerging substances across a significant portion of Europe and decided in their Joint Programme of Activities for 2013 (http://www.norman-network.net/sites/default/files/list_scientific_activities_norman_2013_to_members_8feb2013.pdf) to actively cooperate with the ICPDR. The specific JDS3-related actions were:

- Development and validation of a NORMAN methodology for large volume active sampling for effect-based monitoring, chemical screening and effect-directed analysis (EDA) (lead UFZ, Leipzig, Germany);
- Development of a NORMAN methodology for continuous screening of large rivers using passive sampling in order to assess the applicability of this temporally- and spatially integrative sampling approach as a water quality monitoring tool (lead RECETOX, Brno, Czech Republic);
- Non-target screening of all JDS3 surface water samples with routine gas chromatography- mass spectrometry (GC-MS) and liquid chromatography-high resolution-MS (LC-HR-MS) techniques (lead Environmental Institute, Kos, Slovak Republic);
- Organisation of a collaborative trial on non-target screening of selected water samples from the Danube river with GC-MS and LC-HR-MS methodologies (lead Environmental Institute, Kos, Slovak Republic).

The EU FP7 SOLUTIONS project (www.solutions-project.eu) was funded in autumn 2013, using the Danube River Basin as its case study area and the JDS3 data as the main input for drafting the list of Danube RBSPs. This provided a unique opportunity for SOLUTIONS laboratories to analyse already collected JDS3 samples for the presence of hundreds of additional target organic pollutants, and to perform immunochemical analysis of anthropogenic markers (Bahlmann et al., 2015) and toxicological profiling of concentrated water samples by a battery of bioassays (Schulze et al., 2015).

The toxicological profiling was based on the previously launched NORMAN interlaboratory study for validation of a battery of *in vitro* bioassays for testing of chemicals in concentrated surface water samples (lead RWTH Aachen University, Germany). Complementary to the above toxicological profiling a detection of the genotoxic pollution in investigated sections of the Danube river by micronucleus assay in peripheral erythrocytes of *Alburnus alburnus* (biomarker response analysis) with the goal of identifying the hotspots of genotoxic pollution was carried out (Deutschmann et al., 2015).

THE CHALLENGE

Considering a 'pollution dilution' effect in large rivers such as the Danube, the effect-based screening requires significant pre-concentration and extraction of large water volumes for subsequently splitting the sample extract for analyses by a number of different bioassays and multi-target analyses. At the same time, the transport to the laboratory and the preparation of extracts of hundreds of litres of water present a big challenge. A newly developed mobile large-volume extraction device (LVSPE) was therefore used to extract water samples of up to 1000 litres during the JDS3 (Scholz 2013; Schulze et al., 2014).

Also tackling the 'dilution problem' of spot sampling in large rivers, an 'active' passive sampler system was installed on board the survey ship equipped with a battery of passive samplers for screening of trace organic pollutants and their toxic potentials. Three types of passive samplers were applied: two partitioning samplers for hydrophobic compounds (silicone rubber (SR) and low density polyethylene (LDPE) sheets), and an adsorption sampler for polar compounds based on styrene-divinylbenzene solid phase extraction disks, SDB-RPS Empore Disks (ED), respectively. During the sampling the survey laboratory ship moved downstream along a defined stretch and collected samples which contain water pollutants integrated in time and space along that stretch. Samplers were exchanged every 4 – 6 days in order to cover the pre-defined river stretches.

Largely unknown long-term effects on aquatic life and human health are caused by chemical pollution (Schwarzenbach et al., 2006; Richardson, 2007). To ensure that all contaminants with their degradation products and metabolites are detected, a non-targeted approach is required (Ferrer and Thurman, 2012). During the JDS3, high performance liquid chromatography electrospray ionisation quadrupole-time-of-flight mass spectrometry (HPLC-ESI-QTOF-MS) in two different laboratories and GC-MS were used for non-target screening of all JDS3 samples with the major goal to search for as many compounds as possible while focusing on compounds not previously known to be present in the Danube river and its tributaries.

RESULTS

LVSPE samples

LVSPE was successfully applied at 22 JDS3 sampling sites to realise effect-based screening on a river basin scale for the first time. The sam-

NORMAN Association (N° W604002510) - Network of reference laboratories, research centres and related organisations for monitoring of emerging environmental substances.
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ples were analysed with LC-HR-MS for semi-polar to polar organic compounds as well as with a set of 9 *in vitro* and 2 *in vivo* bioassays to assess the mode of action of organic compounds present in the samples. The chemical screening resulted in the detection of 91 (out of 264 targeted) compounds in at least one sample. Among substances detected at relatively high concentrations were mostly pharmaceuticals, their transformation products, artificial sweeteners, corrosion inhibitors and industrial chemicals. Widely used and legacy herbicides and their TPs were also frequently detected.

Despite the expectedly overall low concentrations of organic compounds compared to other rivers in Europe (Loos et al., 2010), all extracts were effective in one or more bioassays with the endpoints mutagenicity, dioxin-like and PXR mediated activity, oxidative stress responses, and estrogenicity as well as growth inhibition and Photosystem II inhibition of green algae. Samples JDS33 (downstream Novi Sad, Serbia) and JDS63 (tributary Siret, Romania) were among the most toxic samples, which were effective in almost all bioassays.

Passive sampling

Despite the low- or sub- ng/L concentrations of most organic pollutants present in the free dissolved phase, passive sampling enabled clear identification of spatial gradients of a broad range of organic pollutants in the water column, including polychlorinated biphenyls (PCBs), organochlorine compounds (OCs), polyaromatic hydrocarbons (PAHs), alkylphenols, selected polar pesticides and pharmaceuticals. In many cases, the integrative character of passive sampling allowed for measurement of compounds down to pg/L levels where methods based on low-volume spot sampling of water applied in the previous JDS2 survey failed to detect them (Sengl, 2008). Passive samplers in most cases confirmed similar spatial distribution of pollutants along the river, as was observed in the JDS2.

Selected toxic/bioactive potentials of extracts of SR and ED passive samples are currently under evaluation. Preliminary results indicate that SR extracts contain significant amounts of dioxin-like compounds assessed by CALUX bioassay.

Whereas data from spot sampling reflected the pollution at the individual JDS sampling sites at a single moment, passive samplers continuously sampled pollutants for several days, including river stretches between individual JDS sampling sites. The information provided by spot sampling and passive sampling should therefore be considered as complementary (Vrana et al., 2015).

Non-target screening

Analysis of the Danube surface water samples at a basin-wide scale was conducted for the first time with two LC-HR-MS instruments. Suspect screening of 168 substances by ultra-HPLC-QTOF-MS showed that 154 of the studied analytes were found to be present in at least one sample. Initial results from non-target screening by ultra-HPLC-QTOF-MS revealed the presence of more than 3370 different organic compounds listed by name, based on a match with available mass spectral libraries. The follow-up evaluations resulted in unequivocal identification of 56 additional substances dominated by pesticides, pharmaceuticals and personal care products. The remaining tentatively identified suspect compounds, unknowns (proposed molecular formula) and total unknowns (only accurate mass and retention time available) still need to be investigated and those results can be expected in the near future.

The 'suspect screening' by the second LC-HR-MS instrument showed that 110 out of 315 'searched for' substances were determined in at least one sample and 50 compounds were present in more than 20 samples. Although the lists of target/suspect substances in two LC-MS laboratories differed, there was a good agreement on the overlapping compounds (Stipanicev et al., 2015).

Both techniques could achieve low-ng/L detection limits of a wide range of substances with direct injection of the water sample, which significantly reduces the need for laborious sample preparation. The statistical software of the ultra-HPLC-QTOF-MS equipment at Croatian Waters (Zagreb, Croatia) allowed for analysis of differing pollution patterns of thousands of detected 'features' and compounds for the river stretches and countries within the basin.

The GC-MS results were complementary to those obtained by LC-MS. Chemical structures of 298 and 288 substances in 68 and 22 samples collected by two different methods (Liquid-Liquid Extraction (LLE) and LVSPE, respectively) were proposed, but up to 38% of detected substances remained unidentified. A rough estimation of the compounds' concentrations was made based on the comparison of their ion signal with that of the internal standard, which allowed for establishment of their pollution profiles across the basin and preliminary risk assessment by comparing the concentration data with available Predicted No Effect Concentrations (PNECs). A retrospective analysis of 'digital sample banking' GC-MS data proved to be successful. It revealed the presence of several pollutants which would otherwise remain undetected. A statistical chemometric software program was used to find pollution patterns of thousands of detected organic compounds.

Collaborative trial on non-target screening

An additional 1000 L JDS3 sample (JDS58; Giurgiu (RO) – Ruse (BG)) was collected for the purpose of a NORMAN Collaborative Trial on non-target screening. An overview of the results is in 'NORMAN goes Non-target' elsewhere in this bulletin.

CONCLUSIONS

The NORMAN Association and the ICPDR have successfully cooperated within the JDS3, in which NORMAN activities strongly supported the development of a methodology to identify the RBSPs at a large European river basin scale. Several unique approaches were applied for the first time, including LVSPE and passive sampling for collection of samples allowing for detection of the highly-diluted pollutants and assessment of their (eco)toxicological effects, and non-target screening of the entire river basin. The latter is contributing to the recent developments in the NORMAN network, where the JDS3 dataset is used as a model example for archiving ('digital sample banking') of the raw full-scan mass chromatograms for retrospective screening of emerging pollutants. The JDS3 samples were also analysed by a number of FP7 project SOLUTIONS laboratories, using the Danube Basin as a case study, creating a critical mass of the data needed for the first draft prioritisation of the (20) Danube RBSPs (Slobodnik et al., 2015) according to the simplified NORMAN prioritisation framework (Dulio et al., 2013). The results will feed directly into the next Danube River Basin Management Plan and the Joint Programme of Measures to be adopted at the end of 2015.

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SOLUTIONS for present and future emerging pollutants in land and water resources management

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INTRODUCTION

In line with major objectives of NORMAN, and involving several NORMAN members, the new Collaborative Project SOLUTIONS under FP7 started in October 2013. Involving 39 partners from 17 countries in and beyond Europe the 5-year project addresses major challenges posed by emerging pollutants in land and water resources management. NORMAN supports SOLUTIONS as one of the critical advisors on the SOLUTIONS Stakeholder Board together with representatives from the European Commission DG Environment, European Environmental Agencies, environmental and chemical agencies from Germany, Sweden, Canada and the U.S., international river commissions and representatives of water works and water supply.

Monitoring programmes under the Water Framework Directive (WFD) have accumulated vast amounts of data on contamination and on the ecological status of surface waters in the EU. At the same time, a wealth of chemical property and emissions data from registration of chemicals (e.g. REACH) is becoming available. Although toxic effects on aquatic life are frequently observed, it remains a great challenge to link occurrence of chemicals with the ecological status of waters, to identify major chemical stressors, and to find solutions for the abatement of pollution-related risks.

Typically, complex mixtures of priority pollutants, emerging substances, by- and transformation products, and natural compounds occur in aquatic systems. The sheer number of potentially harmful chemicals challenges chemical monitoring, and consequently there is the danger that adverse impacts on aquatic communities and human health from unknown or unexpected chemicals and mixtures remain unrecognised.

Substances of emerging concern include a multitude of polar and even ionic compounds for which many of the classical analytical tools and predictive models do not apply. These substances and mixtures thereof may affect a multitude of toxicity pathways in organisms, populations and communities. An applicable conceptual framework and harmonised sensitive bioanalytical tools are lacking to cover these pathways in monitoring. Chemical analytical tools with analytical detection limits below their predicted no-effect-levels

(PNEC) are often lacking as well. While there is increasing knowledge on the production and use of chemicals, there is also a lack of understanding regarding sources, transport pathways, transfer times, fate, and mixture effects, together with insufficiently developed modelling capacity to reliably predict risks to ecosystems and human health.

Monitoring, modelling and assessment of chemicals in European water resources are further challenged by the co-existence of the vast number of daily used pesticides and biocides, personal care products, pharmaceuticals, and additives to food, textiles and plastics with legacy chemicals whose production and use have been forbidden for decades. Being often very persistent the latter are stored as parent compounds or metabolites in sediments and still contribute to risks. However, it is not only present and historical contamination that are of interest. Production and use of chemicals are highly dynamic and prioritisation and assessment tools developed today should also help to predict and address upcoming chemical risks.

OBJECTIVES

The overall goal of the FP7 Integrated Project SOLUTIONS is to produce consistent solutions for the large number of legacy, present and future chemicals posing a risk to European water resources with respect to ecosystems and human health. To this end, SOLUTIONS

- develops a consistent conceptual framework for the assessment, prioritisation and abatement of pollutants and mixtures thereof to protect European water resources and to minimise ecological and human health risks.
- delivers efficient tools for the identification of substances and mixtures posing risks by developing a new generation of monitoring approaches and tools for the early detection and identification of harmful substances. At the same time SOLUTIONS provides improved understanding and capacity for exposure, effect and risk modelling compiling a full chain of conceptually integrated models and databases accessible via a user-friendly computer tool to support decisions in environmental and water policies.
- demonstrates the added value of the new generation of tools in trans-European case studies in the Danube, Rhine, and rivers of the Iberian peninsula with links to existing monitoring programmes such as the Joint Danube Survey.

A specific focus of SOLUTIONS is on user-friendly products exploiting innovative science to provide solutions for water resources and chemicals management. To meet this objective we

- synthesise the new approaches and condense them into user-friendly guidelines, computer tools and recommendations for direct support of the implementation of WFD.
- evaluate potential opportunities and obstacles for cooperation between the WFD and other existing policies (e.g. REACH).
- assess abatement options and control measures for emerging pollutants in waste and drinking water treatment for effective risk reduction.
- deliver a common knowledge base on a wide range of toxicants, an evidence-based compilation of substances with emissions that might require regulation, and comprehensive lists of River Basin Specific Pollutants -RBSPs- for the case study in the Danube river basin as a result of the integrated application of the new generation of monitoring and modelling tools.
- identify upcoming risks from emerging pollutants of the future on the basis of scenarios on economic development, technology, demography, climate change and other aspects.

APPROACH

SOLUTIONS is structured into 4 highly integrated sub-projects resulting in the workflow illustrated below. Sub-project SP1 on Concepts & Solutions provides the conceptual framework for the entire project, defines the anticipated products, and organises the dialogue with stakeholders in order to make sure that we provide solutions for major problems on emerging chemicals and water resources management. SP1 guides and fully relies on the sub-projects SP2 on Tools, SP3 on Models, and SP4 on Cases which develop most of the underlying tools, models and data that are integrated and developed into solutions for major problems.

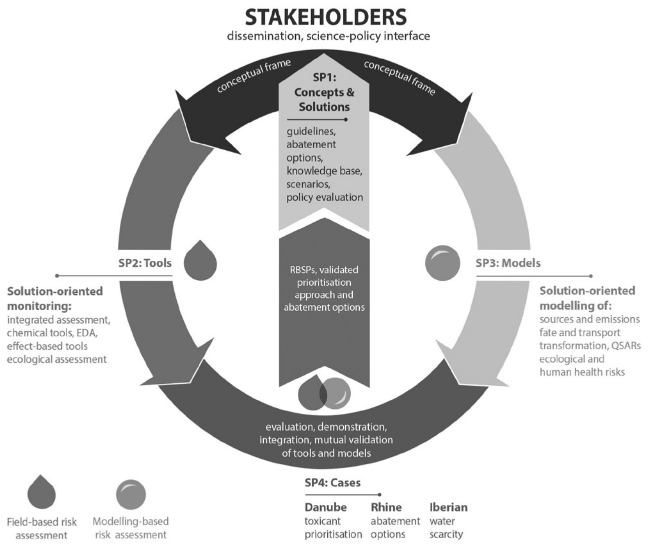

Figure 1: SOLUTIONS Approach

CONCEPTUAL FRAMEWORK

SOLUTIONS developed a conceptual framework for the whole project, which is also the basis for the new decision support tool RiBaTox being developed to support the implementation of WFD and other regulations which intend to protect European water resources and reduce toxic risks to ecosystems and human health. The solutions-oriented approach provides four entry points: chemicals, environmental findings, abatement options and societal developments that need to be assessed or prioritised. Starting from these entry points SOLUTIONS develops the approaches, models and tools to support the sustainable use of chemicals, the identification of RBSPs and European scale Priority Pollutants, to assess abatement options and to analyse legal and policy instruments.

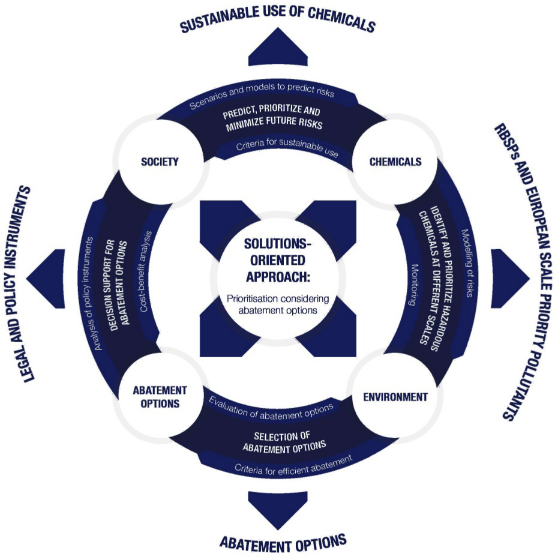

Figure 2: SOLUTIONS Conceptual Framework

SOLUTIONS AND JDS3

While the project officially started in October 2013, several SOLUTIONS partners had laid the foundation for two major tasks in the project a month earlier. Participation in Joint Danube Survey 3 (JDS3) in September 2013 provided a unique set of samples, data and experiences from the biggest river expeditions in the world that help to develop a consistent concept for future water quality monitoring and that provide the basis for the suggestion of River Basin Specific Pollutants (RBSP) for the Danube river. Although the data evaluation is an ongoing process the report with first interesting results will be available soon via http://www.danubesurvey.org/.

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The French Watch List for the 2nd WFD cycle

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INTRODUCTION

In France the Ministry of Ecology has launched a process for the definition of a national watch list of substances to be regularly monitored in surface water (water and/or sediments). A national screening campaign involving 182 substances (100 analytes measured in water, 134 in sediments and 48 in both matrices) was performed in 2012 at 200 sites (metropolitan France and overseas territories). In addition to chemical analysis, *in vitro* (reporter/natural gene response in cultured cell lines) and *in vivo* (gene response in zebrafish embryos) mechanism-based bioassays were deployed on a sub-set of sampling points in order to establish toxicological profiles. In parallel a national monitoring campaign took place in coastal waters. Passive sampling techniques and direct extraction techniques were tested through the implementation of in situ systems integrators POCIS (Polar Organic Chemical Integrative Sampler) and extraction by SBSE (Stir Bar Sorptive Extraction) directly in the water samples. Sediment samples were also collected.

The substances were selected as a result of a prioritisation exercise performed by the national expert Committee on Prioritisation, CEP, on an initial list of 2400 candidate substances, based on criteria adapted from the NORMAN scheme (Dulio & von der Ohe, 2013, ISBN: 978-2-9545254-0-2). A large set of contaminants (PAHs & degradation products, alkyl perfluorinated compounds, plasticisers, pharmaceuticals, pesticides, antioxidants, petrol additives, industrial products and personal care products) were analysed, with a total of 400 data collected for each substance for the water matrix (3 sampling campaigns) and 150 for the sediment matrix (1 sampling campaign).

The features of this ambitious screening study, which involved more than 20 different partners from research laboratories to river basin / national water authorities, and allowed the gathering of more than 45 000 monitoring data for a total budget of 3 millions Euros, were described in the last NORMAN Bulletin (n.3, 2012). We present here the main findings of the campaign and the final list of substances that are now part of the French national Watch List.

OCCURRENCE IN WATER AND SEDIMENT

Overall, out of the 82 substances analysed in water, 60 were quantified in rivers (i.e. at least one concentration value above the limit of quantification - LQ), during the three sampling campaigns and 23 substances were quantified in lakes in metropolitan France. For the sediment matrix, out of the 134 measured compounds, 85 were quantified in rivers and 59 in lakes in metropolitan France. At least one substance was quantified for each category of use, phthalates and parabens being the most frequently found compounds (quantification at 95% of the sites – including reference stations – regardless of the pressure type). As regards the level of occurrence of the investigated substances, and its association with particular

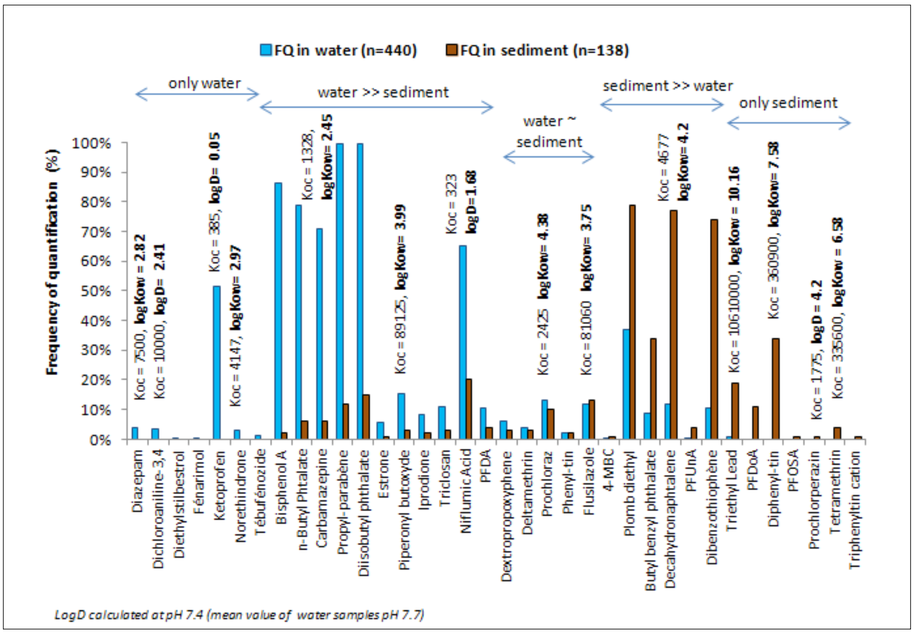

Figure 1: Frequency of quantification in water and sediment for substances investigated in both matrices

types of pressure, in the water matrix, for 21 out of the quantified 60 substances, a risk of exceedance of the estimated Lowest PNEC (as defined in Dulio and Andres, 2014) values was observed. The highest frequency of PNEC exceedance was observed for three compounds used as plant protection products / biocides: acetochlor (herbicide recently withdrawn from the market); deltamethrin (an insecticide); and triclosan (a biocide widely used in products such as soap and toothpaste). For the sediment matrix, 50 out of the 85 quantified substances exceeded the PNEC value at least once. Among these substances, the highest frequency of PNEC exceedance was observed for five PAHs, followed by a surfactant (4-nonylphenol di-ethoxylate) and a pesticide (terbutryn, a banned herbicide on the new list of Priority Substances under Directive 2013/39/EU). Results for substances measured in both matrices are presented in Figure 1.

In order to improve data exchange on emerging contaminants at European level it was decided to share these datasets via the NORMAN network in the common data reporting format defined by NORMAN. The raw data of this screening study are now available in the EMPODAT database (http://www.norman-network.net/empodat/) and via this tool they were contributed to the EC in support of the on-going review of the WFD Priority Substances List.

PRIORITISATION FOR FINAL NATIONAL WATCH LIST

Further to this screening campaign, 64 substances (44 for water and 47 for sediment) were identified as candidates for inclusion in the national Watch List for future monitoring in the French surface aquatic environment (2016–2021) (as a result of a prioritisation exercise based on frequency of quantification, frequency and degree of PNEC exceedance and hazardous properties).

The final step before the inclusion of the final substances on the Watch List was a national survey among routine laboratories. The aim of the survey was to ensure that the required analytical performances (LQ<PNEC) can be fulfilled by routine laboratories in charge of regular monitoring. The analyses during the screening study were performed by academic laboratories based on their performance and proven capability. In order to allow data comparability, all the analyses concerning a substance were carried out with the same analytical method in a single laboratory. But when a substance becomes part of a regular monitoring programme, analyses are to be performed by a large number of different routine laboratories subcontracted by water agencies. An additional step was therefore needed in order to confirm the achievable limit of quantification for each substance before the definition of the final list.

In order to take into account the current analytical capability of routine laboratories while stimulating improvement of the performance by laboratories, two different sub-lists were defined: a) List A of substances for which analytical methods are already available and immediately ready for use by routine laboratories; b) List B of substances for which analytical methods are available at research level but analytical performance needs to be improved in order to allow quantification limits below PNEC in long analytical series at routine level.

We present here some examples of substances quantified in the screening study (water matrix) and then selected for integration in the final Watch List for continental surface water (Table 1). The figure reports the results of the campaign in terms of frequency of quantification, degree and frequency of exceedance of the Lowest PNEC, the Lowest PNEC values and the scores obtained in the prioritisation exer-

CAS Number	Name	Lowest PNEC (µg/L)	Frequency of quantification	MEC95/ Lowest PNEC	Frequency exceedance Lowest PNEC	Hazard score	Final score	LQ screening study (µg/L)	LQ List A (µg/L)	LQ List B (µg/L)
84-69-5	Diisobutyl phthalate	1.8	99.7%	2.74	0.35	0.75	2.57	0.02	0.5	
80-05-7	Bisphenol A	1.6	86.2%	0.75	0.08	0.83	1.86	0.001	0.05	0.02
52918-63-5	Deltamethrin	0.0001	4.0%	74.90	0.11	0.42	1.80	0.0001		0.001*
84-74-2	n-Butyl Phthalate	10	78.8%	0.08	0.00	0.92	1.68	0.02		0.05
95-76-1	3,4-Dichloroaniline	0.016	3.4%	106.00	0.09	0.67	1.55	0.001	0.015	
85-68-7	Butyl benzyl phthalate	7.5	8.9%	0.02	0.00	0.92	1.51	0.02		0.05
84-66-2	Diéthyl phthalate	73	83.1%	0.02	0.00	0.42	1.44	0.03		0.05
34256-82-1	Acetochlore	0.006	19.8%	73.33	0.44	0.33	1.37	0.001	0.005	
10605-21-7	Carbendazime	0.015	48.3%	5.44	0.02	0.42	1.33	0.001	0.015	0.005
94-13-3	Propylparaben	2.65	99.7%	0.04	0.00	0.42	1.32	0.0008	0.03	0.01
120-47-8	Ethylparaben	8.36	100.0%	0.04	0.00	0.42	1.32	0.0005	0.03	0.01
99-76-3	Methylparaben	2	99.2%	0.13	0.00	0.42	1.31	0.03	0.03	0.01
3380-34-5	Triclosan	0.05	11.0%	15.20	0.17	0.50	1.25	0.003	0.05	
53-16-7	Estrone	0.1	5.6%	0.52	0.00	0.75	1.15	0.005	0.001	
604-75-1	Oxazepam	25.34	60.5%	0.06	0.00	0.33	1.11	0.005	0.005	
22071-15-4	Ketoprofene	3.12	51.7%	0.05	0.00	0.42	1.10	0.002	0.01	
1113-02-6	Omethoate	0.00084	1.7%	7.02	0.03	0.33	1.09	0.0001		0.0005
82419-36-1	Ofloxacine	0.113	23.7%	3.31	0.11	0.42	1.08	0.005	0.01	
298-46-4	Carbamazepine	2.5	70.9%	0.17	0.00	0.25	1.06	0.003	0.005	
171118-09-5	Metolachlor ESA	43	75.9%	0.01	0.00	0.08	0.98	0.001	0.01	
152019-73-3	Metolachlor OXA	16.6	70.4%	0.02	0.00	0.08	0.95	0.001	0.01	
121-75-5	Malathion	0.006	4.0%	0.19	0.01	0.25	0.93	0.0001		0.005
723-46-6	Sulfamethoxazole	0.59	38.1%	0.08	0.00	0.25	0.90	0.002	0.005	
68-22-4	Norethindrone	0.04	3.1%	0.37	0.00	0.42	0.88	0.003		0.001
335-76-2	Perfluorodecanoic acid	0.00005	10.6%	48.65	0.28	0.08	0.87	0.001		0.002*
4394-00-7	2-(3-trifluoromethyl-phenoxy)nicotinamide	0.55	65.3%	0.56	0.02	0.08	0.85	0.001		0.01
50-18-0	Cyclophosphamide	19700	0.9%	0.00	0.00	0.67	0.82	0.001		0.001
67747-09-5	Prochloraz	0.55	13.2%	0.14	0.00	0.17	0.77	0.001		0.001
51-03-6	Piperonyl butoxyde	0.24	15.5%	0.25	0.01	0.25	0.74	0.001	0.02	0.005

Table 1: Examples of results for substances selected for inclusion in the French Watch List

cise. The LQs used by research laboratories during the screening study and the target LQ that laboratories will be required to apply for routine analysis are also highlighted in Table 1.

Analytical gaps were identified mainly for phthalates and for some pesticides (malathion, prochloraz and omethoate) and for these substances monitoring will be postponed to 2019.

Six substances (bisphenol A, carbendazime, propylparaben, ethylparaben, methylparaben, piperonyl butoxyde) will be part of the Watch List with a defined LQ starting from 2016 but further improvement of the LQ will be required for the laboratories to reach the final target LQ in 2019.

It is noteworthy that this list introduces for the first time in France, pharmaceuticals and compounds found in personal care products to be part of the national routine monitoring programme.

In conclusion, a total number of 118 organic substances (75 in water, 38 in sediment and 5 in both matrices) will be part of the first French Watch List. The substances will be measured for 2 years in rivers (1 year in lakes) during the next WFD cycle (1 year for List B compounds). Measurement of these substances will be deployed on 25% (about 375 sites) of the surveillance national monitoring network (WFD - Annex V - 1.3.1.), 6 times per year for pesticides and 4 for the other compounds.

This process is intended to be repeated in the next WFD cycle in order to acquire missing information about the level of exposure of emerging contaminants in the aquatic environment and allow regular updating of the list of River Basin-Specific Pollutants. Moreover, it is envisaged that in the next round effect-based profiling will be more systematically used as a complementary approach to the review of the Watch List, including as part of the prioritisation step.

ACKNOWLEDGEMENTS

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CAPACITIE: Cutting-Edge Approaches for Pollution Assessment of Cities

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INTRODUCTION TO CAPACITIE

CAPACITIE is a Marie Curie Initial Training Network, funded by the European Commission within the 7th Framework Programme. The project consists of 16 partner organisations, in addition to the University of York, which is the coordinating and host organisation for the duration of the project. The associate and partner organisations span the industrial, regulatory, consultancy, research and governmental sectors. CAPACITIE includes 12 PhD projects. Each of the projects is related to addressing a variety of issues linked to pollution monitoring in cities. The PhD projects span several disciplines related to the monitoring of pollutants and the development of new technologies for pollution monitoring. The Environment Department is the host department for the project, with the Chemistry, Electronics, Sociology, Computer Science and Physics departments also hosting CAPACITIE PhD students. The CAPACITIE Project is a YESI (York Environmental Sustainability Institute) featured project. YESI aims to develop novel interdisciplinary projects between different departments across the University of York and a wide variety of diverse external organisations and partners.

POLLUTANTS IN THE CITY ENVIRONMENT

More than half of the world's population lives in cities and nearly two billion extra urban residents are expected in the next 20 years. Many of the fastest growing cities in the world are highly polluted, resulting in adverse effects on human health. Urban pollution can also impact the health of the natural environment which will affect the delivery of a range of ecosystem services. There is therefore an urgent need to better understand the factors and processes affecting the pollution of cities and the potential negative impacts of this on human health and the environment. To achieve this, improved approaches for monitoring different forms of pollution (air, water, noise) are needed.

The CAPACITIE Project will explore a wide range of technologies for pollution monitoring, including: mobile phones; passive sampling devices; miniaturised sensing devices; robotics; and state-of-the-art analytical techniques (such as time of flight mass spectrometry). These technologies provide a number of advantages over current monitoring methods in that they allow us to:

- Quantify levels of pollution at greater frequencies and spatial resolutions than is currently possible;
- Monitor locations that in the past have been difficult to sample (e.g. hostile environments or systems with accessibility issues); and
- Characterise human and ecological exposure to the plethora of chemicals that have never been monitored before.

Effective application of the different technologies will provide a much better understanding of the degree of exposure of humans and wildlife to pollutants and hence the risks of these pollutants to ecosystem and human health. The technologies could also be used to inform mitigation measures both in the short term and over longer timescales.

DELIVERABLES OF CAPACITIE

The CAPACITIE Project will produce a new generation of researchers who not only have the skills to develop and apply cutting-edge technologies to monitor pollutants in the natural environment, but also have a detailed understanding of the needs of end users of monitoring data (such as governments, regulators and local authorities) and of the social and ethical issues around the adoption and use of selected technologies (such as safety, generation of sensitive data and information security).

To deliver the above aim, a cohort of early stage researchers (ESRs) will work on a series of research projects addressing different aspects of pollutant monitoring in city environments. The city environment has been identified as the case study for the project, as cities: are under pressure from a wide range of pollutant pressures; are likely to show large variability in pollutant levels over short scales of time and space; can include many areas that are inhospitable and inaccessible; and encompass a range of environmental media types. While the focus of CAPACITIE is on city environments, the techniques, technologies and skills delivered through this programme are highly generic and transferable to a range of environmental monitoring challenges.

The CAPACITIE Project research is comprised of 12 individual PhD projects, the overall aim of which is to address different aspects of pollution monitoring of city environments. The projects are grouped into four inter-related workpackages, according to the aspect of the problem that each project is assessing. Two additional workpackages will focus on the overall training vision of the project and ensuring that the outputs of this research will have an impact.

CAPACITIE WORKPACKAGES

Workpackage 1

While a number of novel technologies already exist, uptake by the end-user sector is slow in Europe due to the burden of regulated methodologies and related issues associated with technologies developed by the academic community which do not meet the specific needs and requirements of end users. In order to develop new effective monitoring approaches for environmental pollutants it is therefore essential to not only focus on technological developments but also to understand the needs of different users of the monitoring data and the barriers and opportunities for employing these technologies in the real world. This will significantly increase the likelihood that new technologies will be adopted by end users. Therefore WP1 involves social science based projects aimed at fully understanding the needs of end users of monitoring data and how best to engage different stakeholders in monitoring activities. The information generated will be used to inform the developmental work done in the experiment-based projects.

Workpackage 2

In recent years, there has been increasing concern that humans and the environment will be exposed to many pollutants that are not monitored and which may be causing harm. These so called 'emerging pollutants' (EPs) originate from a variety of product types including: human pharmaceuticals, veterinary medicines, nanomaterials, personal care products, paints and coatings. Some EPs, such as the natural toxins and degradation products of man-made chemicals, may also be formed within the natural environment by animals, plants and microbes. Numerous classes of EPs have been shown to be released to the environment and EPs have been detected in a range of environmental compartments including surface waters, groundwaters, drinking waters, fish and earthworms across the globe. There is now recognition that these substances should be considered in monitoring programmes and that we should work to understand the implications of these substances in terms of human health endpoints and environmental risks. As the list of EPs of potential concern is enormous, the challenge is to develop approaches for identifying the EPs that really matter and then developing analytical methods for detecting and characterising them.

WP2 will explore how to better prioritise EPs in the city environment using transformation products in the indoor air and surface water environments

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as a case study. WP2 will also further develop and apply some of the cutting edge analytical technologies to understand the exposure of humans and the environment to emerging pollutants in the indoor environment and surface waters in cities.

Workpackage 3

Substantial progress has been made over the last decade in the production of compact and low cost sensors for detecting environmental pollutants. These compact systems can increase the density and coverage of monitoring networks, to support compliance assessment and to inform policy and research. WP3 will build on recent developments in compact, low cost sensor technologies to develop new multi-species sensors for measuring key air and water pollutants in cities.

Legacy monitoring technologies can mean that large conurbations with populations in the hundreds of thousands are represented by only a single point observation. A variety of new technologies are however now available for detecting pollutants in the environment that could greatly extend the coverage of pollution monitoring in both time and space. Technologies of potential utility include passive sampling devices, mobile 'phones, wireless sensor networks and robots. There is also increasing interest in the use of environmental specimen banking for understanding pollution issues that may have developed over time. While some of these technologies are already being applied to understand pollution problems, others have yet to be fully developed for pollution monitoring applications or effectively adopted by end users. WP3 will therefore also explore how a range of potential new monitoring technologies, including robots, mobile 'phones and specimen banks, can be used most effectively to understand exposure to pollutants in city environments.

Workpackage 4

The broadening of pollution monitoring programmes and the adoption of technologies that allow monitoring at higher spatial and temporal resolutions will mean that the amount of monitoring data produced in a city system will increase by orders of magnitude. Efficient methods for capturing and storing this information will therefore be needed. Improved methods will also be needed for combining and analysing data from different sources and appropriately responding to this data in order to enhance the health of the human population and the environment. Ideally, these analyses and responses will be done in real time. WP4 will therefore develop ICT technologies for data collection and analysis and explore how to effectively use the generated information for short- and long-term decision making.

THE CAPACITIE PROJECT ONE YEAR IN

The CAPACITIE Project was initiated in October, 2013, although the official kick-off event took place in March, 2014. All of the ESRs are now in place on the project and have made substantial progress towards each of their project objectives. Information on each of the ESRs and their specific projects can be found in the first edition of the project's newsletter – this also contains detail on the kick-off event, which was well-attended by all project academics, researchers and partners. Now around eight months into their research, each of the ESRs has made significant progress within their PhD projects. The September 2014 and November 2014 editions of the project's newsletter include updates from each of the researchers.

Training and Events

As a Marie Curie Initial Training Network, CAPACITIE includes many opportunities for ESRs to develop their technical and transferable skills, through the delivery of a number of training events, seminars and outreach activities. So far, three training courses have been held at the University of York. The first course was a one-day event, which focused on generic research skills.

The second training course (Environmental Pollution and Monitoring) took place in July 2014 and was organised by the University of York. The course included theory and practical exercises focused on the processes affecting the inputs to – and behaviour and effects of – chemical pollutants in the environment and how these are monitored. This training also included external site visits and teaching from external organisations (such as Drax Power Station, the Food and Environment Research Agency, Yorkshire Water and the City of York Council.

The third training course (Policy and Regulation of Pollutants in the Environment) took place in September 2014 at the University of York. The course was run by staff from the Electronics, Computer Science and Chemistry departments. The aim of this course was to introduce the ESRs to a variety of technologies and techniques for monitoring environmental phenomena and processing the data from environmental sensor technology. This included a range of theoretical and practical learning sessions.

Three project seminars have taken place as part of the CAPACITIE training programme for the ESRs. These have included research on: city pollution modelling; the fate of nanoparticles in the environment; and subjective environmental concern of objective environmental issues.

The CAPACITIE team have also been involved in two external outreach events. These outreach events include the York Festival of Ideas 'Science out of the Lab' event and York Researchers' Night. At both of these events, the CAPACITIE Project held open exhibitions in which the public interacted with the project team in order to aid adults' and children's perspectives of pollution in the city environment. As part of these events, a children's board game was developed and a participatory GIS survey application was also produced in which members of the public could give their opinion on the most and least polluted areas of the City of York.

CAPACITIE'S SECOND YEAR

With a successful first year complete, the CAPACITIE programme for year two aims to be even more exciting and action-packed! The plan for the year ahead includes: a number of visiting seminar speakers; a writing retreat event in which the ESRs will draft a joint-review paper; the second year meeting (March 2015); and the fourth and fifth training courses. Training Course Four is focused on 'Policy and Regulation of Pollutants in the Environment' and will be held in Berlin at the Umweltbundesamt and Ecologic offices (both of which are partners on the project) in April 2015. The 'Pollution in Megacities' training (Course Five) is planned for the autumn of 2015 and will be held in Seoul, South Korea. In this one-week intensive course, ESRs will learn about the major pollutant pressures faced by Seoul; the potential implications of these in terms of human health and the health of the environment; how different types of pollutants are monitored in the city; and how the city is working to mitigate against pollution both in the short- and longer-terms. Watch this space!

Website:
www.york.ac.uk/yesi/capacitie - Follow us on Twitter: @CAPACITIEUoY

SCORE: Flushing out Europe's drug habits

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INTRODUCTION

Europe consumes around 360 kg of cocaine every day. How this was estimated is down to scientists normally associated with contaminants of emerging concern (CECs), many from NORMAN member institutes. Most of us are aware of pharmaceuticals as environmental pollutants, but what about the illicit side of drug taking? As with pharmaceuticals, illicit drugs are also found in sewage, and around seven years ago Ettore Zuccato and colleagues, from the Mario Negri Institute in Milan, published a paper that would change how we view the occurrence of illicit drugs in the environment [1]. The paper for the first time used the concentrations of illicit drug residues measured in sewage from Milan, Lugano and London to estimate the amount of cocaine, opiates, cannabis and amphetamines used in these cities. The advantage of the approach was clear in that it allowed the near real-time estimation of illicit drug use, together with the evaluation of spatial and temporal trends in the consumption of these substances. This quickly led to the European Monitoring Centre for Drugs and Drug Addiction (EMCDDA) exploring the potential of this approach to complement and extend the existing epidemiologically based tools to illicit drug monitoring [2]. The approach was thereafter refined as similar studies were reported from cities across Europe, North America and Australia [3]. Understanding the uncertainties associated with such measurements would be imperative to establishing this new approach in monitoring illicit drug use. The uncertainties associated with sampling were the first to be addressed by Christoph Ort and co-workers at Eawag [4]. Other sources of uncertainty have also been identified and recently evaluated: chemical analysis, stability of drug biomarkers in sewage, back-calculation of drug use (specific case of cocaine), and estimation of population size in a catchment [5]. An interlaboratory study has shown that the uncertainty, expressed as relative standard deviation (RSD%), related to the analysis of drug residues was between 6 and 26%. Extensive reviews of the available literature showed the greatest variability to be in the different methods used to estimate population, between 7 and 55%, meaning that choosing the most reliable estimation is of primary importance in reducing uncertainty. The back calculation of cocaine use had a RSD of 26%, but the remaining steps in estimating drug loads could be kept below 10% if the best practice outlined in our paper is followed [5].

By 2010, there were a large number of research groups publishing data on illicit drug analysis, as well as an equally large number wanting to start working in this field. What was missing however, were international studies comparing use between major cities and an evaluation of the different analytical procedures being used in different labs. In December 2010, a group of like-minded researchers met in Dublin to discuss the possibility of performing a collaborative, Europe-wide study on the analysis of sewage for estimating the use of illicit drugs on a European scale. It was clear that to perform a comparative study, certain aspects of the approach would have to be strictly controlled since different laboratories would be doing the analyses, using their own in-house developed analytical methods. Furthermore, we would be reliant on existing automated sampling equipment at the WWTP inlet, and there is no EU standard sewer design, all being quite different. To overcome all this, a best-practice consensus document (available upon request) and an analytical intercalibration study were agreed, and all of the sewer networks and sampling systems were characterised by the use of a questionnaire devised by the group's sewer expert. In 2011, intercalibration showed that the analytical data could be safely compared, with sampling and sewer differences not likely to result in major uncertainties. The approach was thereafter simultaneously applied in 19 European cities, making it possible to directly compare illicit drug loads in Europe over a 1-week period [6]. Our main findings from 2011 were distinct spatial patterns in drug use across Europe. Cocaine use was higher in Western and Central Europe and lower in Northern and Eastern Europe. Total consumption for Europe as a whole is extrapolated to 356 kilos daily, which would

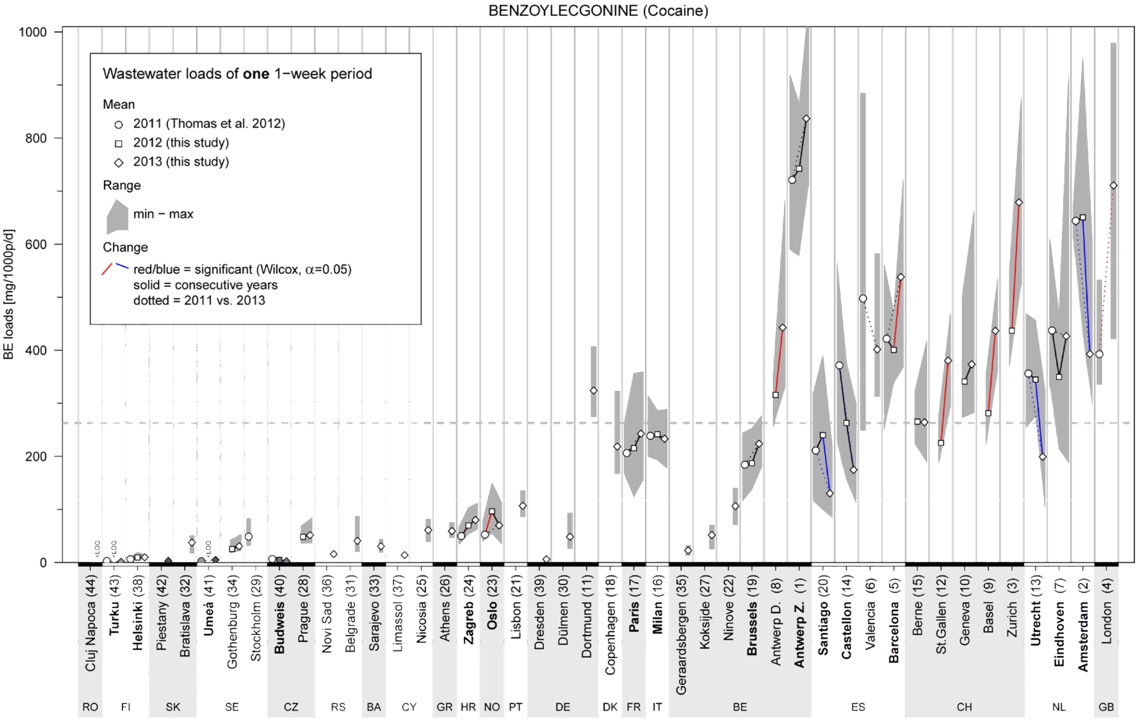

Table 1: Cocaine use in selected European cities, 2011-2013 [7]

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account for approximately 10 – 15 % of the global supply of cocaine (as estimated by the United Nations Office on Drugs and Crime). High per capita ecstasy loads were measured in Dutch cities, as well as in Antwerp and London. In general, cocaine and ecstasy loads were significantly elevated during the weekend compared to weekdays. Per capita loads of methamphetamine were highest in Helsinki, Turku, Oslo and Budweis, while per capita loads of cannabis were similar throughout Europe. Additional studies have been performed in 2012 and 2013 with increasing numbers of cities (23 and 42 respectively) and repetitive intercalibration exercises that allowed an assessment of not only spatial differences, but also temporal patterns in drug use across Europe [7]. Spatial differences were confirmed to vary greatly among European metropolitan areas and the results in general agreed with traditional surveillance data. Temporal changes were substantial in individual cities and years, but the overall means were relatively stable.

The group's activities are coordinated by the SCORE group (Sewage Analysis Core Group Europe) made up of Sara Castiglioni (Mario Negri Institute), Alexander van Nuijs, Adrian Covaci (University of Antwerp), Erik Emke, Pim De Voogt (KWR), Lubertus Bijlsma, Félix Hernández (University Jaume I), Christoph Ort (Eawag), Barbara Kasprzyk-Hordern (University of Bath), Malcolm Reid and Kevin Thomas (NIVA). Coordinating such transnational and multidisciplinary research action is not a trivial task, especially without direct funding. All the analyses are performed in-kind by the individual partners; proof of the collaborative spirit of all the research groups involved and must be commended.

Small contributions to host work shops and intercalibrations have been provided by the Research Council of Norway and the European Monitoring Centre for Drugs and Drug Addiction (EMCDDA). As they are the responsible European agency for reporting factual information on illicit drugs, it has been important for SCORE to work closely with them to gain acceptance of the technique and to start to work closely with the epidemiologists who are responsible for estimating the scale of Europe's drug problem. In December 2012, the EMCDDA in Lisbon hosted three illicit-drug-related meetings, bringing us closer together. In May 2013, the EMCDDA hosted the first international multidisciplinary conference on detecting illicit drugs in wastewater: "Testing the waters" (http://www.emcdda.europa.eu/events/2013/testing-the-waters), bringing together international experts working in relevant fields including drug epidemiology, pharmacokinetics, statistics, forensic science, analytical chemistry and environmental engineering.

WHAT NEXT FOR ILLICIT DRUG TESTING IN SEWAGE?

We believe that the main focus of research in the field will be focused towards a better understanding of the uncertainties associated with different aspects of sewage analysis, as well as expanding the suite of drugs, and hopefully areas, where community scale data are required. The EU Marie Curie Initial Training Network SEWPROF (A new paradigm in drug use and human health risk assessment: Sewage profiling at the community level; www.sewprof-itn.eu) will play a key role in developing inter-disciplinary and cross-sectoral research capability for the next generation of scientists working in this newly-emerging field. Moreover, the SCORE collaboration will continue through the COST Action ES1307 «Sewage biomarker analysis for community health assessment» [http://www.score-cost.eu], which will allow the network to expand and provide a supportive platform to aid in the communication and trans-disciplinary cooperation that is essential to the success of this technique. The SCORE group continues to coordinate European, and potentially broader, comparative studies, along with laboratory performance studies whilst liaising with the EMCDDA and other international governmental agencies such as the United Nations Office on Drugs and Crime. A second transdisciplinary conference "Testing the water 2015" is already planned for this year [http://testingthewaters2015.ch/]. We certainly believe that measurements in sewers are an important addition to the methods that exist today for estimating drug prevalence and that one day soon the data will be commonly used alongside questionnaire-based approaches.

The present paper has been written on behalf of the other members of the SCORE group (Sewage Analysis Core Group Europe): Alexander van Nuijs, Adrian Covaci (University of Antwerp); Erik Emke, Pim De Voogt (KWR), Lubertus Bijlsma, Félix Hernández (University Jaume I); Christoph Ort (Eawag), Barbara Kasprzyk-Hordern (University of Bath), Malcolm Reid (NIVA).

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The first full-scale advanced ozonation plant in the Dübendorf WWTP running; the new Swiss water protection act approved

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NEUGUT WWTP IN DÜBENDORF

The Neugut plant in Dübendorf is the first wastewater treatment plant (WWTP) in Switzerland where a full-scale advanced treatment of wastewater with ozone has been installed [1]. The plant has a capacity of 150 000 population-equivalents and is currently operating with 105 000. It is cleaning daily 20–50 million litres of wastewater using a primary clarifier, followed by biological treatment with nitrification, denitrification, biological P-removal and subsequent sand filtration. As early as 2009, the first discussions started about adding an ozonation treatment, and on October 2, 2012 the foundation stone ceremony took place. The project was supported by the supervisory board and the local communities served by the plant, the Swiss Federal Office for the Environment (FOEN), the canton of Zurich, and scientifically by Eawag, the Swiss Federal Institute of Aquatic Science and Technology [2]. For the implementation, several favorable conditions were present at Neugut, including a reserve capacity sufficient until 2050, an installed sand filtration unit and the reserve area for the installation of the reactor. After about a year of construction, the ozonation plant came into operation on March 24, 2014 (Figure 1). The WWTP was supported by the companies Holinger AG and Ingenieurbüro Gujer AG for the construction and operation of the ozonation stage. The operation has been running smoothly from day one. In May 2014, the first results were presented, showing that the overall removal of 80% of the five indicator substances could comfortably be achieved using an ozone concentration of 3.5 mg/L (corresponding to 0.7 g ozone /g DOC), regulated by the water flow. The investment costs added up to CHF 3.27m, and with additional energy consumption of 0.03 kWh/m^3 the operating costs of the ozonation plant account to CHF 0.023/m^3.The Swiss water protection act has now been approved and more WWTPs will be upgraded. The planning and construction of other WWTPs are drawing on the experience gained at Neugut.

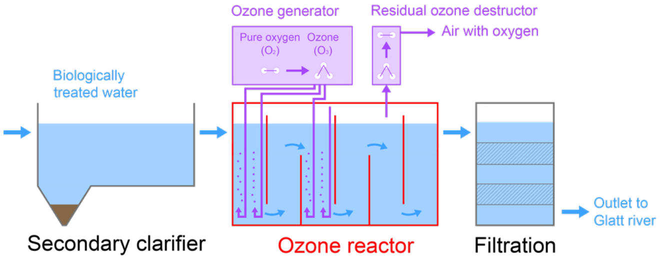

Figure1: Schema of the ozone reactor as implemented at the Neugut WWTP.

THE STORY OF THE NEW SWISS WATER PROTECTION ACT

Switzerland is located at the source of fresh water resources with two large rivers, the Rhine and Rhone, originating in the Swiss Alps. The observed concentrations of micropollutants are therefore lower than in other European countries such as Germany. Nevertheless, concentrations of selected compounds still exceed environmental quality standards at which adverse effects to aquatic organisms cannot be excluded [3]. From this viewpoint, and also from the perspective of a responsibility for the downstream inhabitants in neighbouring countries, FOEN decided to launch the project "strategy MicroPoll" in 2006 to investigate the pollution situation of Swiss surface waters and assess potential measures to reduce the load of micropollutants from urban areas [4,5]. The focus was on measures at municipal wastewater treatment plants, since they are a major source of many organic pollutants.

Current WWTPs are only capable of reducing the overall load of micropollutants by about half. Since hydrophilic compounds in particular – including many pharmaceuticals, personal care products and cleaning agents – still remain in the treated wastewater [6], it is technical measures at the WWTPs that can achieve the most substantial and effective reduction of micropollutants. The FOEN initiative was taken in line with other actions taking place in Europe: the International Commission for the Protection of the Rhine (ICPR) planned to develop a joint and comprehensive strategy for reducing and avoiding micropollutant inputs from urban wastewater and other sources; North Rhine-Westphalia and Baden-Württemberg (Germany) also investigated advanced wastewater treatment; and similar activities related to micropollutants took place in countries such as The Netherlands, UK and Sweden.

The Swiss project "Strategy MicroPoll" eventually resulted in a proposition of the Swiss government in the year 2009 to adapt the water protection ordinance (GSchV). The overall goal was to enhance water quality by the elimination of 80% of micropollutants in wastewater treatment using technical measures. The focus was on three groups of WWTPs: (i) large WWTP to reduce the sources of high loads; (ii) WWTPs at surface waters which have an impact on drinking water resources, for their protection; and (iii) WWTP at rivers with a high fraction of wastewater, to protect the ecosystem. On these criteria, about 100 out of the 700 Swiss WWTP would need to be upgraded and overall about half of the current load of micropollutants could be removed. Five indicator substances were defined for use in evaluating the effectiveness of the measures taken.

After the public consultation, it was found that 80% of the comments supported the targeted measures, but were in favour of a financing plan based on the 'polluter pays' principle and a solution for the whole of Switzerland. In 2010, ideas were floated on the way to finance the proposed measures. The final outcome was the establishment of a Swiss fund to finance the initiative, paid for by all Swiss inhabitants connected to a WWTP. With this money, 75% of the investment costs at the WWTPs were to be financed. The investment cost for the 100 WWTP under consideration was estimated to be in the order of CHF 1200m. The increase in costs for wastewater treatment was estimated at CHF 130m per year, which equates to about 10–15 % of the current costs of wastewater treatment. CHF 9 per year per Swiss inhabitant with a connection to a WWTP would be sufficient to finance 75% of the investment costs (for comparison: current average costs are CHF 112). In April 2012, the adaption of this new water protection act (GSchG) was proposed and accepted first by the federal council, then the council of states and finally the national council on March 3 2014. The implementation of the new water protection act and the start of the financing is planned for January 2016. Within 20 years, the following groups of WWTPs will need to be upgraded: (i) WWTP with more than 80 000 connected inhabitants; (ii) large WWTP (> 24 000 inhabitants) in the catchment of lakes; and (iii) WWTP (>8 000 inhabitants) on rivers with a fraction of wastewater greater than 10%. The energy consumption is expected to increase by 5–25% in a WWTP, and nationally by 0.1%. This additional energy demand should be compensated by energy optimisation and recovery at the WWTP.

EVALUATING AND CONTROLLING THE ADVANCED WASTEWATER TREATMENT

The technologies proposed for the advanced wastewater treatment are ozonation or treatment with powdered activated carbon (PAC). These technologies are well known from drinking water treatment and were tested within FOEN's federal project "Strategy MicroPoll" at two sites at pilot-scale in Switzerland: at the Regensdorf WWTP close to Zurich by Eawag [7], and the Lausanne WWTP on Lake Geneva by EPFL [8]. In these plants, and other plants installed in Germany, a broad range of micropollutants can be reduced by over 80%, reducing the overall toxicity of the effluent at the same time [9,10,11]. Other technologies could reach the same goals (e.g. adsorption to granular activated carbon, tight membrane filtration, advanced oxidation processes such as UV/H_2O_2 or O_3/H_2O_2), but current considerations of technical feasibility and cost favour the treatment with ozone or PAC. Recently, Envilab AG and Eawag have develop with FOEN a new selection of twelve substances to be used for the evaluation of the effectiveness of the measures. These compounds represent a wide variety of compounds typically present in municipal wastewater, are insufficiently eliminated in conventional wastewater treatment, and can be easily analysed in a single run with LC/MS/MS [12]. Out of this group, at least six compounds have to be selected: four from the group of “very well eliminated compounds” (amisulpride, carbamazepine, citalopram, clarithromycin, diclofenac, hydrochlorothiazide, metoprolol, venlafaxine), and two from the group of “well eliminated compounds” (benzotriazole, candesartan, irbesartan, mecoprop).

To ensure a good performance of the advanced treatment, appropriate control and operation strategies need to be developed. The effectiveness of the treatment technology needs to be assessed not only for chemical, but also for ecotoxicological quality control. In the treatment with ozone, transformation products are produced, which are so far not assessed in much detail. Moreover, the effects on complex ecosystems of removing micropollutants from wastewater should be studied to gain insight into how the pollutants affect their structure and function [13].

FURTHER INVESTIGATIONS AT NEUGUT WWTP

Further assessments are currently taking place at the Neugut WWTP. Eawag is involved with two projects funded by FOEN and the EU project DEMEAU with investigations at the WWTP. Demeau (Demonstration of promising technologies to address emerging pollutants in water and wastewater [14]) is a three-year EU project, funded within FP7 until August 2015, with the overall objective of promoting the uptake of knowledge, prototypes and practices from previous EU research, enabling the water and wastewater sector to face emerging pollutants. Eawag focuses on demonstrating the potential of ozonation for wastewater treatment at the Neugut WWTP in a collaboration by the Departments of Environmental Chemistry, Process Engineering, Water Resources and Drinking Water as well as the Swiss Centre for Applied Ecotoxicology (Ecotox Centre)[15]. Removal processes and the influence of the source water composition on the efficiency of eliminating micropollutants with ozone are being studied, together with ecotoxicological investigations. In addition, the transformation products produced by ozonation are being investigated with chemical analysis as well as kinetic studies in more detail. Appropriate online control of the technology to assure constant high water quality with minimal energy consumption is an important task to improve the long-term stability and robustness of the processes. The control of the ozonation process by monitoring the difference in UV absorbance between the reactor inlet and the outlet is being investigated, partly funded by FOEN [16,17]. Furthermore, aspects of environmental impact and cost assessment in the life cycle (LCA/LCC) of the technology are being addressed by researchers at the University of Applied Sciences and Arts, Northwestern Switzerland (FHNW) within DEMEAU to support decision-making and in overcoming market barriers for novel technologies. Ecotoxicological investigations have shown a temporary increase of toxicity after ozonation in certain tests, which can be reduced again by a biological filter such as sand filtration [9,10,11]. Based on these investigations, a biological treatment after ozonation is recommended. Within the project ReTREAT, funded by FOEN in a project framework for the promotion of technologies, different biological post-treatments (fixed-bed and moving-bed bioreactors, a biological activated carbon filtration) are being tested for their suitability and efficiency to reduce ozonation transformation products and ecotoxicological effects. The Ecotox Centre is therefore investigating different levels and mechanisms of effects with *in vitro* as well as *in vivo* bioassays in the laboratory and in flow-through systems directly on the WWTP.

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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 summarises the activities carried out so far and points up forthcoming results. More information on each of these activities is provided on the network website www.norman-network.net .

Milestones and achievements 2014

WG-1 PRIORITISATION (VALERIA DULIO, INERIS, FR)

The publication of the NORMAN Framework for prioritisation of emerging substances in April 2013 (V. Dulio and P.C. von der Ohe, 2013, ISBN: 978-2-9545254-0-2) is an important achievement of the working group, which has also been active in the collection and regular updating of monitoring data, physico-chemical data, review of Lowest PNEC values and other hazardous properties for the compounds on the NORMAN List of emerging substances, as a basis for their prioritisation. Thanks to this work, WG-1 has contributed as a stakeholder to the work of the European Commission for the implementation of the first EU Watch List ("NORMAN proposal for candidate substances for the 1st EU Watch List - Art 8 of 2013/39/EU Directive" and accompanying set of Factsheets, submitted to EC in August 2014) and is actively involved in the next review of the list of Priority Substances of the WFD.

An important milestone in 2014 was the workshop "Methodologies for prioritising hazardous chemicals in European waters" (Paris, 24–25 June 2014) organised by NORMAN WG-1 in collaboration with the EU IP SOLUTIONS project. The final aim of this workshop was to assess the current state of prioritisation methodologies, identify the current gaps and barriers and make recommendations for further development and improved integration of innovative approaches in prioritisation methodologies. The workshop conclusions confirmed that non-target screening and effect-based analysis are promising monitoring-based tools to overcome the present limitations of prioritisation schemes, which are focused on a limited set of target compounds. The most effective and successful route for the future could be the combination of "substance-based" and "monitoring-based" approaches as complementary tools. This event set out the steps the group would be taking to improve the current methodology in line with the conclusions of the workshop.

Finally, the extension and review of the NORMAN List of emerging substances has been discussed among experts, involving considerable work to identify on the one hand the new substances that need to be added to the list and on the other hand the substances that, while remaining relevant environmental contaminants, no longer deserve to be labelled as "emerging substances". They will not be deleted from the NORMAN list but they will be identified as "former emerging substances". The new list, recently published on the NORMAN website, includes more than 900 substances with, among others, additional biocides, flame retardants, PFASs, etc.

WG-2 ON BIOASSAYS (HENNER HOLLERT, RWTH AACHEN UNIVERSITY, DE)

NORMAN promotes via its Working Group on Bioassays (since 2011 under the leadership of RWTH Aachen) the use of biotests in environmental monitoring and strongly supports validation and intercomparison of these tests.

A blind interlaboratory study (ILS) applying biotests to evaluate complex surface water extracts was organised by NORMAN in 2013–2014, using 7 bioassays in 11 different laboratories in Europe (see, in this Bulletin, "The NORMAN interlaboratory study on biotesting of spiked water extracts").

With this ILS the Bioassays Working group also collaborated with the EDA-EMERGE project to develop a methodology where the biotest battery selected and validated by NORMAN was applied as a proof of concept on about 30 samples of approx 1000L obtained with large-volume active sampling from Joint Danube Survey 3 (see below WG-3).

WG-3 ON EDA (WERNER BRACK, UFZ, DE)

One important initiative of NORMAN in 2013-2014 was the development and validation of a NORMAN methodology for large-volume active sampling for effect-based monitoring, chemical screening and EDA. Application of bioassays together with non-target screening for effect-directed analysis of water samples often needs sample enrichment. Active, time-integrated on-site large-volume solid phase extraction (LVSPE) was developed to overcome the disadvantages of grab sampling (which is not representative, compared to time-integrated approaches) and passive sampling (which might result in low enrichment or bias, depending on the complexity of the environmental mixture). About 30 samples of approx 1000 L were taken during JDS3 by the UFZ group and submitted to chemical analytical screening. Performance for chemical screening is very good. Moreover, large-volume sample extracts were subjected to different bioassays (for this second part of the study, most data are already available, but not finally evaluated). Based on the results of this action and together with results from the associated project SOLUTIONS, a joint NORMAN–SOLUTIONS validated methodology for integrated effect/chemical screening based on large-volume active sampling will be addressed to European regulators (for publication).

The EDA WG is also working on the development of a Guidance document on EDA. While EDA is an approach of increasing relevance for the identification and prioritisation of emerging pollutants in European surface waters and related sediments and biota, there is still a complete lack of guidance on general principles for performing EDA, depending on the research or monitoring objectives and the required outcome. NORMAN and, particularly, its WG on EDA are an ideal platform for developing and publishing these principles. Topics are the general planning of EDA and the role of EDA in monitoring programmes (EDA as a tiered approach), criteria for the selection of bioassays, fractionation and analytical procedures, quality control and confirmation approaches. A draft is work in progress and consultation with the members was launched at the end of 2014 (planned to be published in 2015).

WG-4 ON ENGINEERED NANOMATERIALS (RALF KAEGI, EAWAG, CH)

The analysis of engineered nanomaterials (ENMs) is not trivial – comprehensive information on the material analysed is only obtainable by applying a set of different analytical techniques. Furthermore, certified reference materials are lacking and sample preparation procedures are not unified. Quality assurance of measurement results is therefore difficult to guarantee. An interlaboratory comparison study on gold nanoparticles (Au-NP) was launched by WG-4 in 2014 in collaboration with the COST Action ES1205 (ENTER), with the aim of allowing comparison of the performance of different techniques on a set of known and well characterised samples. The main questions addressed are: i) total concentration of Au in each sample, ii) size distribution of Au-NP in samples containing a single particle size or a mixture of up to three different sizes, and iii) based on the data obtained, the laboratories should decide whether the mixture is classified as a nanomaterial or not (according to EC recommendation). A range of analytical techniques based on different measurement principles for NP characterisation and quantification were included as part of this study. The NORMAN network and the COST Action ES1205 (ENTER) offer a larger network of laboratories which are equipped with various analytical techniques. The study is still on-going. A workshop is planned for spring 2015 in Paris to discuss the results from the ILS study (funded by COST ES 1205) and judge whether: a) comparable data can be gener-

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ated and b) the EC recommendation is applicable when applying state-of-the-art techniques (on well characterised samples).

WG-5 ON WASTEWATER REUSE AND CONTAMINANTS OF EMERGING CONCERN (DESPO FATTA-KASSINOS, NIREAS, UNIVERSITY OF CYPRUS, CY)

The activities of WG-5 are focused on the following three main aspects: a) the risks associated with wastewater reuse – evolution and spread of antibiotic resistance in the environment; b) the risks associated with micro-contaminants' uptake by crops; c) assessing which of the information is valid and reliable to be used in regulatory frameworks (i.e. Water Framework, Urban Wastewater Treatment and Wastewater Reuse Directive). Because antibiotic resistant bacteria and resistant genes are increasingly perceived as contaminants of emerging concern, it is considered important to systematically gather and evaluate information on the performance of the currently applied wastewater treatment systems in removing antibiotic resistance. To this purpose a screening campaign was launched by NORMAN in 2014 (see, in this Bulletin, "NORMAN WG-5: Wastewater reuse and contaminants of emerging concern").

WG-6: INDOOR ENVIRONMENT AND CONTAMINANTS OF EMERGING CONCERN (EVA BRORSTRÖM-LUNDÉN, IVL, SE)

Articles and consumer products used indoors may contain a variety of both well-known chemicals and emerging substances. Chemicals are emitted in the indoor environment, and indoor air and dust is an important pathway of chemical exposure for humans as well as a source for exposure to the outdoor environment.

These considerations have given birth to this new working group on the indoor environment and emerging contaminants under the leadership of IVL and IVM and in collaboration with a strong core group of members (University of Antwerp, University of Umea, University of Stockholm, etc.). It is also the first example of a working group addressing an environmental compartment other than the water compartment which has been so far the dominating focus of the NORMAN network and this confirms the fact that the mission of NORMAN is to address emerging contaminants in all environmental compartments. The kick-off meeting of the new group took place in Amsterdam on 8–9 December.

The main objective of the meeting was to define the scope of the working group in relation to relevant on-going projects and to agree on the overall strategy and final aims for the coming years. The following subjects were addressed: chemicals and chemical groups of concern for the indoor environment; emissions of emerging substances indoors and identification of important pathways of chemical exposure for humans indoors and pathways to the outdoor environment via air or WWTPs; harmonisation of sampling and measurement methods for air and dust; the need to organise interlaboratory studies for non-target screening in indoor dust; the need to organise a systematic compilation of occurrence data from indoor dust and air and the need to reach consensus on a common set of metadata, as a priority action before data collection; policy issues (What are the policy frameworks / institutional bodies to be addressed for indoor environment aspects?). A number of initiatives will be part of the NORMAN Joint Programme of Activities (2015 and beyond).

PASSIVE SAMPLING EXPERT GROUP (IAN ALLAN, NIVA, NO)

A number of initiatives were promoted by NORMAN in the field of passive sampling between 2009 and 2014 (see http://www.norman-network.net/?q=node/59). Those activities have already delivered a good package of results and experience in the use of passive sampling, but there are still points that need to be clarified in order reassure decision-makers about the use of these tools in regular monitoring. To encourage this discussion the NORMAN expert group decided to organise a meeting in order to define the strategy and a roadmap of the further actions to be promoted by NORMAN for 2015 and beyond.

The main aim was to have a critical analysis of the remaining barriers to the application of passive sampling techniques and to define the concrete actions needed to promote the implementation of these tools in environmental monitoring programmes.

The meeting took place in Lyon (27–28 November 2014) and was organised by IRSTEA as a NORMAN initiative in collaboration with AQUAREF. The outcomes of the meeting will be published by mid-2015 in a common paper prepared by the organising committee and the participating experts and will constitute the background for future NORMAN actions aimed at improving the performance and applicability of these devices in water quality monitoring.

QA/QC ACTIVITIES

An interlaboratory study of *in vitro* bioassays for testing of surface water samples spiked with selected emerging contaminants (2013–2014): details of this intercomparison study are reported above (see WG-2) and in the corresponding note (see, in this Bulletin, "The NORMAN interlaboratory study on biotesting of spiked water extracts").

Collaborative trial on non-target screening of selected river water samples from the Danube river with the GC-MS(MS) and LC-HR-MS(MS) methodologies available in participating laboratories was organised in 2013-2014 by the Environmental Institute (the first time it has been done worldwide in environmental samples) in collaboration with Eawag and UFZ.

NORMAN EMPODAT

The size of the EMPODAT database is constantly increasing, with more than 3.5 million datasets available at the end of 2014 (compared to 1 million data items at the end of 2013). France has been one of the main contributors in 2013 and 2014, with monitoring data from water agencies as well as the results from the national screening campaign on surface water and groundwater. Datasets were also provided by other member states, including The Netherlands, Italy, Slovakia and Germany. In the pipeline there are the results of the Joint Danube Survey 3 conducted in 12 member states in 2014, screening studies data from Sweden, etc. An overview of the improvement in terms of distribution of data entries by category of use appears in the table below.

As regards the improvement of the database facilities, effort has also been made in the development of two new Ecotox modules in EMPODAT: the first one to allow for a regular compilation of EQS / PNEC values, either already existing (national values from Member States) or derived by NORMAN; and the second one to allow for a systematic gathering of "raw data" and associated metadata from ecotoxicity tests. In the latter module metadata are compatible with the new CRED system, in order to allow in the future a simplified assessment of the reliability and relevance of the tests based on automated database queries.

Since April 2013, NORMAN is partner of the Information Platform for Chemical Monitoring (IPCheM) currently being established by the European Commission, with the EC Joint Research Centre in the lead.

Since 2014, a single-substance version of the CHEMPROP software has been available for all NORMAN members (registration required on the UFZ website). With this tool, it is possible to derive information on

Category	New entries in 2014	Total	Growth%
Plant protection products	1,440,260	1,824,509	78.9%
Plant protection products/biocides	524,494	643,787	81.5%
Industrial Chemicals	222,175	352,000	63.1%
Pharmaceuticals	86,141	163,151	52.8%
Other	83,453	106,338	78.5%
Flame retardants	79,273	121,594	65.2%
Plasticisers	76,040	93,215	81.6%
Disinfection by-products (drinking water)	38,801	47,212	82.2%
Industrial Chemicals/biocides	32,754	55,218	59.3%
Personal care Products	18,882	42,616	44.3%
PFAS	17,113	18,699	91.5%
Gasoline additives	14,608	28,562	51.1%
Biocides	8,062	9,598	84.0%
Algal toxins	2,859	2,893	98.8%
Personal care Products/Biocides	2,440	18,154	13.4%
Moth repellent / Antimicrobial agent	1,908	1,941	98.3%
Food additives	1,019	1,058	96.3%
Vio-terrorism / Sabotage agents	954	966	98.8%
Biocide transformation products	953	1,105	86.2%
Personal care Products/Food additives	481	489	98.4%
Trace metals and their compounds	387	88,390	0.4%
Surfactants	262	7,662	3.4%
Industrial chemicals / Flame retardants	25	15,081	0.2%

physico-chemical properties (Koc, water solubility, etc.), ecotoxicity and other hazardous properties (BCF, ED effects, CMR classification, etc.) when experimental data are not available. WG-1 uses the ecotox models to derive Lowest PNEC values for substances without experimental tests.

NORMAN MASSBANK

The aim of NORMAN MassBank is to provide an open access and vendor-independent repository for mass spectral data within Europe, to support the identification of unknown compounds in environmental samples. This is a prerequisite for the improved prioritisation of hazardous compounds in Europe and worldwide. In line with this objective NORMAN MassBank improves the flexible exchange of mass spectral data within NORMAN and is used in the European ITN EDA-EMERGE, the Joint Danube Survey 3 and the European Integrated Project SOLUTIONS. Furthermore, the exchange of mass spectra via NORMAN MassBank decreases the need for standards purchase in each laboratory thanks to improved sharing of data. Since 2012 Eawag has been working on the development of the R package, RMassBank, under the leadership of Emma Schymanski (Eawag), which is necessary in order to allow automated processing of raw mass spectral files for the gathering of huge amounts of high quality mass spectra to be uploaded in MassBank. Continuous upgrading of the RMassBank including a graphical user interface for more user friendly usage is planned for 2015.

Over 7,100 spectra of standard compounds have been added by NORMAN members to date, as well as literature and tentative/unknown spectra for the exchange of data. A workshop on MassBank and RMassBank was organised in September 2014 at Eawag as a satellite meeting of the evaluation workshop of the Collaborative Trial on Non-target Screening (for more details see, in this Bulletin, “NORMAN goes non-target”).

NORMAN WORKSHOPS

Workshops in 2014

Workshop on Passive Sampling techniques for monitoring of contaminants in the aquatic environment: Achievements to date and future perspectives
Organised jointly by NORMAN Network and AQUAREF, hosted by IRSTEA, France (27–28 November 2014, Lyon, France)

Workshop on Non-Target Screening: Towards the harmonisation of methods for non-target screening of environmental samples
Organised by NORMAN Network jointly with SOLUTIONS project, hosted by Eawag (16–17 September 2014, Dübendorf, Switzerland)

NORMAN MassBank Workshop 2014
Organised by Eawag (Switzerland) and UFZ (Germany), hosted by Eawag (17–18 September 2014, Dübendorf, Switzerland)

Workshop on Methodologies for prioritising hazardous chemicals in European waters: the state of play and the need for improvement
Organised by SOLUTIONS project in collaboration with the NORMAN network, hosted by INERIS (24–25 June 2014, Paris, France)

Forthcoming events

Contaminated Sediments: Environmental Chemistry, Ecotoxicology and Engineering
8-13 March 2015, Ascona, Switzerland

- More information at http://www.contased.org/

4th European Water Conference
23-24 March 2015, Brussels, Belgium

- More information at http://ec.europa.eu/environment/water/2015conference/index_en.htm

SETAC Europe 25th Annual Meeting
3-7 May 2015, Barcelona, Spain

- More information at http://www.barcelona.setac.eu/

12th Urban Environment Symposium: Urban Futures for a Sustainable World
1-3 June 2015, Oslo, Norway

- More information at http://hues.se/

Workshop on Emerging Pollutants in Non-industrial Indoor Environments
8-9 June 2015, Kjeller, Norway

- Contact: PernillaBohlin.Nizzetto@nilu.no

Environmental monitoring of biocides in Europe & compartment-specific strategies
25-26 June 2015, Berlin, Germany

- Contact : heinz.ruedel@ime.fraunhofer.de

EDA-EMERGE PhD student conference - “Emerging pollutants and multiple stressors in aquatic ecosystems”
29 June-1 July 2015, Leipzig, Germany

- Contact : stefanie.rotter@ufz.de

14th International Conference on Environmental Science and Technology
3-5 September 2015, Rhodes, Greece

- More information at http://www.cest.gnest.org/

ICCE 2015 – 15th EuChemMS International Conference on Chemistry and the Environment
20-25 September 2015, Leipzig, Germany

- More information at http://www.icce2015.org/index.html

3rd International conference: Environmental monitoring and assessment: Challenges and opportunities
1-2 October 2015, Aarhus, Denmark

- More information at http://dce-conference.au.dk/

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

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