TRAVAUX DU RÉSEAU EUROPÉEN NORMAN

Réseau européen de laboratoires de référence, de centres de recherche et d'organismes associés pour la surveillance des substances émergentes dans l'environnement

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Contexte de programmation et de réalisation

Ce document s'inscrit dans le cadre de l'action 14 de la Convention INERIS - ONEMA 2010, dans la continuité des travaux réalisés en 2009.

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1. INTRODUCTION

Ancien projet de recherche européen financé par la CE (6e PCRD - Priorité 6.3 - Contrat N ° 018486), le réseau NORMAN est opérationnel depuis février 2009 comme association de droit français sans but lucratif « loi 1901 » : Association NORMAN - Réseau de laboratoires de référence, centres de recherche et d'organismes associés pour la surveillance des substances émergentes dans l'environnement.

Il compte aujourd'hui 46 membres de 19 pays (y compris deux organismes canadiens) parmi les plus reconnus dans le domaine de la recherche sur les polluants émergents (RIVM, Cemagref, Fraunhofer Institute, UFZ en Allemagne, UBA Autriche, Université Libre de Amsterdam, Université de Stockholm, NERI au Danemark, EAWAG Suisse, SYKE Finlande, etc).

Le Centre commun de recherche IES ISPRA de la Commission Européenne fait partie des membres du réseau avec des liens de collaboration étroits qui ont amené en juin 2011 à la signature d'un contrat de collaboration entre NORMAN et le JRC, ce dernier s'engageant à offrir, sur chaque programme d'activité annuel, un support financier sur des activités d'intérêt commun.

Comme le montre la présentation ci-dessous, les actions de NORMAN sont étroitement liées aux activités en France dans le domaine des substances émergentes et de véritables synergies ont été créées grâce à l'implication directe de l'ONEMA dans les travaux du réseau.

Les travaux de NORMAN sont organisés autour de modules décrits ci-dessous :

- les bases de données NORMAN,
- les groupes de travail,
- les activités d'assurance qualité,
- les workshops.

2. LES BASES DE DONNEES

La base de données EMPODAT NORMAN (base de données sur l'occurrence des substances émergentes dans l'environnement) a été considérablement améliorée et contient désormais environ 120000 données d'occurrence sur 307 substances dans plus de 20 pays européens. Une batterie d'outils statistiques a été développée permettant une vue d'ensemble rapide de la distribution des substances.
Un module de statistiques sur mesure permet de personnaliser les recherches de substances / paramètres. Mises à jour automatiquement, les « Substance fact sheets : feuille synthétique par substance » ont été créées pour fournir des informations sur les performances des méthodes analytiques utilisées. L'information servira entre autres, à l'exercice de hiérarchisation conformément à la méthodologie qui est actuellement en cours de développement en GT1 (voir ci-dessous).

Par ailleurs, la reprogrammation et la maintenance des modules EMPOMASS (base de données sur les spectres de masse des substances « inconnues ») et EMPOMAP (base de données sur les projets de recherche européens sur le sujet) ont été réalisées en 2010. Concernant EMPOMASS, une étape importante est prévue courant 2011 où UFZ, Leipzig mènera une action consistant à la mise en œuvre d'un serveur de la base de données MassBank (Horai et coll., 2010 ; www.massbank.jp) comme plate-forme pour la collecte et l'échange de données de spectrométrie de masse au sein de NORMAN et de NORMAN vers la communauté scientifique et institutionnelle dans le monde entier. En effet, il est prévu que cette amélioration permette des progrès importants dans l'identification des pics inconnus pour l'analyse qualitative de substances non ciblées par exemple via l'analyse de l'effet direct (EDA) – (voir description du GT-3 ci-après).

3. GROUPES DE TRAVAIL

3.1 GROUPE DE TRAVAIL 1 (INERIS, France) - Hiérarchisation des substances émergentes

L'objectif est l'identification des nouvelles substances qui justifient une attention prioritaire (y compris les besoins en termes d'amélioration des données existantes), basée sur des critères tels que présence dans l'environnement, distribution spatiale et temporelle, usage, niveau de consommation, toxicité et écotoxicité, persistance, potentiel de bioaccumulation, etc. La différence par rapport aux autres méthodologies de hiérarchisation et la justification de cette étude est justement que par définition des lacunes dans le processus d'évaluation du risque pour les substances émergentes existent (ex : pas de renseignements suffisants sur les effets de la substance, performance insuffisante de la méthode d'analyse nécessaire pour quantifier le niveau d'occurrence de la substance dans l'environnement, etc). Ces lacunes ne permettent donc pas d'évaluer correctement le risque associé et peuvent entraîner la désélection de ces substances dans les processus usuels de hiérarchisation.

La méthodologie proposée par NORMAN est donc basée sur deux principales étapes

1. une première classification des substances dans un nombre défini de catégories d'action,
2. classement subséquent et hiérarchisation des substances au sein de chaque catégorie d'action.

Six types spécifiques de catégories ont été identifiés représentant les mesures à prendre par la communauté scientifique et les pouvoirs publics afin de couvrir les lacunes dans les connaissances actuelles lesquelles feront partie des futures actions NORMAN.
La méthodologie vise à couvrir les substances émergentes dans tous les compartiments de l'environnement. Toutefois, dans cette première étape les indicateurs prioritaires sont développés pour le milieu aquatique seulement.
Les substances candidates pour cet exercice sont les substances de la liste actuelle de NORMAN (mise à jour en 2010), qui se compose de plus de 700 substances (liste disponible sur le site internet www.norman-network.net).
Une première ébauche de la méthodologie pour la définition du cadre de la définition des priorités a été préparée et discutée au cours de la première réunion du GT en février 2010 à Bruxelles. Suite aux échanges et aux commentaires reçus, un deuxième projet de document de travail a été préparé et discuté lors de la 2ème réunion du GT organisée en novembre, à Paris. Un test d'exécution de la méthodologie est en cours. Les premiers résultats (listes prioritaires pour les catégories d'action différentes) seront disponibles en 2011.

Signalons que cette méthodologie Norman est à la base de méthodologie nationale mise en œuvre dans le cadre du Plan Micropolluants du MEDDTL par le Comité d'Experts pour la Priorisation des substances aquatiques, qui débouchera en 2011 sur la production d'une liste de substances candidates à la campagne exceptionnelle à mener en 2012 dans les eaux de surface.

3.2 GROUPE DE TRAVAIL 2 (INERIS, France) – Biomarqueurs et bioessais pour la surveillance des milieux aquatiques stratégies pour l'interprétation des résultats.

En 2010, la coordination du GT (auparavant sous la responsabilité du RIVM) a été reprise par INERIS. La proposition de « position paper » (projet), initialement prévue pour juin 2010 est encore en cours de préparation et est destinée à être diffusée, pour consultation parmi les participants du groupe de travail à partir de 2011. Un inventaire des outils et des stratégies pour interpréter les résultats est en préparation et devrait être finalisé en juin 2011. En 2010, une étude comparative a été menée réunissant 6 participants. Les résultats des participants sont attendus en juin 2011. L'évaluation et l'interprétation des résultats sera la base de travail pour la préparation d'un deuxième exercice sur différents sites en Europe en 2011.

3.3 GROUPE DE TRAVAIL 3 (UFZ, Germany) – Analyse des effets directs pour l'identification des substances

2010 a vu le lancement d'un nouveau groupe de travail sur l'analyse orientée sur l'effet pour l'identification des substances dangereuses (EDA).

La justification de ce GT découle de la forte valeur ajoutée offerte par les approches axées sur les effets pour identifier des composés dangereux. Ce type d'approches devrait avoir sa place dans les programmes de surveillance dans le cadre des contrôles d'enquête, en particulier.

Les résultats peuvent être utilisés pour fournir une des indications complémentaires aux méthodologies de hiérarchisation conventionnelles. À cet égard, ce groupe de travail représente le lien entre les activités du GT-1 sur la hiérarchisation des contaminants émergents et du GT-2 sur les bioessais. La réunion de lancement du GT a eu lieu à Leipzig les 19-20 octobre 2010. Au cours de la réunion il y a un consensus pour souligner combien les approches axées sur l'effet ont vu leur intérêt croître auprès des pouvoirs publics. Toutefois, les participants ont conclu qu'une stratégie soumise aux autorités devrait inclure

i) un exposé clair explicitant le rôle de cette approche,

ii) un protocole simplifié de l'EDA prêt à être utilisé dans les réseaux et

iii) l'application de ce protocole sur site pilote afin d'en démontrer l'applicabilité opérationnelle.

L'un des premiers résultats de la réunion a été la préparation et la soumission en janvier 2011 d'une proposition de projet de recherche sur l'EDA. Parmi les tâches prévues pour 2011 :

- publication d'un livre sur EDA dans la série de Handbook of Environmental Chemistry ;
- développement et mise en œuvre d'une banque de donnée de spectres de masse haute résolution pour NORMAN ;
- organisation d'un atelier sur les nouveaux aspects de l'EDA dans l'identification de composés candidats basés sur les effets indésirables dans les échantillons de terrain (prévue automne 2011) ;
- organisation de la réunion annuelle du GT-3 (automne 2011) ;
- planification d'un programme de démonstration qui pourrait avoir lieu en 2012.

4. ACTIVITES QA/QC, ETUDES INTERLABORATOIRES

4.1 Utilisation de l'échantillonnage passif pour les substances émergentes (WRI, Slovakia)

Un intense travail préparatoire a été réalisé en 2010, sous la direction de l'Institut de recherche de l'eau - WRI, SK pour l'organisation d'une campagne interlaboratoire sur l'échantillonnage passif appliqué aux contaminants émergents qui débutera au printemps-été 2011.

L'étude de l'applicabilité de ces outils de surveillance pour les substances émergentes fait partie des activités de réseau de NORMAN depuis 2009. Suite à la réunion du groupe d'experts organisée en 2009 à Prague, une note de positionnement (Position Paper) "échantillonnage passif de polluants émergents dans le milieu aquatique : état de l'art et perspectives" a été publiée au cours de l'été 2010. Ce document offre une vue d'ensemble exhaustive de l'état de l'art pour les différents types d'échantillonneurs passifs pour la surveillance des contaminants émergents dans l'eau, les sédiments et les organismes vivants, mais aussi pour l'évaluation de l'écotoxicité (ex. utilisation d'échantillonneurs passifs comme mimétiques pour la bioconcentration, etc). Le document est disponible sur le site de NORMAN et un résumé est fourni en annexe.

L'exercice interlaboratoire qui aura lieu en 2011 sera organisé comme "Surveillance sur Site chimiques" (CM sur place) organisé par NORMAN et le Centre Commun de Recherche (JRC ISPRA) en appui à la stratégie de mise en œuvre de la Directive-cadre sur l'eau. L'exercice, qui sera ouvert aux participants provenant de laboratoires commerciaux, universitaires ou institutionnels, vise à rendre compte de la variabilité des données issues des différents échantillonneurs passifs. Les substances cibles comprendront des pesticides, des pharmaceutiques, des biocides, des hormones stéroïdes et des retardateurs de flamme bromés polaires.

4.2 Essai interlaboratoire sur des métabolites de pesticides dans l'eau potable (IWW, Germany)

Cette étude interlaboratoire sur les métabolites de pesticides et le glyphosate a été organisée dans le cadre du Proficiency Testing AQS Bade-Wurtemberg, en collaboration avec le Centre de l'eau IWW (Mülheim an der Ruhr). Compte tenu de l'importance des métabolites de pesticides comme contaminants émergents à l'échelle européenne, la portée de l'exercice a été étendue au-delà du niveau national sous l'égide de NORMAN, donnant ainsi une occasion intéressante pour les laboratoires européens d'accroître la qualité et la comparabilité des données analytiques pour cette catégorie de polluants émergents Grâce à une participation très élevée des laboratoires (82 laboratoires), il était possible d'inclure une évaluation de la méthode sur les résultats. Cette évaluation a montré que dans la plupart des cas, il n'y a pas de différence significative entre les méthodes.

4.3 Essai interlaboratoire sur les alkyles perfluorés dans les échantillons environnementaux

Le rapport final de l'essai interlaboratoire organisé en 2009 est maintenant finalisé et envoyé aux participants (et bientôt disponible sur le site Web de NORMAN). L'étude a été réalisée par l'Institut pour les études environnementales (IVM) en collaboration avec NORMAN, INERIS et QUASIMEME et en même temps qu'une étude sur le matériel humain organisé par Prof. Bert van Bavel (MTM, Orebro University). En conséquence, le rapport se compose de deux parties : échantillons humains (préparé par MTM) et échantillons environnementaux (préparé par IVM).

Pour la partie de l'environnementale, les échantillons fournis étaient de l'eau de surface, des poissons marins (Sandre) et des boues. Les participants provenant de laboratoires mondiaux étaient autorisés à appliquer leurs méthodes internes. Les résultats ont été recueillis et évalués statistiquement en utilisant les statistiques de Cofino. Les Z-scores ont été fournis individuellement aux participants.

Le grand nombre important de laboratoires participant à cette étude internationale confirme l'intérêt pour l'analyse des PFC tant dans les matrices humaines qu'environnementales.

Cette étude a montré que la performance des laboratoires participant à la partie humaine de l'étude était meilleure que la performance dans la partie environnementale. Ceci pourrait être en partie causé par les faibles niveaux de PFC dans les échantillons environnementaux. Cependant, il existe probablement d'autres sources possibles qui ont contribué à la variance élevée des résultats dans cette étude, et ceci est expliqué en détail dans le rapport. Une autre remarque porte sur les matrices analysées : pour la première fois, les boues d'épuration ont été incluses dans l'étude. Les variations importantes sur cette matrice montrent que plus d'efforts sont nécessaires pour améliorer les méthodes d'analyses dans les boues.

4.4 Mise en œuvre du protocole NORMAN pour la validation de méthodes au sein de la normalisation européenne (IWW, Germany)

La nouvelle proposition d'élément de travail basé sur le protocole de NORMAN pour les méthodes de validation a été préparée par l'IWW en juillet 2010 et va maintenant être soumise par la France au CEN TC230.

5. EVENEMENTS EN 2010

5.1 Séminaire sur les polluants spécifiques : "WFD River Basin Specific Pollutants Monitoring – Identification and Monitoring" (JRC)

L'atelier s'est déroulé du 10 au 11 juin 2010 à Stresa, en Italie et a été organisé comme un atelier annuel de NORMAN en collaboration avec CCR IES. L'objectif de l'atelier était de fournir un forum de discussions pour les états membres et les groupes intéressés par les approches pour une sélection harmonisée des polluants spécifiques dans les bassins versants (RBSP) et leur surveillance. Une attention particulière a été donnée aux substances émergentes dans la mesure où leur hiérarchisation et leur suivi dans le milieu aquatique sont particulièrement difficiles. Le séminaire visant à produire des recommandations claires aux états membres sur la façon de procéder pour ces polluants spécifiques, un questionnaire avait été préalablement distribué aux représentants des états membres permettant la collecte d'informations exhaustives sur les procédures appliquées pour la sélection des polluants spécifiques par bassin. De plus, quatre ateliers de travail avec des thèmes spécifiques ont permis des échanges sur la disponibilité des données ; l'identification des substances candidates ; la sélection des polluants spécifiques et la surveillance de ces polluants.

Parmi les conclusions de cet atelier, on citera :

- le besoin de renforcer les échanges et des données de concentration au niveau de l'union européenne (c.-à-d. partage des données grâce à une base de données commune au niveau de l'Europe). La base de données EMPODAT de NORMAN a été identifiée comme un outil possible pour améliorer ces échanges ;
- le besoin de format de données commun (concentration + métadonnées) nécessaire pour améliorer l'interopérabilité des bases de données et exploitation des données de surveillance disponibles. A cette fin, un modèle commun de collecte est déjà disponible. Il a été utilisé au cours de la collecte des données DG ENV-EEA et est également adopté par NORMAN. Sa mise en œuvre au niveau des états membres est nécessaire pour une utilisation optimale des ressources ;
- le besoin de campagnes exploratoires à l'échelle européenne avec une implication répartie des divers états membres et des planifications et mise en œuvre collectives ;
- le renforcement des échanges d'expériences au niveau de l'UE sur l'utilisation de techniques de « screening » non ciblé pour le contrôle d'enquête (l'activité sera lancée par le CCR et NORMAN).

Plus de détails sont disponibles sur le site Web de NORMAN et figurent également dans le rapport du séminaire qui est publié sous le titre de «Workshop report River basin specific polluants – identification and monitoring ».

5.2 Séminaire sur les banques d'échantillons : "Environmental specimen banking (ESB) and emerging substances" (UBA, Germany)

Le séminaire s'est déroulé les 21 et 22 juin 2010 à Berlin.

Les banques d'échantillons qui existent déjà ne sont pas encore organisées en réseau, chacune d'elles possède ses propres caractéristiques et programmes de travail. Le déroulement du séminaire consistait en une présentation des banques et des programmes existants ainsi qu'en deux groupes de discussion en vue de l'harmonisation sur les questions suivantes : "Quels polluants ?" et « Quels échantillons environnementaux ? ».

NORMAN a présidé les groupes de deux discussions afin d'étudier la possibilité d'une collaboration plus étroite pour l'analyse des contaminants émergents.

Les banques d'échantillons existant en Europe peuvent faire bénéficier des données sur les tendances spatiales ou temporelles à NORMAN, et NORMAN peut fournir des recommandations aux banques d'échantillons lorsqu'il s'agit de l'analyse de contaminants qui n'étaient pas mesurés dans le passé et qui sont aujourd'hui considérés comme des préoccupants. Avant même d'envisager une coopération institutionnelle entre l'Union européenne, les banques et NORMAN, un pas en avant doit être proposé vers la création d'un réseau de banque d'échantillons.

Une lettre d'intention est en cours de rédaction par la communauté des « banques d'échantillons » pour montrer leur volonté de coopération.

5.3 Séminaire sur les nanoparticules : "Enginnered nanoparticles in the environment ; analysis, occurrence and impacts" (BfG, Germany)

Le séminaire a eu lieu les 19 et 20 octobre 2010 à Coblence, avec plus de 70 participants. La réunion a mis en évidence les questions clés qui sont encore ouvertes dans le domaine des nanomatériaux, par exemple, sur les méthodes analytiques appropriées pour l'analyse de nanoparticules dans des matrices environnementales, leurs comportements (par exemple vis à vis des barrières naturelles) ? Cela semble aujourd'hui possible uniquement dans des conditions très spécifiques et de manière limitée. Toutefois, les conclusions du séminaire soulignent l'importance de la prise en compte des modifications de surfaces des nanoparticules ainsi que les scénarii d'émissions puisque un changement des conditions initiales peut permettre le passage de barrières. Basé sur ces conclusions et l'expression de l'intérêt des participants, un groupe de travail sur les nanomatériaux sera lancé en 2011.

Les présentations du séminaire sont disponibles sur le site Web de NORMAN.

Le tableau fourni en annexe compile l'ensemble des travaux du réseau NORMAN.

6. CONTRIBUTIONS DE L'INERIS AUX ACTIVITES DU RESEAU NORMAN EN 2010

Dans le cadre des travaux présentés ci-dessus l'INERIS s'est impliqué dans :

1. l'organisation des activités qui relèvent de son rôle de Secrétaire Exécutif de l'Association, directement lié au Comité Directeur et responsable de la gestion quotidienne courante de l'Association et du bon fonctionnement des interactions entre les Membres de l'Association, avec, notamment :
   - l'organisation des réunions du Comité Directeur (deux réunions en mai et octobre 2010) et de l'Assemblée Générale (Paris, 6 décembre 2010)
   - la coordination des activités scientifiques et des livrables programmés pour 2010
   - la préparation du programme annuel d'activités scientifiques pour 2011 sur la base des propositions du Comité Directeur et de l'Assemblée Générale ;

2. étapes de négociation avec JRC pour la signature d'un accord de collaboration entre NORMAN et JRC qui a été signé en juin 2010 à Stresa, Italie, à l'occasion du colloque de NORMAN (« River Basin Specific Pollutants – Identification and Monitoring ») ;

3. les activités scientifiques (programme d'activité 2010) suivantes :
   - coordination des activités du Groupe de Travail N°1 sur la priorisation des substances émergentes et lien avec le travail du Comité Experts Priorisation (CEP) au niveau national en France ;
   - participation dans le Groupe de Travail N°2 sur l'application des bioessais et des biomarqueurs dans les programmes de surveillance des milieux aquatiques ;
   - participation comme expert dans le Groupe de Travail N° 3 sur les approches EDA ;
   - participation dans le comité d'organisation du colloque NORMAN – JRC (« River Basin Specific Pollutants – Identification and Monitoring », Stresa, juin 2010), avec contribution notamment au niveau de la préparation du questionnaire envoyé aux représentants des états membres, évaluation des réponses au questionnaire, préparation des questions pour les 4 sessions de discussion (groupes de travail), rédaction du rapport du colloque ;
   - participation au colloque NORMAN-UBA (« Environmental specimen banking (ESB) and emerging substances", Berlin, juin 2010) avec une présentation sur les activités du réseau NORMAN et l'animation de la session de discussion « What Chemical ?» suivie par la préparation du rapport final ;
   - collecte des contributions et rédaction du Bulletin de veille scientifique du réseau NORMAN (publication mars 2011 - dissémination via le site web du réseau et distribution par courrier).

ANNEX

NORMAN activities - status 2010

Name of the activity	**Status December 2010**
SWB - Scientific Watch Bulletin (2nd issue) Contact person : valeria.dulio@ineris.fr	Contributions will be provided on: - Environmental Specimen Banks – follow-up of previous contribution in 2009 (Fh-IME) - Cyclic methyl volatile siloxanes (cVMS) in the environment: recent findings in the light of the work presented at a session on cVMS held at the SETAC Europe meeting in May in Seville and at a EU member states siloxanes workshop held on 10-11 June 2010 in Helsinki (ITM – University of Stockhom) - Current concerns related to wastewater reuse and xenobiotics (University of Cyprus) - Organophosphorous flame retardants and the ENFIRO project (Life Cycle Assessment of Environment-Compatible Flame Retardants: Prototypical Case Study) coordinated by IVM – Pim Leonards (IVM) - Nanoparticles in the aquatic environment – brief on the outcomes of the NORMAN workshop on nanoparticles organised by BfG in October 2010 (BfG) - Metabolites and transformation products of emerging contaminants in the environment: brief of the TransCon2010 conference organised by EAWAG in September 2010 (EAWAG) - Disinfection by products in drinking water – occurrence and impact on human health (Veolia) - Summary of the recently published Position Paper on "Passive sampling of emerging pollutants in the aquatic environment: state of the art and perspectives" - Summary of PFC ILS conducted in 2009 - Summary on RBSP workshop. Planned deadline for publication of the bulletin: December 2010.
EG-1 (2009) - Expert Group meeting N°1 "Toxicity profiling" with publication of position paper (IVM) Contact person timo.hamers@ivm.vu.nl	The meeting of the EG took place on 9 October 2009 in Amsterdam, Position Paper due to be published by the end of the year.
EG-2 - Expert Group meeting N°2 "Use of passive sampling for emerging substances" with publication of position paper (VUVH) Contact person: Branislav Vrana vrana@vuvh.sk	Position paper "Passive sampling of emerging pollutants in the aquatic environment: state of the art and perspectives" has been finalised – available on the NORMAN website and circulated to all members, DG ENV (WG-E and CMEP representatives) for wide dissemination. An interlaboratory calibration study is under preparation (will be executed in 2011 – meeting of the organisation committee on 24 November in Bratislava). Objective of the intercomparison exercise: - present variability in data by comparing results from various passive samplers sent by participating laboratories exposed to water at a single (reference)

Name of the activity	Status December 2010
	site; - target substances: polar pesticides, pharmaceuticals, biocides, steroid hormones, brominated flame retardants; - it will be open to participants from commercial, academic and regulatory laboratories.
AW-1 - Workshop1 "WFD River Basin Specific Pollutants Monitoring - Information exchange on current approaches, best practices and identification of needs with particular focus on emerging pollutants" (JRC) Contact person: Georg Hanke georg.hanke@jrc.ec.europa.eu	The workshop took place on 10-11 June in Stresa, Italy and was organised as a Norman annual workshop in collaboration with JRC IES. The objective of the workshop was to provide a common forum for MS and interested groups for presenting, discussing and streamlining approaches for a harmonised selection and monitoring of RBSP in the WFD context. Particular attention was given to emerging contaminants, as their prioritisation and monitoring are particularly challenging. The workshop aimed to produce clear recommendations on how to proceed. Speakers's presentations available on the NORMAN website The workshop report is ready (draft circulated for comments to the participants). The final report will be published in the coming weeks as "JRC scientific and technical report".
AW-2 – Workshop2 "Environmental specimen banking (ESB) and emerging substances (UBA, Germany) Contact person: jan.koschorreck@uba.de	The workshop took place on 21-22 June in Berlin. EU-ESBs are not yet organised as a network, each of them has its own characteristics and work programmes. The scientific programme of the workshop included: 1) presentation of the EU ESB programmes; 2) two discussion groups in view of harmonisation on the following issues: "What chemical?" and "What specimen?" NORMAN chaired the two discussion groups in order to investigate the potential for analysis of emerging contaminants. NORMAN is interested in ESBs for retrospective analysis (time and spatial trends) of substances that were not measured in the past and which are today regarded as substances of emerging concern. However, before the establishment of formal links with NORMAN, EU-ESBs need to make a step forward in the creation of a network among ESBs. The final report will be available early 2011
Workshop on "Enginnered nanoparticles in the environment; analysis, occurrence and impacts". Contact person: Thomas Ternes ternes@bafg.de	The workshop took place on 19-20 October in Koblenz. A brief will be submitted to the NORMAN Bulletin. Speakers's presentations available on the NORMAN website. Report available by the end of the year.
AW-3 – Workshop3 "Improving information systems / Databases" Contact person: Jaroslav Slobodnik slobodnik@ei.sk	Postponed to early 2011
WG-1 - Working group N°1 "Prioritisation of emerging substances" (INERIS)	A first draft of discussion paper for the definition of the prioritisation framework was prepared and discussed in

Name of the activity	Status December 2010
Contact person: valeria.dulio@ineris.fr	the first meeting of the WG in February 2010 in Brussels. Further to the comments received, a second draft of the position paper was prepared and circulated among the WG members for consultation. 2nd WG meeting: 22-23 November, Paris. A first run test of the methodology is under way. This activity will continue in 2011.
WG-2 - Working group N°2 "The value of bioassays and biomarkers in water quality monitoring programmes: strategies for the interpretation of results" (INERIS / RIVM / IVM) Contact person: wilfried.sanchez@ineris.fr	Delay with respect to the planned deadlines, partly due to change in coordination of this WG. In 2010 the coordination of the WG (previously under the responsibility of RIVM) was taken over by INERIS. An inventory of biological test tools and strategies for interpretation of the results, plus bioassays and biomarkers currently available is under preparation and should finalised by June 2011. In 2010 organisation of an intercomparison study on two sites in France in Sept 2010 including fish and invertebrate biomarkers and bioassay in water and sediments (6 laboratories participated in the study). Results will be disseminated and will be the basis for the preparation of a second exercise lead by INERIS on different sites in Europe in 2011.
WG-3 – Working Group on "Effect-directed analysis for hazardous pollutant identification" Contact person: werner.brack@ufz.de	Kick-off meeting of the WG took place in Leipzig on 19-20 October. Preliminary outcomes of the meeting in particular as to the activities that will be carried out by the WG in 2010 – 2011: - Preparation of a position paper on EDA applications in the framework of the current legislation and research needs; - Submission of a ITN project on EDA (deadline Jan 2011); - Preparation of a "Simplified EDA protocol" for implementation in the short term as part of environmental monitoring programmes; - Organisation of a pilot study for demonstration of the applicability of EDA approaches (possible execution in 2012); - Creation of a common mass spectra database to support the identification of unknowns linked to NORMAN EMPOMASS database.
IL-1 – QA/QC activities: "PT on metabolites of pesticides in drinking water" (IWW) Contact person: David Schwesig d.schwesig@iww-online.de	Completed as planned. Final report available on the NORMAN website
IL-2 - QA/QC activities: organisation of interlaboratory study on "Perfluorinated Compounds in Water, Fish and Sludge" (IVM / QUASIMEME) Contact person: Stefan.van.Leeuwen@ivm.vu.nl	Experiment part of the ILS is completed. The report is now finalised and was sent to the participating laboratories.

Name of the activity	Status December 2010
Drafting of a new working document for method validation (future CEN Technical Specification) based on the NORMAN validation framework Contact person: David Schwesig d.schwesig@iww-online.de	New Work Item Proposal based on NORMAN protocol for methods validation was prepared by IWW in July 2010 and is now going to be submitted by France to CEN TC230.
Regular update and maintenance of NORMAN Databases Contact person: Contact person: Jaroslav Slobodnik slobodnik@ei.sk	The NORMAN EMPODAT database has been significantly upgraded being now a host of more than 146,000 occurrence data on 296 substances in 20 European countries. A battery of statistical tools was developed allowing for fast overview of the distribution of substances in the different matrices, countries, and data quality categories. A customised statistics module allows for personalised substance/parameter searches. Automatically updatable "Substance fact sheets" were created for each substance providing also information on the performance of the used analytical methodologies. The information will be used for future prioritisation of substances directly in the database, according to the prioritisation methodology which is currently under development in WG-1. . The list of NORMAN substances was significantly extended (745 substances) in cooperation with WG on Prioritisation and implemented in all database modules. Further, reprogramming and maintenance of EMPOMASS and EMPOMAP modules was carried out during 2010. First datasets of bioassays data were collected in the requested format.

Fraunhofer IME

Use of environmental specimen banks for investigations on emerging pollutants - recent case studies and outlook for future applications

Environmental specimen banks (ESBs) could play an important role in gathering exposure information especially of emerging substances (refer to NORMAN Bulletin 1, p. 2-4, December 2009). Past studies revealed that consumption patterns of chemicals and tissue concentrations in biota are correlated (e.g., for musk fragrances). It could also be proven that concentrations in exposed biota decreased after banning or phasing out compounds of concern (e.g., lead, tributyltin, alkylphenols). Moreover, the use of archived biological samples allows the fast analysis of samples from different years and regions under comparable conditions. Thus results of retrospective monitoring could help to assess the relevance of compounds in question with respect to concentration levels and temporal trends (exposure monitoring).
The following case studies taken from recent publications should demonstrate the potential of the application of ESBs. Two studies are covering perfluorinated compounds (PFC) while the third example deals with a brominated flame retardant, hexabromocyclododecane (HBCD). One PFC, perfluorooctane sulfonic acid (PFOS) is already covered by the Stockholm Convention on Persistent Organic Pollutants (POPs; http://chm.pops.int/), while HBCD is currently under review.

Case study 1: Analysis of perfluorooctane sulfonic acid (PFOS) in historical eel samples from the Rhine

Although PFC were used for many applications since the 1950s only in recent years their environmental relevance became apparent. Meanwhile the persistent, bioaccumulative and toxic potential of several PFCs has been proven.
Kwadijk et al. (2010) investigated the occurrence of PFC including perfluorooctane sulfonic acid (PFOS) in eel (*Anguilla anguilla*) and other matrices collected from several locations in The Netherlands. Eel was caught using electric fishing. For each site, fillets from 30 individuals with a length of 30-45 cm were randomly selected and homogenized using a stainless steel blender. Samples were then stored at -20 °C until analysis. For the locations Lobith at the river Rhine and two inland lakes (Hollands Diep and Haringvliet East) historical eel tissue samples were available which were collected from 1978 onward for monitoring purposes (only since 1990 for Haringvliet East). Thus time series spanning up to 30 years could now be measured for PFOS levels for these locations. PFOS levels were quite comparable for eel from the Rhine site (27 - 120 ng/g wet weight, ww) and from Haringvliet East (43 - 93 ng/g ww), but lower for eel from the third site (Hollands Diep: 5.9 - 42 ng/g ww). The authors found a statistically significant upward trend in PFOS concentration at Lobith between 1978 and 1991 ($p < 0.005$; $n = 14$). Highest values were detected in the samples from 1988 and 1991. From 1999 on, a decreasing trend of PFOS levels in eel was detected ($p < 0.0005$; $n = 8$). The current levels of the Rhine eel are quite comparable to those from the beginning of the time series in 1978. In contrast to the first period for the Rhine site, no significant trend was detected in eel from Hollands Diep for the period 1979 - 1994. However, a downward trend comparable to the Rhine site was also observed for nearly the complete time series available for the site Haringvliet East (period 1991 - 2006; $p < 0.03$; $n = 14$). Summarizing, the retrospective analysis revealed that PFOS concentrations increased by factors of 2 - 4 until the mid-1990s, followed by a decrease to the levels at the start of the time series. The authors comment that this concentration course now detected for The Netherlands was also reported for PFC in biota from other industrialized countries. However, interestingly the declining trend started before the PFOS phase-out of 3M became fully effective (2002).

If a correlation to consumption patterns is assumed, possible explanations for the declining trend could be that emissions were reduced more efficiently or industry started to substitute PFOS and its precursor compounds even before the production stop became effective. Paul et al. (2009) reported that the global production was highest and quite constant in the period 1990 - 2002 (based on production of the precursor compound POSF), and that it dropped by about 80 % after 3M's production stop became effective in 2002.

Case study 2: Levels of perfluorinated compounds (PFC) in herring gull eggs from German coastal waters

A retrospective monitoring was performed to assess concentration trends of PFCs in marine biota from the German Environmental Specimen Bank (ESB). Archived annual pool samples of eggs of herring gull (*Larus argentatus*) covering the periods 1988 - 2008 (North Sea; islands Trischen and Mellum) and 1991 - 2008 (Baltic Sea; island Heuwiese) were analyzed for a set of PFCs. The sampling sites are located in National Parks. However, the island Mellum is influenced by the estuary of the river Weser, and the island Trischen by the estuary of the river Elbe. The Baltic Sea island Heuwiese, on the other hand, is in a quite pristine region with negligible anthropogenic impacts. The water exchange with the open Baltic Sea is also reduced by surrounding islands. Correspondingly, North Sea eggs had higher PFC concentrations than Baltic Sea eggs in most years. Compounds detected with highest levels were perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA). The median values for PFOS in herring gull eggs were about 70 ng/g ww and 80 ng/g ww for the North Sea sites Mellum and Trischen, respectively, and 60 ng/g ww for the Baltic Sea site. However, while the PFOS time series for North Sea eggs showed varying concentrations with highest values between about 1993 and 2002, Baltic Sea eggs revealed a significant increasing trend from about 20 ng/g ww in 1991 to about 160 ng ww in 2008. Thus concentration differences for PFOS between North Sea and Baltic Sea eggs diminished in recent years. Eggs from Heuwiese had lower PFOA levels (mostly in the range of the limit of quantification of 0.5 ng/g wet weight, ww) than North Sea eggs which showed especially in some years quite high concentrations (median PFOA values: about 10 ng/g ww; maximum concentrations up to 120 ng/g ww). Beside PFOS and PFOA also the C7-, C10-, and C11-perfluorinated acids and the C6- and C7-sulfonic acids were found at low concentrations in the herring gull eggs. The authors conclude that the voluntary cease in production of PFOS and respective precursor substances declared by 3M by 2002 is not mirrored so far in continuously decreasing PFOS concentrations in wildlife. It seems that the situation may be different at specific sites as the increasing PFOS levels in the herring gull eggs sampled from the Baltic Sea island Heuwiese reveal.

Generally, a delay of several years can be expected between concentrations courses in freshwater and marine biota (compare PFC maximum for PFC in freshwater fish in the study by Kwadijk et al. 2010).

Case study 3: Analysis of Hexabromocyclododecane (HBCD) in herring gull egg samples from German coastal waters

Hexabromocyclododecane (HBCD) is a brominated flame retardant applied mainly in extruded and expanded polystyrene foams which are used as thermal insulation in the building industry. In 2001, the estimated annual HBCD demand in Europe was 9500 tons (no current usage data available). During recent years, emissions control programs have been implemented by the HBCD industry in order to reduce potential environmental burdens from production and processing.

The German Federal Environment Agency initiated a retrospective monitoring study for HBCD with archived samples from the German ESB. The aim was to determine the course of HBCD burden in the marine environment over a 20-year period. For this purpose pooled

annual samples of whole eggs of herring gulls (*Larus argentatus*) were applied. Eggs had been collected between 1988 and 2008 from three islands in the North and Baltic Seas. They were analyzed for three diastereomers of HBCD (alpha, beta- and gamma-HBCD). Analyses were performed by HPLC-MS/MS analysis with electrospray negative ionization after enantiomer-specific separation on a chiral column. As in most biomonitoring studies, alpha-HBCD diastereomers were pre-dominant in all eggs investigated although the technical product consists mainly of gamma-HBCD. For all eggs so called enantiomer fractions (EF) for alpha-HBCD showed a significant deviation from the racemic mixture (EF 0.34 - 0.48 instead of 0.5 for the racemic mixture of both enantiomers). For eggs from the Baltic Sea island Heuwiese the EF values were higher as compared to those for eggs from both North Sea sites. The determined contents of total HBCD (sum of all three diastereomers) were in the range 13.8 - 74.8 ng/g lipid weight (lw) and 4.17 - 107 ng/g lw for eggs from the two North Sea islands and between 25.1 and 98.7 ng/g lw for the eggs from the Baltic Sea island. At all sites an increase of HBCD levels was observed until about 2000. Afterwards, levels decreased significantly (e.g., by about 60 percent for the gull eggs from the Baltic Sea site). For the North Sea site Trischen (influenced by the Elbe estuary) HBCD concentrations of eggs in 2008 were in the same range as in the period 1988 - 1994. The corresponding decrease at the site Mellum in the western part of the North Sea was delayed. Here HBCD egg burdens decreased not until 2008 to levels of about 50 % of the peak concentration measured in the year 2000.
The observed declining HBCD burdens may be regarded as a result of the implemented emission control measures for HBCD production plants or of a reduced use of this flame retardant in recent years.

Outlook

The presented studies are examples how ESBs can contribute exposure data for the risk assessment of emerging substances (e.g. for the assessment under REACh or the Stockholm Convention on POPs). An additional impetus to use ESB data for this purpose may come from the further implementation of the Global Monitoring Plan under the Stockholm Convention. In the revision of the Guidance for a Global Monitoring Program (current version: UNEP 2004) specimen banking will be covered more detailed in a separate chapter (based on Decision SC-4/31 of the Conference of the Parties; UNEP 2010). Even in the current version of the UNEP Guidance it is recommended to store the remaining homogenized tissue samples after analysis to permit retrospective analyses for the later determination of environmental trends and other purposes. Although environmental specimen banks are currently established mainly in developed countries, in future also developing countries may use ESBs as monitoring tools. A symposium on this topic was hold at Ehime University in Matsuyama (Japan) in December 2009. The symposium proceedings with selected papers from the meeting are available online (Isobe et al. 2010).
The potential use of ESBs for the risk management of chemicals in Europe was topic of a recent workshop. In collaboration with NORMAN the German Environmental Agency organized a first Conference on European Environmental Specimen Banks which was held in Berlin in June 2010. About 70 participants from European ESBs, EU institutions of chemical safety management, EU Member State government bodies and other interested parties joined the meeting. The scientific programme of the workshop included presentations on the EU ESB programmes from different views (geographic: north, central and south Europe; ecosystems: marine, limnetic, terrestrial). Further contributions reviewed different aspects of European ESBs in the context of chemical safety management. Results from studies of emerging substances were also presented as posters. Finally, the potential for harmonisation between ESBs was explored in two discussion groups. These sessions covered the questions ‘What chemical?’ and ‘What specimen?’. The final discussion also covered the

possible cooperation of NORMAN with ESBs. Most participants agreed that the retrospective analysis of chemicals in archived samples can give important information on the exposure of wildlife to potential emerging substances. These data may also be used to identify a compound as emerging substance (e.g., if environmental concentrations increase). For broader usage of such data it would be helpful to add results from such studies to the NORMAN EMPODAT database. On the other hand, NORMAN could give input to ESBs on compounds relevant for monitoring. For example, the results of the NORMAN activity on prioritisation of emerging substances will be helpful for ESBs to identify new target compounds. The participants recommended that a proposal on future cooperation should be elaborated in a working group. A detailed report of the Conference on European ESBs will soon be available on the NORMAN website.

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

Passive sampling of emerging pollutants in the aquatic environment: state of the art and perspectives
Position Paper

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This document has been written as a follow-up to the expert group meeting organised by the NORMAN association on 27th May 2009 in Prague. It reflects the position of the NORMAN association experts and invited speakers on the topic of passive sampling and its application in the monitoring of emerging pollutants in aquatic environment.

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Executive Summary

Passive samplers represent an innovative monitoring tool for the time-integrated measurement of bioavailable contaminants in water and sediment. Passive sampling technology is proving to be a reliable, robust and cost-effective tool that could be used in monitoring programmes across Europe. These devices are now being considered as a part of an emerging strategy for monitoring a range of priority and emerging pollutants.

Passive sampling is based on the deployment *in-situ*, or use in the laboratory, of non-mechanical devices of simple construction capable of accumulating contaminants dissolved in water or sediment pore water. Such accumulation occurs via diffusion, typically over periods of days to weeks. Contaminants accumulated in exposed samplers are subsequently extracted and their concentration levels measured, allowing the quantification of time-weighted average (TWA) concentrations in water or equilibrium pore water concentrations in sediment. These devices can be deployed in most aquatic conditions (fresh and saline) and associated water treatment facilities, thus making them ideal for monitoring across the entire water cycle and even in remote areas with minimal infrastructure. Passive sampling can also be employed in batch sediment extractions to provide estimates of contaminant concentrations in pore water or assessment of bioavailable concentrations of contaminants in sediment.

In 2009, the NORMAN association organised a meeting of experts in the field of passive sampling. As a result of this meeting a position paper was produced, which reflects the view of the experts on the topic of passive sampling and its application in the monitoring of emerging pollutants in the aquatic environment and indicates future research and development needs in this area.

The position paper discusses functional principles of passive samplers and problems associated with the effects of environmental variables (temperature, water turbulence and sampler fouling) on their performance. Further, it lists the established or expected/potential performance of passive samplers for monitoring of the most discussed groups of emerging substances (such as cyanobacterial toxins, antifouling agents, brominated flame retardants, endocrine disrupting compounds, fluorinated surfactants, organosiloxanes, pharmaceuticals, polar pesticides, sunscreen filters etc.) and availability of calibration data that enable estimation of TWA concentrations. The document also shows the applicability of the passive sampling concept in risk-oriented monitoring of emerging substances in sediments and in determination of the bioaccumulative exposure of organisms. The great potential of this technology in combination with toxicological assays to determine the biological relevance of mixtures of toxicants with specific modes of action, and present at low concentrations, is also demonstrated.

If passive sampling is to become accepted and used in a regulatory context for monitoring water quality across Europe, then there is a need for the development of improved validation methods and setting-up of the appropriate quality control and quality assurance schemes for the technology. Successful demonstration of the performance of passive samplers alongside conventional sampling schemes, and inter-laboratory studies that demonstrate reproducibility of data produced by different designs of passive samplers, are urgently needed to facilitate the acceptance of passive sampling in routine regulatory monitoring programmes in the future.

I. Introduction

Improvements in analytical methods, primarily the introduction of more sensitive and specific mass spectrometry techniques, have increased awareness of the presence of emerging substances from many sources at trace levels (low ng L^{-1}) in the aquatic environment [1]. These substances include industrial chemicals and products, consumer products such as pharmaceuticals (both prescription and non-prescription drugs) and personal-care products, pesticides, natural bioactive compounds such as cyanotoxins and hormones, and metabolites of all these chemicals. Previous research focused mainly on non-polar and mono-polar compounds such as PCBs (polychlorinated biphenyls), PAHs (polycyclic aromatic hydrocarbons), chlorinated solvents, or chlorinated pesticides such as DDT or lindane. More recently attention has turned to the modern polyfunctional and often ionisable pesticides, biocides, drugs and personal care products. Currently there is a lack of knowledge regarding the fate and effects of many chemicals released into the environment either as products or accidentally. Although most of these compounds are present in the environment at low concentrations, many of them raise considerable toxicological concerns, particularly when present as components of complex mixtures [2].

Exposure assessment in the aquatic environment is based primarily on analytical measurements of chemical compounds in samples from various environmental compartments – water, sediments, soils, air – as well as from organisms from different trophic levels within a food chain [2]. Understanding and quantification of processes which emerging compounds can undergo in the environment, such as adsorption and partitioning between solid and aqueous phases, formation of complexes in solution as well as abiotic and biological transformation, are also urgently required. Both effective sampling and analytical methods are therefore essential to obtain reliable data on the concentrations, speciation and fate of these compounds in the aquatic environment.

While a lot of effort has been put into research and development of increasingly sensitive instrumental analytical methods for the measurement of emerging substances in various matrices in the aquatic environment, less interest has been paid to the development of suitable sampling techniques. Until recently, sampling methods for emerging substances were the same as those routinely used for monitoring priority pollutants in the aquatic environment. These are based on periodic collection of spot or grab bottle samples of water. The subsequent laboratory analysis of the sample provides a snapshot of the levels of pollutants at the time of sampling. There are, however, drawbacks to this approach in environments where contaminant concentrations vary over time, and where episodic pollution events such as spills or storm water runoff can easily be missed. This problem is particularly relevant to polar (hydrophilic) emerging substances. The residence times of these compounds in aquatic systems are generally lower than those of hydrophobic organic compounds. However, the presence of these more hydrophilic compounds in these systems (wastewater, surface water) may occur as a result of relatively episodic events (frequent, short duration and high concentration peaks). Thus, there is an urgent need for the development of suitable sampling and analytical methods capable of detecting and identifying contaminants in an integrative manner for an adequate assessment of the environmental risk posed by emerging substances.

One solution to this problem is to increase the frequency of sampling or to install automatic sampling systems that can collect numerous water samples over a given period. For example, the pooling of samples collected hourly into a 24 h composite sample, or continuous on-line monitoring for specific sets of compounds can be used to provide representative data. These methods are both costly and in many cases impractical, since a secure site and additional infrastructure or personnel are required to protect, operate and maintain the mechanical automatic sampling devices. Over the last decade alternative

methods for monitoring water quality have been sought to overcome some of the difficulties. A developing alternative strategy to these traditional sampling methods is to employ passive sampling devices that can be deployed over extended time periods (days to weeks) to provide time-weighted average (TWA) concentrations [3,4].

Passive sampling is a relatively easily applied sampling technique, based on the use of non-mechanical samplers of simple construction, often consisting of a single polymeric sorbing phase. In most cases these samplers do not require any external energy source to function. These devices can be deployed in most aquatic conditions (fresh and saline) and associated water treatment facilities, thus making them ideal for monitoring across the entire water cycle and even in remote areas with minimal infrastructure. Furthermore, these samplers assist with the sensitivity of subsequent analytical methods as they pre-concentrate and preserve chemicals sampled within these polymeric receiving phases. This enables improved sensitivity for a greater range of compounds and improved stability of chemicals within the sample without additional treatment (e.g. pH adjustment) unlike more traditional grab sampling techniques. In some cases, the use of passive samplers can also help to reduce or even eliminate the use of excessive volumes of toxic extraction solvents.

Passive samplers have been used for environmental monitoring since the 1970s, when the first samplers for the assessment of ambient air quality and workplace exposures to potentially hazardous air pollutants were developed and applied. To date, a number of sampler designs are commercially available and there are now established standards and official methods (e.g. ASTM, EPA, NIOSH, CEN and ISO protocols) for the use of these devices, which form part of legal frameworks. More recently, worldwide monitoring networks have been set up using passive air samplers to monitor persistent organic pollutants on a global scale [5,6].

In contrast, the application of passive samplers in monitoring water quality is some way behind the situation for air, and the technologies available for monitoring soils and sediments are even further from recognition. Since the introduction of the semi-permeable membrane device (SPMD), designed at USGS by Huckins et al. [7] in the early 1990s, passive samplers have become widely used for monitoring persistent organic pollutants and other non-polar organic compounds in the aquatic environment. Nearly ten years later, the passive sampling technology suitable for sampling hydrophilic organic compounds including modern pesticides, pharmaceuticals and personal care products has been reported in the work of Alvarez (POCIS sampler) [8] and Kingston et al. (Chemcatcher concept) [9]. Since then, the number of publications on development, performance optimisation and field application of passive samplers for emerging substances has grown rapidly.

A number of recent reviews have been published describing the design, calibration procedures, figures of merit and applications of the different devices for monitoring the aquatic environment [3,10,11,12]. Booij summarised in a report for the ICES Marine Chemistry Working Group the established or expected/potential performance of various passive samplers of compounds that are listed under WFD and other directives or conventions [13]. Recently, several review papers addressing passive sampling of emerging pollutants have been published [14,15]. In addition, a book describing the SPMD [16] and a general text describing many passive sampling techniques for environmental monitoring [17] are available.

II. Concept of passive sampling

Passive sampling is based on the deployment *in-situ* or use in the laboratory of devices capable of accumulating contaminants dissolved in water or sediment pore water. Such accumulation occurs via diffusion, typically over periods of days to weeks. Contaminants accumulated in exposed samplers are subsequently extracted and their concentration levels measured, allowing the quantification of TWA concentrations in water or equilibrium pore water concentrations in sediment. It enables temporally-representative sampling or sampling of the truly dissolved concentration of contaminants in water or aquatic sediments. Even for those chemicals that are present at extremely low concentrations in the dissolved phase and are primarily accumulated in biota via the dietary uptake, passive samplers generally extract sufficient amounts of residues for analysis. Passive sampling can also be employed in batch sediment extractions under laboratory conditions to provide estimates of contaminant concentrations in pore water or assessment of bioavailable fraction of contaminant in sediment [18,19].
Passive sampling is based on the diffusion of analyte molecules from the sampled environmental medium (water or sediment pore water) to a receiving phase in the sampling device. The diffusion occurs as a result of a difference between chemical potentials of the analyte in the two media (Figure 1). The net flow of analyte molecules from one medium to the other continues until equilibrium is established in the system, or until the sampling is stopped. The mass of chemical sorbed in the sampler following a given exposure period is initially proportional to the TWA concentration in the environmental medium to which the sampler was exposed (integrative samplers) and subsequently once equilibrium is achieved to the concentration in the environmental medium with which the device is at thermodynamic equilibrium (equilibrium samplers). The main advantage of kinetic or **integrative sampling** is that even contaminants from episodic events commonly not detected with spot sampling are collected by the sampler. This permits the measurement of time weighted average (TWA) contaminant concentrations over extended time periods using a single sample (extract from the passive sampler). This gives a more representative picture of contaminant levels than that obtained with the use of infrequent spot samples. To achieve **equilibrium sampling**, for a given sampler the sampling period needs to be sufficiently long to establish thermodynamic equilibrium between the water and the sorbent phase of the sampler. To achieve equilibrium within reasonable sampling periods samplers of relatively low capacity for the analytes of interest or with modified surface area to volume ratios may be required [20]. Application of the sampler-water distribution coefficient then enables the calculation of the analyte concentration in the sampled medium.

Analytes are accumulated in a suitable sorbent material within the passive sampler, known as a receiving phase. This can be a solvent, chemical reagent, absorbent polymer or a porous adsorbent material. Whereas most samplers of hydrophobic compounds are based on diffusion and absorption in non-porous polymers, most samplers of polar organic compounds (i.e. majority of emerging compounds) and metals are based on diffusion through porous membranes and sorption to selective **adsorbent materials**. The difference in selection of materials applied in sampler construction results in different sorption phenomena that define the driving force of the sampling process (Figure 2). In general, accumulation of hydrophilic organic compounds to porous adsorbents is more complex than absorption and dissolution of hydrophobic chemicals in non-porous polymers (polyethylene or polydimethylsiloxane). This is because adsorption distribution coefficients (unlike partition coefficients in solvents and sub-cooled liquid polymers) described by sorption isotherms can be concentration-dependent. Competitive adsorption of analytes and possible interferences are also possible. The polar organic compounds are mainly retained by specific interactions with functional groups at the surface of the adsorbent. Although the use of adsorptive polymers with specific interactions is preferred in certain cases, the risk always exists of saturating the fixed number of superficial bonding sites when these polymers are applied to a

complex sample matrix. Finally, many compounds may speciate into multiple forms depending on their pK_a parameters and the pH of the sampled medium. Where a sorbent phase only accumulates a single form of a specific compound such as the neutral species, these phenomena will also influence the observed uptake. Sampling description is thereby complicated by the presence of several species with different diffusion and sorption properties that may dynamically change during the sampling process, depending on a milieu of properties of both the sampled medium, the receiving phase and of the individual compound.

Recently, a novel absorptive equilibirum passive sampler for polar organic compounds has been reported by Magnér et al. [21]. This is based on a plastic material, polyethylene-co-vinyl acetate-co-carbon monoxide (PEVAC). This receiving phase operates as a homogenous, non-porous liquid in which the analytes are retained by dissolution rather than by specific interactions with the surface of the polymer. The PEVAC material showed enhanced sorption of several polar pesticides and pharmaceuticals compared to the silicone material. Identification of suitable absorbent polymer materials with high retention capacity of polar compounds presents a promising approach in future development of passive sampling technology and may replace currently used complex adsorption-based samplers for which data conversion into aqueous concentrations is often difficult.

For devices that operate in the kinetic or integrative mode, the sampling rate is given by the product of the overall analyte mass transfer coefficient and the active surface area of the sampler (R_S = k_o A). Sampling rate may be interpreted as the volume of water cleared of analyte per unit of exposure time (e.g. mL h^{-1} or L day^{-1}) by the device and is independent of the analyte concentration in the sampled medium. It can be affected and modulated by the analyte diffusion and partition properties in the media along the diffusional path, and is determined in laboratory calibration studies.

Often the main barrier to mass transfer is the water boundary layer (WBL) located at the external surface of the sampler. In such a case the sampling rate is significantly affected by environmental variables such as water temperature, turbulence and biofouling. If laboratory calibration data is to be used for calculation of TWA concentrations, the effect of these variables has to be either controlled or quantified. For samplers used to measure concentrations of non-polar organic analytes, one method of overcoming some of the problems associated with the impact of fluctuating *in situ* environmental conditions (temperature and turbulence) on sampling rate is the use of performance reference compounds (PRCs) [22]. These are analytically non-interfering compounds (typically deuterium or ^{13}C labelled analogues of the compounds to be measured) and are loaded onto the receiving phase of the sampler prior to deployment. These PRCs are eliminated from the receiving phase during the deployment period. Where the kinetics of uptake and elimination are isotropic, that is the rate constants for the elimination of the PRCs are affected by environmental variables in a manner similar to the uptake rates of pollutants, these elimination rate constants can be used to correct the sampling rates of pollutants in field deployments. There is also some evidence that the elimination rate constants of PRCs can be used to compensate for the impact of biofouling on uptake; however, more work is needed in this area [23,24,25].

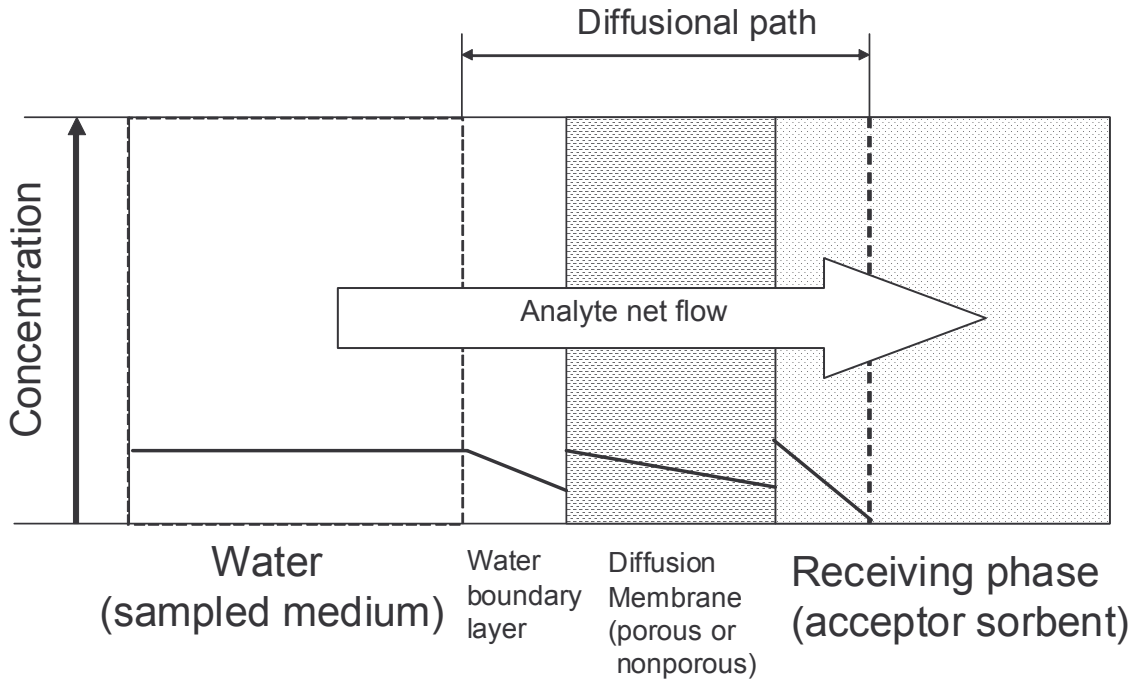

Figure1. *Functional principle of a passive sampling device, showing the concentration profile of a compound during diffusion and accumulation from bulk of the sampled medium to the sorbent (receiving phase) through a permeable (porous or non-porous) membrane. High affinity to the sorbent inside the sampler drives the diffusion of analyte molecules from the sampled medium into the sampler until the thermodynamic equilibrium is established. (adapted from Mills et al. [14]).*

The correction for the effect of environmental variables in samplers where the sequestration process depends on adsorption of the analyte presents one of the major challenges in the development of the technology. In many cases, uptake of analytes (polar organic compounds and metals) into these devices is WBL-controlled and thus sensitive to changes in flow turbulence. The PRC concept cannot, however, be generally used to correct calibration data for changes in field conditions because of the complex character of the desorption kinetics that may not be isotropic with the adsorption [26]. Mazzella et al. [27] and Budzinski et al. [28] have recently demonstrated isotropic exchange in certain exposure scenarios, but this concept still remains to be fully explored. In cases where PRC loss is not isotropic with uptake of target analytes, an alternative *in situ* calibration approach is to load PRCs into co-deployed sampling phases from which elimination is observed and which may subsequently be related to uptake. An *in situ* calibration technique, using PRC-loaded absorbent polydimethylsiloxane (PDMS) disks deployed alongside the Empore^{TM} adsorbent disk samplers as a surrogate calibration phase, has been proposed by Shaw et al. [26] and shows promise for future applications. Alternatively a passive flow monitor based on dissolution gypsum has been developed which may predict the sampling rate in response to *in situ* flow conditions [29]. Differences in mass transfer in absorption- and adsorption-based samplers are illustrated in Figure 3.

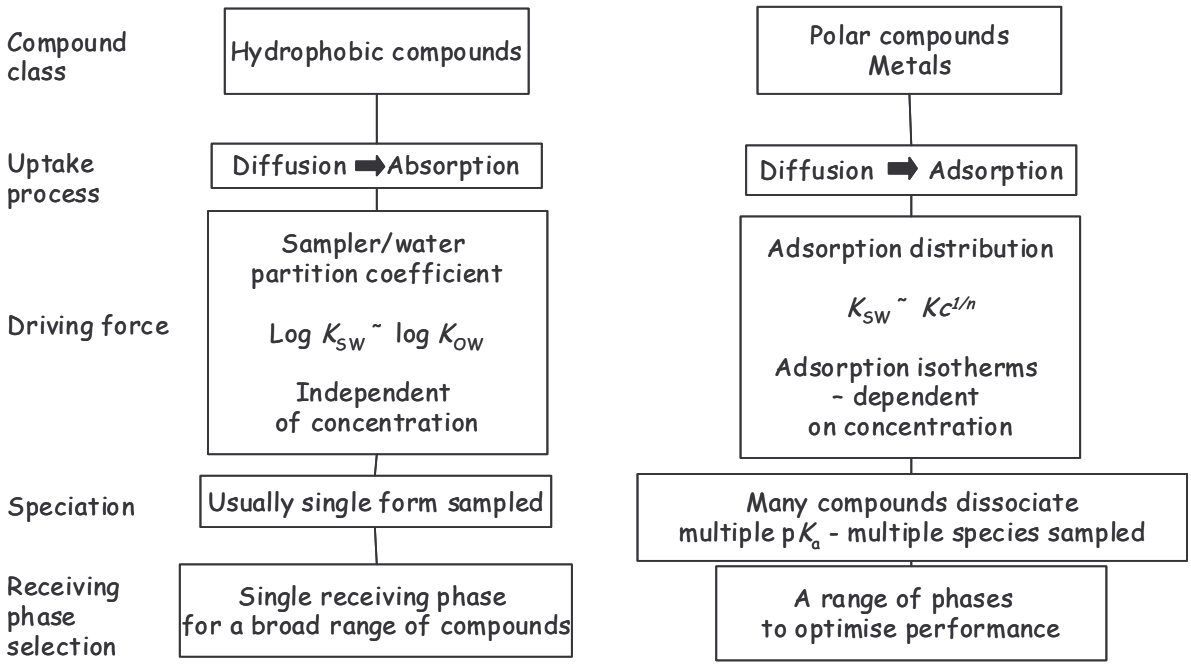

Figure 2. *Differences in passive sampling in (left) absorption- and (right) adsorption- based samplers. The majority of emerging substances are polar or semi-hydrophobic. Thus, the use of adsorbent-based samplers presents the most suitable sampling approach for these compounds.*

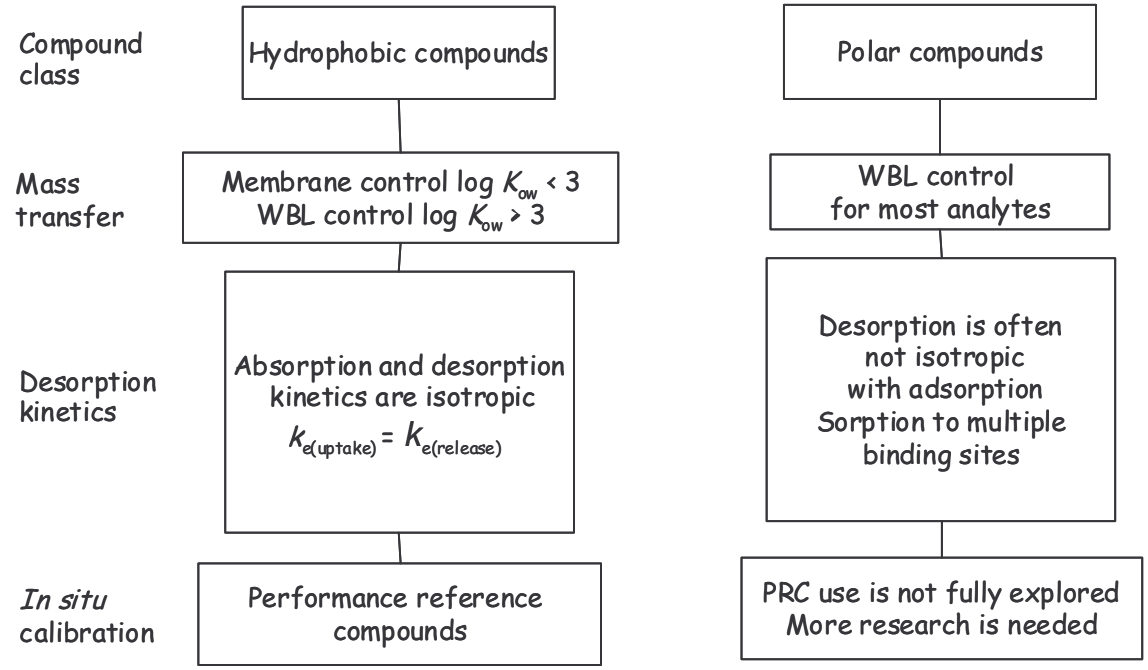

Figure 3. *Differences in mass transfer in (left) absorption- and (right) adsorption-based samplers*

III. Applications in aquatic monitoring of emerging compounds

A detailed description of sampler designs available for monitoring emerging polar organic compounds has recently been published by Söderström et al. [15]. Applications of passive samplers for some important groups of emerging substances are discussed in the following section. Table 1 lists the most discussed emerging pollutants in the aquatic environment, the established or expected/potential performance of passive samplers of these compounds and availability of calibration data that enable calculation of TWA concentrations.

III.1. Algal toxins

Algal toxins are a group of natural products which may occur in fresh, brackish and marine waters. However, possibly because of anthropogenic eutrophication and global climate changes, and subsequent blooms of potentially toxin-producing cyanobacteria, the incidence of contamination of water bodies with these compounds seems to have increased over recent years[30]. Algal toxins are structurally, functionally and phylogenetically diverse group of compounds with variable chemical and toxicological characteristics. These pollutants may cause serious health problems as documented by cases of human and animal intoxications as well as by the results of laboratory studies [30]. Based on the toxicity data, the World Health Organization (WHO) suggested the tolerable daily intake (TDI) value for microcystin-LR (a widespread hepatotoxin produced by cyanobacteria) is 0.04 μg kg^{-1} body weight, and corresponding safety guideline value 1.0 μg L^{-1} is recommended for drinking waters. There are no obligatory guidelines for other cyanobacterial and algal toxins. However the presence of these compounds in water is highly undesirable and tools for proper monitoring are necessary.

Owing to the quite high spatial and temporal variability of the occurrence and subsequent development of algal blooms, and hence potentially of co-occurring toxin production, passive samplers may prove to be a useful tool for monitoring of natural toxins. The first use of integrative passive sampling for algal toxins was described in the work of MacKenzie et al. They developed a passive sampler (SPATT bag) based on synthetic resin enclosed in porous sachets and used it for monitoring a group of marine toxins known as paralytic shellfish poisons [31]. The device was designed as an early warning of developing cyanobacterial blooms to protect consumers and prevent the harvesting of contaminated seafood products. This work was continued by other authors. Fux et al. evaluated various sorbents in the SPATT system [32]. Rundberget et al. redesigned the device and used it for monitoring of various natural toxins on the southern coast of Norway [33]. Shea et al. described the development of a monophasic device for monitoring of brevetoxins, highly toxic compounds produce during red tide events. Devices constructed of polydimethylsiloxane sheets were successfully used for integrative sampling [34]. Kohoutek et al. employed POCIS for the monitoring of microcystins in freshwater. The study was focused on evaluation of various configurations of the sampling device [35], and described calibration procedures and monitoring of the toxins under conditions of natural algal blooms. Concentrations of toxins obtained by passive sampling correlated well with the overall concentration of dissolved microcystins, demonstrating the suitability of passive sampling for the determination of TWA concentrations [35].

III.2.Antifouling compounds – organotins

Due to their bioaccumulation potential and toxicity, organo-metallic substances are considered as emerging pollutants of concern. In some cases organo-metallic compounds (e.g. some organic forms of tin) are more toxic than inorganic complexes or free forms of the parent metal. Passive sampling devices have been used to measure a number of organo-metallic species, including those of lead, mercury and tin.

Følsvik et al. [36,37] reported the use of SPMDs for monitoring organotin compounds using SPMDs. Both dibutyl- and tributyltin were accumulated by the devices, but no accumulation of monobutyltin was observed during several weeks of SPMD exposure in a Norwegian fjord. Using this method, it was possible to identify concentration gradients of organotin compounds at the sampling site. Later, a variant of the Chemcatcher® sampler was developed and calibrated for the measurement of the TWA concentration of organotin compounds. [38,39]. Using gas chromatography (GC) with either ICP-MS or flame photometric detection, favourable limits of quantification for the device (14-day deployment) for the different organotin compounds in water were in the range of 0.8–25 ng L^{-1}, and once accumulated in the receiving phase the compounds were stable over prolonged periods [39].

III.3. Brominated flame retardants

Polybrominated diphenyl ethers (PBDEs) are widely used as flame retardants in products such as furniture, textiles, plastics, paints and electronic appliances. Due to their extreme hydrophobicity (log K_{ow} values 4–10), these compounds are dissolved in the aqueous phase at extremely low (sub-ppb) concentrations. Nevertheless, because of their possible environmental risks due to their persistence and bioaccumulation, the inclusion of certain PBDE congeners in monitoring programmes is justified. Booij et al. [40] used SPMDs for sampling and *in situ* pre-concentration of PBDEs from water at several sampling stations in the Scheldt estuary and the North Sea along the Dutch coast. The application of integrative sampling enabled the back-calculation of extremely low concentrations (in range 0.1-5 pg L^{-1}) of PBDE congeners in water from SPMD-accumulated amounts. Rayne and Ikonomou [41] employed SPMDs for sampling PBDEs in water in the Fraser River near Vancouver, Canada. The concentrations of PBDE found in SPMDs, their physicochemical properties, and their SPMD uptake parameters were used in an aquatic transport model to reconstruct the patterns of PBDE in pollution sources. The reconstructed patterns of accumulation in SPMDs closely approximated the composition of known technical mixtures of PBDEs.

III.4. Endocrine disrupting compounds

Over the last two decades the presence in the environment of endocrine disrupting compounds, such as those which mimic or block the action of endogenous hormones on steroid (oestrogen and androgen) receptors and subsequently alter the normal functioning of the endocrine system in wildlife and humans, has emerged as a major environmental issue [42,43]. Natural oestrogens (such as oestrone, E1, and 17-β oestradiol, E2) and synthetic oestrogens (e.g. 17-α-ethinyloestradiol, EE2, the active component of oral contraceptives) are very powerful endocrine disruptors. They derive mainly from excreta of humans and livestock [44]. Anthropogenic industrial chemicals such as nonylphenol (NP), bisphenol A (BPA) and phtalates are, however also known to influence the hormonal system of aquatic organisms. Wastewater treatment plants are important sources of pollution, since many endocrine disrupting compounds are not fully removed by the treatment processes. Several studies have demonstrated applicability of passive samplers for integrative sampling of these compounds during exposure periods up to several weeks [126,128,129,142]. For many compounds, calibration data that enable quantitative translation of amounts accumulated by the sampler into TWA concentrations are available (Table 1).

III.5. Fluorinated *surfactants*

Fluorinated surfactants (also referred to as poly- and perfluoroalkyl compounds, including perfluoroalkyl carboxylic acids, perfluoroalkyl sulfonates, fluorotelomeric acids, alcohols, etc.) have been used for decades to make stain repellents that are widely applied to fabrics, carpets and paper. They are still used in the manufacture of paints, adhesives, waxes, polishes, metal coatings, electronics and caulks. Due to concern over their persistence and global occurrence in humans and wildlife, two of these fluorinated surfactants,

perfluorooctanoic acid (PFOA) and perfluorooctanesulfonate (PFOS) are within the family of compounds currently attracting the greatest attention as emerging pollutants.[45] It is difficult to identify the origin of pollution by fluorinated surfactants found in wastewater. Although no quantitative studies aimed at monitoring of these substances with passive sampling methods have been reported, Casey et al. [46] reported identification of these compounds in POCIS extracts at levels above associated controls. Recently, Günther et al. described the application of a passive sampler based on active carbon adsorbent [47]. Further research in development of passive samplers suitable for monitoring of these compounds in water is needed.

III.6. Organosiloxanes

Another important class of emerging pollutants is the organosiloxanes. These polymers comprise a backbone of alternating silicon-oxygen units with organic side chains attached to each silicon atom. Over the last 30 years organosiloxanes (silicones), both cyclic and linear forms, have been extensively used in a number of consumer products. These include for example anti-perspirants, and hair and skin care items. It has been estimated that in the USA adult women are exposed to up to 307 mg of organosiloxanes daily [48]. The most commonly used organosiloxane is decamethylcyclopentasiloxane (abbreviated to D_5) although others such as octamethylcyclotetrasiloxane (D_4) and their linear versions can be used in products [48]. These compounds have unusual physico-chemical properties combining high hydrophobicity (e.g. D_5 has a log K_{ow} of 6-8, depending on the literature reference used)) with a high Henry's Law constant and low water solubility [49]. Owing to these properties, most (c. 90%) of the organosiloxanes used in personal protection products are expected to be evaporated to the atmosphere during and after use, with the remainder being discharged into the wastewater. Several organosiloxanes are under assessment for classification as very persistent and very bioaccumulative in the environment. Hence there is an urgent need for monitoring levels of these compounds in different environmental compartments.

Analytically, siloxanes are difficult to measure at trace levels as they are ubiquitous atmospheric environmental contaminants, they are contained in sample vial caps, septa, gas chromatographic columns and they give problems of cross-contamination by laboratory workers using personal care products containing these substances. The maintenance of good procedural blanks and rigorous quality assurance and quality control measures are needed to ensure confidence in any quantitative results. For these reasons reliable environmental monitoring data are sparse. Most analytical methods for both cyclic and linear siloxanes employ headspace gas chromatography/mass spectrometry techniques [49], although large volume direct injection methods using *n*-hexane have also proved to be useful [50]. Sparham et al. [49] have recently analysed D_5 in the Rivers Great Ouse and Nene, UK (concentration range < 10-29 ng L^{-1}) and in treated wastewater (concentration range 31-400 ng L^{-1}). There are few other quantitative studies for D_5 and the other organosiloxanes of environmental concern.

Owing to the low concentrations of organosiloxanes found in the aquatic environment, the use of passive samplers in monitoring campaigns may offer the opportunity to pre-concentrate these compounds prior to instrumental analysis. To date, however, there is little experience of their use with this class of pollutants. Work in this area is being undertaken by researchers (Mills and Greenwood) at the University of Portsmouth, Portsmouth, UK. Preliminary findings show that pre-cleaned thin sheets of low density polyethylene (LDPE) membrane can be effectively used as passive samplers for D_4 and D_5. Work is currently being undertaken to identify PRCs that are suitable for use with the samplers and that are appropriate for the organosiloxanes of major environmental concern. Polydimethylsiloxane (PDMS) sheets cannot be used for this purpose because of background contamination with these smaller siloxane polymers. This makes it difficult to obtain good procedural blanks. Even with extensive washing it is still hard to remove all traces of D_4 and D_5 from these

materials. Other polymers such as polyethylene terephthalate (PET), polyoxymethylene (POM), polytetrafluoroethylene (PTFE) and polycarbonate could potentially be used as either equilibrium or kinetic samplers for these compounds. Because the organosiloxanes are volatile, care must be taken during field deployments not to lose the sequestered analytes during retrieval and transport of samplers and in subsequent laboratory processing. Extensive QA and QC procedures must also be employed. Data from the Portsmouth group on the initial field use of the LDPE samplers for measuring this class of compounds are expected in 2011.

III.7. Pharmaceuticals

Concern over pharmaceutical residues (and personal care products) entering the aquatic environment has been growing since the mid-1990s. Both classes of compounds enter the environment largely as a result of human use, although some come from veterinary use. Several studies have reported the presence of a wide range of these chemicals at ng L^{-1} and sub ng L^{-1} concentrations in various water bodies. A complex mixture of chemicals is often present comprising the parent molecule, associated metabolites and environmental degradation products. Some of these substances may subsequently enter the food chain. The biological effects of pharmaceutical residues on aquatic organisms have been reviewed recently [51].

Effluent from wastewater treatment works is the most common source of pharmaceutical residues in streams and rivers. Some of these chemicals are resistant to treatment. Often the treatment process can break down conjugated drug metabolites to release the parent molecule back into the environment. A range of tertiary treatment processes (e.g. chlorination, ozonation and UV light) can be employed to reduce these levels, but these are expensive to operate continuously at the treatment plant.

Pharmaceuticals have a wide range of physico-chemical properties and concentrations in the aquatic environment and this can make their measurement challenging. Many drugs are either weak acids or bases with pK_a values in the range 4-10. The degree of ionisation will therefore differ in different water bodies that have pH values typically over the range 5.5-8.4 (i.e. from soft to hard fresh water and sea water). Likewise, these substances have a range of log K_{ow} values, but most are considered polar compounds. In some cases the chirality of the drug molecule also needs to be considered. Most compounds of environmental concern can be analysed using LC/MS/MS instrumental methods after extraction and concentration. Typically a wide range of analytes can be separated and quantified at the trace level in a single analysis.

There is a need to obtain reliable data on the fate of pharmaceuticals in the aquatic environment. These data can then be used to develop appropriate models and assist in the risk assessment process. As most discharges of these substances are sporadic and seasonal it is difficult to obtain such information using spot or grab sampling alone. Passive sampling therefore offers a number of opportunities in this area and this has been summarised by Mills et al. [14]. Recently, Söderström et al. [15] reviewed performance characteristics of samplers suitable for monitoring pharmaceuticals and other polar organic pollutants in the aquatic environment.

Two types of passive sampler (polar version of the Chemcatcher and POCIS) have been used for measuring TWA concentrations of pharmaceuticals (and some personal care products). The devices use either an immobilised (Chemcatcher) or loose (POCIS) receiving phase. The Chemcatcher uses a 47 mm Empore™ disk, usually based on divinylbenzene co-polymer chemistry, although ion-exchange (both anion and cation) receiving phases can be used for certain classes of analyte. The POCIS uses a commercially available solid-phase extraction adsorbent (typically c. 200 mg Oasis HLB) that is specially designed to sequester

pharmaceuticals. The same diffusion-limiting membrane (polyethersulphone) is used in both devices. This membrane has a low surface energy and this can limit biofouling of its surface during field use. The uptake rates of the two devices for these more polar analytes are low (typically less than 1 L d^{-1}) compared with the sampling of non-polar compounds by, for example, SPMDs. This can limit their usefulness in some applications, but – unlike non-polar compounds – polar compounds are usually present at higher concentrations, so that sampling rates below 1 L d^{-1} are not an obstacle.

Although a number of laboratory and field studies have been carried out using the POCIS, there is an urgent need for reliable calibration data (Table 1). In many cases different calibration systems (e.g. flow through and static with renewal) [52] and different water turbulences and temperatures have been used and this increased the variation in the data obtained. Much of the field data reported is therefore either qualitative (presence or absence of a pollutant) or semi-quantitative (amount extracted from the receiving phase) rather than using uptake rates to calculate actual water concentrations (ng L^{-1}).

III.8. Polar pesticides

Use of pesticides can have unintended effects on the environment. Over 98% of sprayed insecticides and 95% of herbicides reach a destination other than their target species, including non-target species, air, water, bottom sediments, and food [53]. There are four major routes through which pesticides reach water, including: spray-drift outside of the intended application area, percolation, or leaching, through soil column, with water runoff or concomitant soil erosion, or through accidental or negligent releases [54]. There is an increased demand for environmental monitoring of pesticides because some of them are either already identified as priority substances under the Water Framework Directive (e.g. atrazine, simazine, diuron, isoproturon), or may become priority substances in the future or are relevant as river basin-specific pollutants in selected European regions [55]. An EU "Thematic Strategy on the Sustainable Use of Pesticides" calls for environmental monitoring to be done for other new pesticides in order to verify whether the concentrations in the aquatic environment are "safe" [56].

The first passive sampler reported for this chemical class was the POCIS [57,58]. Typically, for sampling of polar pesticides POCIS remains in the time-integrative mode for exposure periods of up to several weeks. This sampler has found application in integrative sampling of a wide range of polar pesticides and, for many of them, calibration data are available that enable quantitative translation of amounts accumulated by the sampler into TWA concentrations (Table 1).

Polar pesticides are often released at high concentrations into streams and rivers in episodic events. These events usually last only a few hours and for these compounds to be detected by passive samplers, a device with a short response time is required. But passive sampling devices fitted with microporous membranes (e.g. polyethersulphone membrane in POCIS), although ideal for long-term monitoring [59], have a lag-phase of several hours which represents the time necessary for the analytes to diffuse through the membrane to reach the receiving phase [24]. In situations where detection of short pollution events in the monitored water body is required, a long lag-phase of the sampling device presents a potential disadvantage. Shaw and Mueller [60] suggested the use of a device fitted with an Empore™ disk bonded polymeric sorbent as receiving phase (without a diffusion limiting membrane) to reduce the response time and make the sampler more reactive to sudden pollution events [61]. The disadvantage of such devices is a fast equilibration of the sampling devices with the water phase, which restricts to a few days the time over which the samplers operate in time-integrative mode. Comparison of the performance of two different types of Empore™ disks as passive samplers showed that the styrene-divinylbenzene-reverse phase sulfonated (SDB-

RPS) Empore™ disk had better performance as sorbent phase for very polar compounds compared to C18 [62].

III.9. Sunscreen and ultra-violet filters

The analysis of sunscreens/organic ultra-violet (UV) filters in water has increased substantially in the last two years. Due to their use in a variety of personal care products, these compounds can enter the aquatic environment indirectly from showering, washing clothes, via wastewater treatment plants and also directly from recreational activities.

In one of the first studies, Poiger et al. [63] detected four organic UV filters (80-950 ng $SPMD^{-1}$) in SPMDs deployed at Lakes Zurich and Greifensee, Switzerland. SPMD-derived water concentrations were in the range of 1-10 ng L^{-1} and corresponded well with those determined in spot samples of water. In a later study, Balmer et al. [64] investigated the occurrence of four important organic UV filter compounds in water, wastewater and fish from various Swiss lakes. Data from passive sampling using SPMDs supported the presence of these UV filters in lakes and rivers and suggested some potential for accumulation of these compounds in biota. Recently, Fent and Zenker et al. [65,66] demonstrated the applicability of the POCIS sampler for monitoring oestrogenic UV filters in surface water. They found that processing of POCIS samples with subsequent instrumental measurements was much less time consuming than processing of fish samples for environmental monitoring. Hydrophilic compounds like benzophenone-4 which do not accumulate in fish lipids could also easily be determined using the POCIS sampler.

IV. Application in sediment monitoring

Until recently sediment monitoring has relied on the determination of total or normalised contaminant concentrations. This approach, however, does not distinguish between freely dissolved and bound molecules and aims to assess the presence of chemicals rather than their activity and availability [67]. Since many laboratory and field studies have demonstrated that biological effects in benthic organisms are not generally related to the total concentration of contaminants in sediments, alternative and more representative measures of the bioavailable fraction of contaminants in sediments are required [68]. In addition, it has been shown that traditional empirical models tend to overestimate pore water concentrations.

Application of passive sampling to sediment monitoring can be undertaken *in situ* with buried passive samplers or in batch experiments in the laboratory following grab sampling or coring (and sectioning). Passive samplers can be used to:

- Determine freely dissolved contaminant concentrations in pore water;
- Estimate sediment-pore water partition coefficients for contaminants of interest;
- Measure contaminant desorption rates;
- Estimate the fraction of contaminants available for desorption within a relatively short time scale or fraction effectively contributing to the partitioning with pore water and/or biota;
- Measure surface water/pore water activity or fugacity ratios to estimate whether sediments act as a source or sink for contamination in the overlying water;
- Measure the total contaminant amount in sediment that is available for release to the aqueous phase within a given time.

The most commonly used passive sampling approach is based on the principle that the passive sampler is exposed to a sediment sample until a thermodynamic equilibrium between the two phases is established. According to partition theory, the concentration of a compound in the sampler is directly proportional (by the equilibrium partitioning coefficient

between sampler and water) to the freely dissolved concentration of sampled compounds in pore water. Because this concentration is considered to be the driving force for the uptake of the contaminants by aquatic organisms, the bioavailability of a substance can be directly assessed using passive samplers. However, depending on sampler characteristics (e.g. surface area and volume), equilibrium may not be established for the most hydrophobic compounds during exposure and therefore performance reference compounds (such as used for surface water deployments) can be used to quantify sampler-pore water exchange kinetics and dissolved concentrations in such situations [67,69].

In all cases it is absolutely crucial to select an appropriate combination of sampler and sediment volumes in order to avoid significant depletion of the pore water phase. The true freely dissolved concentration of contaminant in pore water can be determined when the sampler's sorption capacity is kept well below that of the sediment sample to avoid depletion during the extraction [20,70,71]. When the sorption capacity of sampler to sediment is kept high, samplers can be used to measure the total contaminant amount in sediment that is available for release to the aqueous phase within a given time. This represents the fraction available to take part in partitioning with sediment organisms. The contaminants remaining in the sediment following such extraction can be considered effectively unavailable [72]. This fraction can also be estimated by repeated/successive extractions of the sediment with an adsorbent phase such as Tenax [73,74]. Such procedures also enable the quantification of contaminant desorption rates.

The concentration difference between the *in situ* deployed samplers from the sediment and those from the overlying water give direct information on the fugacity difference between sediment and water, and on the direction of the contaminant diffusion at the sediment−water interface as well [20,71,75]. This enables identification of sites where remedial treatment of sediment may be appropriate. Other parameters, such as sedimentation rates and the spatial resolution of sediment sampling close to the sediment-water interface, are crucial for such measurements.

For metals, the technique of diffusive gradients in thin films (DGT) provides an important contribution to understanding processes that metals undergo in sediments. DGT provide measurements in sediments that can be reported either as the mean flux of labile metal species to the device during the deployment time, or as the mean interfacial concentration in pore water. For a given device and deployment time, the interfacial concentration can be related directly to the effective concentration of labile metal [76]. This concentration represents the supply of metal to any sink, be it DGT or an organism that comes from both diffusion in solution and release from the solid phase. The primary use of DGT in sediments has been to investigate the distribution of solutes (metals) at high spatial resolution and to interpret the dynamics of the pollutant release from sediment [76]. Pore water concentration profiles with a fine resolution can be obtained by deploying DGT probes vertically in sediment and across the sediment–water interface. Modelling of metal accumulation in DGT with increasing exposure time can allow the estimation of sediment–water partition coefficients for metals of interest.

It is crucial that the risk assessments of contaminants in sediment are as reliable as possible. It is widely accepted that it is the dissolved fraction of pollutants that is available for interaction with biological tissues and that can thereby cause bioaccumulation and/or biological effects. Several studies have shown that biota concentrations, calculated from partition coefficients based on classical equilibrium partition theory, are often orders of magnitude higher than the actual measured concentration in the sediment-dwelling organisms. But, using the freely dissolved concentration derived from passive samplers, the calculated concentrations in biota are in good agreement with the actual measured values [77].The methodology using passive sampling is leading to a much better understanding of how hydrophobic contaminants interact with sediment. This will allow a better estimation of

(bio)availability, as can be validated through comparison with uptake by organisms. Data obtained with passive samplers can be used in risk calculations for sediment-bound contaminants with regard to any need for remedial measures for contaminated sediments and these studies would be an important input with regard to environmental quality standards for contaminants in water proposed in the EU Water Framework Directive.

So far, the methodology of passive sampling in sediment has been tested and successfully validated in studies focused mainly on priority groups of contaminants that cause major environmental problems, such as polycyclic aromatic hydrocarbons or polychlorinated biphenyls. Nevertheless, this concept can also be successfully applied in risk-oriented monitoring of other groups of contaminants in sediments, including emerging substances. Further research is needed to develop novel solid phases with strong affinity to a broad range of compounds that may be found in sediments. These sampler materials should allow an easy extraction and analysis of accumulated substances [68].

V. Application in monitoring of contaminants in biota

Knowledge of dissolved phase chemical concentrations is a critical part of understanding how aqueous exposure levels relate to the concentrations of residues measured in organisms in various trophic levels of aquatic ecosystems. The freely dissolved concentrations of pollutants represent the driving force for bioconcentration. Thus, passive samplers enable *in situ* determination of the bioaccumulative exposure of organisms at the lowest trophic level (filter feeders, e.g. mussels), in nearly all food chains, to hydrophobic organic compounds [78,79]. The estimation of bioaccumulation factors (BAFs) in certain species of concern (e.g. mussels) has also been demonstrated [79,80]. Moreover, since the contribution of dietary uptake for organic compounds with log K_{ow}s < 5.5 is generally very small, organism exposure assessment can be potentially extended to higher trophic levels for less hydrophobic compounds.

Bayen et al. [81] recently reviewed kinetic studies of the uptake of neutral non-polar chemicals from the aqueous phase into organisms (fish, bivalve, crustacean, insect, worm, algae, and protozoan) and passive samplers. They demonstrated that passive samplers are biomimetic when diffusional partitioning processes mediate concentrations in organisms of concern (i.e., when residue accumulation in organism tissues follows equilibrium partitioning theory). Huckins et al. [78] discussed in detail accumulation into the SPMD sampler compared with that into biomonitoring organisms.

The large number of variables, which potentially affects the accumulation of hydrophobic organic compounds in biota, suggests that it is unrealistic to expect any single passive sampler to be biomimetic of all biomonitoring organisms. Also, it is similarly unrealistic to expect that one or two species of biota mimic bioaccumulation in all organisms of concern. Variables affecting pollutant accumulation in passive samplers are limited to the sampler properties, physicochemical properties of the sampled chemical, exposure site conditions (e.g. temperature and turbulence, and exposure scenario factors such as the constancy of chemical concentrations during the exposure period). The ability to generate chemical-specific calibration data and then adjust these values to site-specific conditions (e.g. using PRCs) [22] means that analyte concentrations obtained using passive samplers are directly comparable across sampling sites.

There are some fundamental similarities in the characteristics and processes affecting the accumulation in biota and passive samplers, especially for hydrophobic organic compounds. Diffusion of non-polar compounds through non-porous polymers used in passive sampler construction mimics the diffusion across bio-membranes. Also, partitioning between the

polymers, organism lipids and the exposure water is similar and can be described by the equilibrium partitioning theory. Finally, the surface-to-volume ratio appears to be a critical parameter for the uptake rate of the more hydrophobic chemicals, both for samplers and organisms.

Monitoring by passive samplers has some advantages over the use of biota. Passive samplers can be prepared to a standardised quality characterised by low initial concentration of contaminants, uniform composition, diffusion and sorption properties. In contrast, test organisms often contain background contamination levels and they are naturally variable in composition. As a result, variability of chemical analysis of biota or sediment is in most cases higher than that associated with analysis of passive samplers. Moreover, the simple polymeric matrix composition of passive samplers provides sample extracts that contain much less matrix interference in comparison with extracts from biota and sediment. Samplers can be applied in almost any environment with a broad range of water quality properties and even in very polluted sites where biomonitoring organisms may not survive. In contrast, biomonitoring organisms can be applied only within a certain geographical range and they do not tolerate extreme exposure conditions (e.g. temperature, pH, pollution, and salinity). The uptake process of pollutants in passive samplers is simple (by diffusion and sorption), whereas it is more complex in organisms since it includes bioconcentration, bioaccumulation and metabolism. The complexity of these processes is increased by behavioural, physiological and anatomical characteristics of biomonitoring organisms.

The uptake capacity of polar organic compounds in biomonitoring organisms is in most cases low. Also, these compounds reach steady state within a short period of time, so that biological sampling of polar organic compounds has a very limited applicability [82]. In comparison with biomonitoring organisms, passive samplers demonstrate better retention of contaminants that are absorbed during peak exposure events. The amount of chemicals accumulated in passive samplers in most cases reflects the dissolved, readily bioavailable, concentration in sampled water, whereas the estimation of contaminant bioavailability from total amount found in an organism body may be difficult, owing to the presence of a non-incorporated portion of the pollutant in its intestines.

For metals, the DGT technique measures directly the variables needed to assess water quality. Uptake of trace metals across living membranes is determined by free ion concentrations when membrane transport is slow and by the total concentration of labile species when membrane transport is fast. Deployment of twin DGT devices with different diffusive gel layers can provide an *in situ* measurement of both labile inorganic and total labile species. Free ion activities can be calculated from labile (free and/or kinetically-labile species in solution) inorganic concentrations.

VI. Application in ecotoxicity assessment

Ecotoxicity assessments are an invaluable tool for the evaluation of water quality and in some countries ecotoxicity assessments are compulsory, for example, with direct toxicity assessments of effluents released to the environment [83]. One of the main advantages of ecotoxicity assessments is that they give an integrated picture of the total toxic burden of the complex mix of chemicals that are present in environmental samples. It is often the case that toxic substances cannot be identified and chemical monitoring methods cannot be targeted, but ecotoxicity assessments can still measure the effect of these unknowns in environmental samples. Such samples can be tested, either at the level of organisms (e.g. daphnids or fish embryos [83],[84]), at the level of cells (e.g. fish cell lines) [84] or at the sub-cellular level (e.g. specific binding of chemicals to receptors using reporter gene assays). An example of such a reporter assay comes from research on endocrine disruptors, where cells have been modified to express oestrogen receptors ([85],[86]). The binding of oestrogens – or

oestrogen-like compounds – to the receptors leads to the production of an enzyme which in turn induces a colour change in the medium (or light emission) that can be quantified easily. Commonly, bioassays are applied to whole water samples, extracts of water samples or extracts of organism tissues. Applying the same bioassays to extracts of passive samplers is straightforward and an increasing number of studies have explored this.

VI.1. Passive samplers as mimics for bioconcentration

Combining bioassays with (grab) water samples has the same limitations (or advantages) as compared to combining chemical analyses with water samples. Grab samples give an accurate picture of the total concentration only at a certain point in time. Grab samples again provide data on toxic effects that relate only to the time of sampling. As an alternative, combining ecotoxicity assessments with monitoring of chemicals in biota, for example by analysing extracts of aquatic organisms, is certainly feasible, and produces more representative results than analysing grab samples, but has the same limitations associated with monitoring of contaminants in biota as discussed in the previous section (i.e. section V.). Combining bioassays with passive sampling circumvents the limitations that are associated with grab samples and chemical monitoring in biota. Furthermore, a passive sampler mimics bioconcentration of freely dissolved chemicals over cell walls, membranes or a filter feeding apparatus or gills. Thus, testing passive sampler extracts in bioassays has a high relevance as this reflects exposure scenarios in the aquatic environment.

VI.2. Which passive sampler suits which bioassay?

Numerous biological assays have already been used successfully in combination with passive samplers. Many studies deal with quantification of environmental oestrogens with reporter gene assays in extracts from SPMDs ([87,88]), POCIS ([89],[90],[91],[92],[93],[94]) and Chemcatchers ([95]). An assay that covers compounds such as PAHs and dioxin-like compounds, the EROD assay, has been used with extracts from SPMDs ([87]) and in combination with the Toximeter ([96]). Several studies describe the use of Chemcatchers and POCIS to measure photosystem II (PS-II) inhibitors ([97],[98],[99],[100]). Microtox, a bacterial whole cell assay that is used to measure baseline toxicity, has also been used in combination with POCIS ([94],[100]), Chemcatcher ([98]) and SPMD ([101]) extracts. Muller et al. tested Chemcatchers extracts in the umuC assay, which is used to assess genotoxic effects in response to the presence of DNA-damaging chemicals within the sampled mixture. [98]. Mutagenicity has been assessed in extracts from SPMDs by Rastall et al. [87]. Shaw et al. used Chemcatchers in combination with two invertebrate bioassays, coral larval settlement and sea urchin larval development, in addition to bacterial luminescence and microalgal photosynthesis [102].

The above listing is certainly not complete but illustrates that the range of bioassays is very diverse, spans across organisational levels – from gene expression to whole organisms – and covers multiple modes of action. In addition, both relatively hydrophobic absorptive passive samplers and adsorptive samplers used to sample more polar chemicals have been used in combination with these multiple end-point bioassays. Although various combinations of passive sampler and bioassays have been explored, it is difficult to list fixed combinations for passive samplers and biotests. The reason for this is that the range of compounds that is targeted by bioassays is often very diverse and no single sampler can adequately target a set of chemicals with diverse physicochemical properties. This issue can be illustrated for an algal test that is used to quantify the effects of herbicides such as diuron and atrazine that inhibit PS-II. Log K_{ow} values for PS-II inhibitors range from below 1 (e.g. metamitron) to 4 (dipropetryn). Metabolites of these compounds can also be active PS-II inhibitors and may further extend the log K_{ow} range of possible PS-II inhibitors. Log K_{ow} ranges for compound classes targeted by other bioassays can be even larger; e.g. PCBs with log K_{ow} values up to 7 are oestrogenic whereas benzotriazole, with a log K_{ow} of 1.4, is anti-oestrogenic. As

passive samplers usually target a range of log K_{ow} values spanning 2 to 3 orders of magnitude [87], it is clear that not all compounds that are active in a bioassay will be sampled in a similar, integrative fashion. Some toxic compounds may reach equilibrium well before others. Thus, even when the concentration ratios of various toxicants in the environment are constant, different integrative sampling windows of individual compounds will cause their concentration ratios in a passive sampler to vary over the deployment time of the sampler. In addition, different compounds with the same mode of action may have very different diffusion coefficients within a given sampler (or over a membrane that envelops the sampling phase), and thus behave differently in response to changing environmental conditions.

Although no single passive sampler covers all compounds that act on a certain organism or have a certain mode of action, this does not negate the rationale of combining passive samplers with ecotoxicity assessments. The use of bioassays is a more holistic approach to assessing the risk associated with exposure, since the technique provides a functional integrative assessment of mixture toxicity for chemicals accumulated by passive samplers to levels sufficient to induce a biological response. So, by combining passive sampling with bioassays it is possible to avoid intensive chemical analyses. However, when using a specific bioassay in a sampling campaign, one has to attempt to identify the main possible toxicants that may be present at the sampling locations and select a sampler that best covers the log K_{ows} of those toxicants.

VI.3. The link between biological and chemical analysis

It is common to express the effect of water samples in ecotoxicity tests as a dilution factor, i.e. at what dilution the sample still leads to a certain effect level in the bioassay [83]. The same approach can be used for a passive sampler and one can express the toxic effect in terms of a certain portion of a sampler extract [89]. An alternative approach was developed by Koči et al., a toxicity measure corrected for the volume sampled by a passive sampler (vtox [103]). Although these approaches are clearly informative, and one can classify more or less polluted sites and derive water quality criteria on this basis, it is difficult to compare chemical and biological analyses directly.

Another system to evaluate effects in bioassays is the toxic equivalent (TEQ) concept. It was first established for effects caused by dioxins and PCBs on the arylhydrocarbon receptor [104]. Subsequently, the concept has been applied to oestrogenic activity, phytotoxicity and other types of toxicity. In essence the TEQ concept revolves around comparing the dose response curve induced by a sample to the dose response induced by a reference compound (see [105]). The biological response to the sample can then be expressed in terms of an amount or concentration of the reference compound. This approach can then be complemented by testing many individual compounds in the bioassay to establish their dose-response curves; from these one can derive their potencies relative to the reference. When a set of compounds has been quantified in an environmental sample by means of chemical analysis, concentrations of these compounds can be multiplied by the potencies of the compounds and added together (assuming concentration addition applies) [106]. The sum of the individual chemicals signifies the toxicity based on chemical analysis and the minimum expected response of the environmental sample in the biological test. This approach is well established and many legal TEQ limits are in place for dioxin-like compounds (e.g. the EU limit for fish = 4 pg WHO-PCDD/F-TEQ /g fresh weight) [107].

Being able to relate results from a bioassay directly to those obtained by chemical analyses has the main advantage that one can assess whether most of the toxicity has been accounted for by the chemical analyses, or whether major toxicants have been missed. In passive sampling, linking biological analyses to chemical analyses has been done in several

studies ([90],[92],[93],[97],[99]). Attention has focused on oestrogens, PAHs and herbicides and recently also on baseline toxicity ([100]).

VI.4. Identification of toxic compounds in passive samplers: effect-directed analysis

Effect-directed analysis (EDA) is another area where ecotoxicity assessments can be used [108]. In EDA, an environmental sample is fractionated chromatographically and next, the various fractions are tested individually for toxic effects. Once toxicity has been detected in a fraction, this fraction can be analysed chemically to identify possible toxicants. This is a very powerful method for identifying major toxicants in a complex environmental sample, particularly when the bioassay data are expressed as TEQ to allow for direct comparisons between data from chemical and biological analyses.

The EDA approach has been applied frequently in sediments [68,109]. As yet, only one example comes from passive sampling. Rastall et al. [110] fractionated SPMD extracts and tested these for activity in a reporter gene assay for oestrogen receptor agonists. They found that oestrogens sampled by SPMDs cover a wide log K_{OW} range, but individual oestrogens could not be identified. This area is one where much progress can be made.

In a recent field study where POCIS were deployed for five weeks in treated sewage effluents, a toxic spill occurred at one of 21 sites. The toxic spill caused a fish kill in the receiving river, and the POCIS from this site recorded the highest baseline toxicity in a bacterial test [100]. Using chemical analyses of water samples taken directly following the fish kill, the toxicant(s) causing fish mortality could not be identified (A. Stockli, personal communication). Although EDA was not attempted with these POCIS, it clearly points to an effective use for passive samplers as monitors for such peak toxic events.

VI.5. How does the bioassay response in passive sampler extracts relate to sampler exposure conditions?

The rate at which a compound is sampled by a passive sampler depends on the properties of the compound, the properties of the sampler and the environmental conditions at the deployment site. For individual chemicals it is fairly straightforward to establish relationships between compound properties, environmental conditions and sampling rates [111]. In contrast, the response in bioassays is the sum of the effects caused by contributions from at best a few (for highly specific endpoints) to a large number of individual compounds. As the composition of the mixtures and the relative abundance of the toxicants can vary widely across sites, and over time, this poses certain limitations on how bioassay results can be interpreted with respect to varying environmental conditions. Interpretation can be even harder when a sampler includes a membrane. For example, it was shown that more polar compounds (log $K_{OW} < 2$) move more rapidly over a polyethersulphone membrane than less polar compounds (log $K_{OW} > 3$) into the SDB sampler phase in the Chemcatcher [99]. For short sampling windows, less polar compounds may be under-represented in the mixture of toxicants which will skew results. Thus, when combining bioassays and passive sampling one has to appreciate the uncertainties caused by the fact that the suites of target chemicals cover a wide range of physicochemical properties. As a result, different mixtures of chemicals with the same mode of toxic action will respond differently to varying exposure conditions.

VII. Quality assurance, quality control and normation

If passive sampling is to become accepted and used in a regulatory context for monitoring water quality across Europe, then there is a need for the development of improved validation methods and setting up of the appropriate quality control and quality assurance schemes for the technology. This would involve a set of activities (e.g. development of standard certified reference materials, setting-up of round robin exercises and the publication of standard methods) as those have been established for the validation of analytical techniques for the measurement of various analytes of importance in different environmental matrices. There is also a need for associated accreditation schemes laboratories involved in passive sampler calibration measurements in the lab and those using passive samplers in the field.

The implementation of the above is not straightforward. For laboratory calibrations of the samplers, there is a need for large volumes of reference materials to be available. For field trials it may be possible to use reference sites that are well characterised and stable in chemical composition. An attempt to compare various water monitoring methods that could potentially be used in support of the Water Framework Directive was undertaken as part of a European Union-funded project [112] and the results of this activity have been summarized [113]. A number of field trials were undertaken in different water bodies across Europe and the results from these multiple comparisons indicated the potential utility of this approach. But these activities are expensive to develop and organize and therefore regulators and other end-users need to be convinced of the value of these alternative monitoring techniques so that they can support the provision of EU funding to enable this important research in support of policy and associated legislation.

Several interlaboratory field trials, where a range of passive sampling technologies will be evaluated at European riverine sites, are being set up in 2010. The first is being facilitated within the framework of AQUAREF (the organisation coordinating French laboratories involved in water monitoring) [114]. A call was made in early 2010 for the participation of research groups across Europe who are involved in either developing or using passive sampling technology. Several field sites were selected and include both surface water and a marine lagoon in France. This trial focuses on the monitoring of pesticides, PAHs and metals. The second exercise is being proposed by the NORMAN network, where the focus of this exercise will be on the application of passive sampling for monitoring pollutants of emerging concern. Further, an interlaboratory proficiency testing scheme aimed at the chemical analysis of a range of hydrophobic organic compounds and metals in two commercially available passive samplers has been launched recently in the Czech Republic. [115] The results of these exercises will be of value in demonstrating the future utility of the technology and will be helpful in the design of similar activities in the future.

Progress has been made on the normation of passive sampling methods. One of the deliverables of the European Union-funded project STAMPS [116] was the development of a British Standards Institution Publicly Available Specification [117]. This specification provides guidance for end-users on the preparation, deployment and associated quality assurance requirements for the use of passive samplers in surface waters. The specification is currently under consideration for development of a CEN/ISO standard [118].

VIII. Application of passive samplers in regulatory monitoring

"Emerging pollutants" can be defined as pollutants that are currently not included in routine monitoring programmes at the European level and which may be candidates for future regulation, depending on research on their (eco)toxicity, potential health effects and public perception and on monitoring data regarding their occurrence in the various environmental compartments. In many cases knowledge of their ambient and background levels in water,

sediments and biota is still limited and even less is known of the long-term ecotoxicological effects of these emerging contaminants. At such an early stage, it is difficult if not impossible to derive appropriate environmental quality standards (EQS) for these chemicals without the use of significant safety factors. Therefore compliance testing against EQS values is not often undertaken for these substances. Most monitoring programmes that include emerging pollutants are in general screening studies [119,120] aimed at obtaining additional information on the occurrence of these compounds in various aquatic environmental matrices, where they are likely to accumulate. Passive sampling may be favoured over matrices such as sediments and biota for such screening. It draws advantage from a simple matrix composition that enables simplified sample extraction, cleanup and the subsequent instrumental analysis. Moreover, field exposure of passive samplers in various matrices such as surface waters, wastewaters and sediment can be standardised. In addition, the use of, for example absorption-based samplers for the screening of non-ionic hydrophobic substances in water and sediments results in limits of detection which are generally substantially lower than those that can be achieved through bottle sampling [121]. Another factor to be taken into account in screening studies is the possible (mostly unknown) temporal variability in the concentration of emerging pollutants in water. Continuous monitoring possible with passive samplers can help in reducing the uncertainty associated with sampling when concentrations vary in time. For example, variable concentrations may be observed for emerging contaminants that are emitted in the urban environment and that can ultimately be released from sources such as landfill and wastewater effluents. This is, however, also valid for compliance monitoring of more conventional pollutants for which EQS have been derived and are in use (e.g. for the EU WFD). Despite the measurement of a different fraction of contaminants in water, passive samplers can be used to support data collected by infrequent bottle sampling [122,123] or through monitoring in biota. This allows continuous monitoring in conditions where this would not be feasible and improves the representativeness of the sampling. The integrative nature of passive sampling combined with extremely low limits of detection for non-ionic hydrophobic organic contaminants may represent the only acceptable way to monitor some of these substances in surface waters. Since passive sampling is based on the measurement of dissolved phase pollutants, further comparison with EQS based on “whole water” concentration values may require additional information to account for the fraction of contaminants associated with other phases such as dissolved organic carbon and suspended particulate matter. In the long term, such a strategy requires the development of water body-specific knowledge of contaminant speciation and partitioning. The additional information on non-dissolved fractions of compounds can be obtained in parallel representative measurements of these compounds in suspended particular matter or bottom sediments. The sum of the representative (e.g. TWA) contaminant concentration in the dissolved phase (provided by passive samplers) and that bound to colloids and particles (provided by sampling of suspended particulate matter) will provide the measure of total concentration that can be applied in compliance checking with EQS.

Moving towards an implementation of passive sampling for regulatory monitoring of emerging substances will require the identification of suitable material for accumulation of target compounds and an accurate characterisation and calibration of the devices. In this regulatory context, passive samplers may be applied to the monitoring of surface waters in both populated and remote areas and other aqueous matrices such as wastewaters and other effluents. Samplers can be deployed simultaneously in different media in order to detect gradients in chemical activity/concentration and understand fluxes of these emerging substances.

IX. Future trends

There are several future trends for the development of passive sampling techniques for emerging substances.

Novel materials will need to be tested as selective receiving phases (e.g. ionic liquids, molecularly imprinted polymers, and immuno-adsorbents), together with membrane materials that permit the selective diffusion of chemicals. Novel synthetic absorbent polymer materials with high retention capacity of polar organic compounds may enable the replacement of currently used adsorption-based samplers for which data conversion into aqueous concentrations is often difficult.

A major challenge in the future development of the technology is the calibration of devices to enable the quantification of the concentration of emerging substances present in water. In comparison with devices designed for sampling hydrophobic organic compounds, sampling of most emerging substances is more complex. In addition to the common factors (temperature, water turbulence and biofouling), other factors (e.g. salinity, DOC level, pH, and the presence of complex mixtures of contaminants) may significantly affect the performance of samplers of emerging substances and these need to be evaluated. There are several routes to reduce uncertainty associated with the passive sampler data. These include quantitative assessment, reduction or control of the known factors which impact on sampler performance. For samplers where analytes are accumulated in the receiving phase by absorption mechanisms, PRCs can be successfully employed for improving the accuracy of the measurement of TWA concentrations of contaminants in the field. However, further research is needed to understand accumulation kinetics in samplers fitted with adsorbent-type receiving phases. Mechanical control of constant water flow conditions around the receiving phase in the field enables sampling rates of WBL-controlled samplers that are unaffected by turbulence [124]. Such devices require an *in situ* use of rotors or pumps that force water motion around the sampling devices. Thus, they cannot be classified as true “passive samplers”. However, miniaturised devices that require only a low energy supply (e.g. batteries or solar cells) for the operation of pumps can be deployed in the same way as passive samplers.

Miniaturised devices present a further trend in technology development. Small samplers are usually less expensive to use because of the lower costs of materials needed for their preparation and the reduced equipment requirements for their deployment. Lower volumes of solvents and reagents are consumed during their subsequent processing. Small samplers also offer the advantage of easy transportation to and from the sampling site. As miniaturised devices should not deplete the bulk matrix, they can be used in situations where space, volume and the flow of water are limited; for example, in groundwater boreholes.

The ability to predict kinetic and thermodynamic uptake parameters for passive samplers using quantitative structure property relationship (QSPR) models describing interactions of sampled compounds with materials used in the construction of devices is also important. This may help to reduce the amount of required laboratory-based calibration experiments.

Development of biomimetic devices capable of simulating the accumulation of toxic chemicals in tissues of aquatic organisms will enable a reduction in the use of chemical monitoring in biota in routine monitoring programmes. It will also decrease the uncertainty associated with the data obtained, as this is based on highly variable samples of biological material.

The combination of the deployment of passive samplers followed by the biological testing of sampler extracts with the aim of detecting and subsequently identifying toxicologically

relevant compounds offers much potential. This approach can provide information concerning the relative toxicological significance of waterborne contaminants and hence help to improve risk assessments for different water bodies.

Finally, further development of QA/QC, method validation schemes, and standards for the use of passive sampling devices is urgently needed. Successful demonstration of the performance of passive samplers alongside conventional sampling schemes as well as inter-laboratory studies that demonstrate reproducibility of data produced by different designs of passive samplers will help to facilitate the acceptance of passive sampling in routine regulatory monitoring programmes in the future.

Table 1. List of most discussed emerging pollutants in the aquatic environment and the established or expected/potential performance of passive samplers of these compounds.

Category / class	Sub-class	Individual substances	Potential of non-polar samplers[a]	Potential of polar samplers[b]	Stage of develop-ment[c]	Sampler calibration data[d]
Natural products	Cyanotoxins	Microcystins	-	+	**d**	[125]
Antioxidants	Antioxidants	2,6-Di-tert-butylphenol	-	+		
		4-tert-Butylphenol	-	+		
		BHA	-	+		
		BHQ	-	+		
		BHT	-	+		
Antifouling compounds	Antifouling compounds	Irgarol	-	+	**d**	[9,99]
	Organotin compounds	Dibutyltin ion	-	+	**d**	[38,39]
		Monobutyltin ion	-	+	**d**	[38,39]
		Tetrabutyltin ion	-	+	**d**	[38,39]
		Diphenyltinion	-	+	**d**	[38,39]
		Triphenyltin ion	-	+	**d**	[38,39]
Detergents	Ethoxylates/ carboxylates of octyl/nonyl phenols	4-Nonylphenol di-ethoxylate (NPE2O)	-	+	**d**	[25,126, ,127]
		4-Nonylphenol mono-ethoxylate (NPE1O)	-	+	**d**	[25,126 ,127]
		4-Nonylphenoxy acetic acid (NPE1C)				
		4-Nonylphenoxyethoxy acetic acid (NPE2C)				
		4-Octylphenol di-ethoxylate (OPE2O)	-	+	**d**	[25,126,127]
		4-Octylphenol mono-ethoxylate (OPE1O)	-	+	**d**	[25,126,127]
		4-Octylphenoxy acetic acid (OPE1C)				

Category / class	Sub-class	Individual substances	Potential of non-polar samplers[a]	Potential of polar samplers[b]	Stage of develop-ment[c]	Sampler calibration data[d]
		4-Octylphenoxyethoxy acetic acid (OPE2C)				
Disinfection by-products (drinking water)	Iodo-trihalomethanes		-			
	Bromoacids		-			
	Bromoacetonitriles		-			
	Bromoaldehydes		-			
	Haloacetic acids (chloro-, bromo-, iodo-)		-			
	Other disinfection by-products	Bromate				
		Cyanoformaldehyde				
		Decabromodiphenyl ethane				
		Hexabromocyclododecane (HBCD)	+	-		
		NDMA	+	-	**d**	
Plasticizers	Phthalates	Benzylbutylphthalate (BBP)	+	-		
		Diethylphthalate (DEP)	+	-		
		Dimetylphthalate (DMP)	+	-		
		Di-n-butylphthalate (DBP)	+	-		
		Di-n-octylphthalate (DOP)	+	-		
	Other	Bisphenol A	-	+	**d**	[25,128,142,129]
		Triphenyl phosphate			**d**	
	Benzophenone derivatives	2,4-Dihydroxybenzophenone	-	+	**d**	[65]
Flame retardants	Brominated flame retardants	1,2,5,6,9,10-Hexabromocyclododecane (HBCD)	+	-		
		Tetrabromo bisphenol A (TBBPA)	+	-		
		Tetrabromo bisphenol A bis (2,3 dibromopropylether)	+	-		
		Hexabromocyclododecane (isomers)	+	-		
		Decabromodiphenyl ethane	+	-		

Category / class	Sub-class	Individual substances	Potential of non-polar samplers[a]	Potential of polar samplers[b]	Stage of develop-ment[c]	Sampler calibration data[d]
	Polybrominated diphenylethers	2,2',3,4,4',5',6-Heptabromodiphenyl ether (BDE 183)	+	-	**d**	
		2,2',4,4',5,5'-Hexabromodiphenyl ether (BDE-153)	+	-	**d**	
		2,2',4,4',5,6'-Hexabromodiphenyl ether (BDE-154)	+	-	**d**	
		2,2',4,4',5-Pentabromodiphenyl ether (BDE-99)	+	-	**d**	
		2,2',4,4',6-Pentabromodiphenyl ether (BDE-100)	+	-	**d**	
		2,2',4,4'-Tetrabromodiphenyl ether (BDE-47)	+	-	**d**	
		2,2',3,3',4,4',5,5',6,6'-Decabromodiphenyl ether (BDE-209)	+	-	**d**	
		Technical Decabromodiphenyl ether	+	-	**d**	
		Technical Octabromodiphenyl ether	+	-	**d**	
		Technical Pentabromodiphenyl ether	+	-	**d**	
	Organo-phosphates	Tri-(dichlorisopropyl)-phosphate		+	p	[130]
		Triethylphosphate		+	p	
		Tri-n-butylphosphate		+	**d**	
		Triphenylphosphate		+	**d**	
		Tris(2-chloroethyl)-phosphate		+	p	
	Chlorinated paraffins	Long chain PCAs (lPCAs, C>17)	+	-	p	
		Medium chain PCAs (mPCAs, C14-17)	+	-	p	
		Technical PCA products	+	-	p	
Fragrances	Fragrances	Acetylcedrene		+	p	
		Benzylacetate		+	p	
		Benzylsalicylate		+	p	
		Camphor		+	p	
		g-Methylionone		+	p	
		Hexylcinnamaldehyde		+	p	
		Isoborneol		+	p	
		Isobornylacetate		+	p	
		Isoquinoline		+	p	
		d-Limonene		+	p	

Category / class	Sub-class	Individual substances	Potential of non-polar samplers[a]	Potential of polar samplers[b]	Stage of develop-ment[c]	Sampler calibration data[d]
		Methyldihydrojasmonate		+	p	
		Methylsalicylate	-	+	**d**	
		p-t-Bucinal		+	p	
		Terpineol		+	p	
	Nitro musks	Muskketone	+	-	**d**	
		Muskxylene	+	-	**d**	
		Musk ambrette	+		p	
	Macrocyclic musks					
	Polycyclic musks	AHTN (Tonalide)	+	-	**d**	
		Galaxolide	+	-	**d**	
		OTNE	+	-	**d**	
		AHDI (Phantolide)	+	-	**d**	
		ADBI (Celestolide)	+	-	**d**	
		ATII (Traseolide)	+	-	**d**	
Gasoline additives	Dialkyl ethers	Methyl-tert-butyl ether (MTBE)	-	-		
Indus-trial chemi-cals	Industrial chemicals	TCEP				
		Triphenyl phosphine oxide				
Perfluoro-alkylated substances	Perfluoroalkylated substances	Perfluorooctane sulfonate (PFOS)		+	p	
		Perfluorooctanoic acid (PFOA)		+	p	
Personal care products	Sun-screen agents	4-Methylbenzylidene camphor	+	+	**d**	
		Benzophenone	-	+	**d**	
		Benzophenone-3	-	+	**d**	
		Butyl methoxydibenzoyl-methane			p	
		Ethylhexyl methoxycinnamate	+	+		
		Eusolex Homosalate				
		N,N-Diethyltoluamide	-	+	**d**	
		Octocrylene				
		Oxybenzone				
	Insect repellents	N,N-diethyl-m-toluamide (DEET)	-	+	**d**	
		Bayrepel				
	Carriers	Octamethylcyclotetrasiloxane (D4)	+	-	p	

Category / class	Sub-class	Individual substances	Potential of non-polar samplers[a]	Potential of polar samplers[b]	Stage of develop-ment[c]	Sampler calibration data[d]
		Decamethylcyclopentasiloxane (D5)	+	-	p	
		Dodecamethylcyclohexasiloxane (D6)	+	-	p	
		Hexamethyldisiloxane (HM or HMDS)	+	-	p	
		Octamethyltrisiloxane (MDM)	+	-	p	
		Decamethyltetrasiloxane (MD2M)	+	-	p	
		Dodecamethylpentasiloxane (MD3M)	+	-	p	
	Parabens (hydroxybenzoic acid esters)	Methyl-paraben	-	+	p	
		Ethyl-paraben	-	+	p	
		Propyl-paraben	-	+	p	
		Isobutyl-paraben	-	+	p	
Pesticides	Polar pesticides and their degradation products	Acetochlor	-	+	**d**	[26,131, 132]
		Amitrole	-	+		
		Bentazone	-	+	**d**	
		Bromofos-ethyl	-	+		
		Carbazole	-	+		
		Carbendazim	-	+	**d**	[99]
		Carboxin	-	+		
		Glyphosate	-	+		
		Chloridazon	-	+	**d**	
		Clopyralid	-	+		
		Chlorpropham	-	+		
		Chlorpyrifos	-	+	**d**	[130]
		Chlorotoluron	-	+	**d**	
		2,4 D	-	+	**d**	[59]
		Dicamba	-	+	p	[59]
		Desethylterbutylazine	-	+	**d**	
		Desmedipham	-	+		
		Desmetryn	-	+		
		Diazinon	+	+	**d**	[99]
		Diclobenil	-	+		
		d-Dichlorvos	+	+	**d**	[57]
		Dinoterb	-	+		
		Endosulfan-sulfate	+	+	**d**	[133]
		Ethoprophos	-	+		
		Ethofumesate	-	+	**d**	
		Fluroxypyr	-	+		
		Heptenophos	-	+		
		Iodofenphos	-	+		
		Imidacloprid	-	+		
		MCPA	-	+	**d**	[59]
		MCPB	-	+	p	
		MCPP (Mecoprop)	-	+	p	[99]
		Metalaxyl	-	+	**d**	[27]

Category / class	Sub-class	Individual substances	Potential of non-polar samplers[a]	Potential of polar samplers[b]	Stage of develop-ment[c]	Sampler calibration data[d]
		Methomyl	-	+		
		Metamitron	-	+	**d**	
		Mevinphos	-	+		
		Phenmedipham	-	+		
		Prometryn	+	+	p	
		Prometon	-	+	**d**	
		Secbumeton	-	+		
		Terbutryn	+	+	p	[99]
		Terbutylazine	-	+	**d**	[134,99]
		Thiabendazyl	-	+	**d**	
		Triadimefon	-	+		
	Other pesticides	Cypermethrin	+	-	**d**	
		Deltamethrin	+	-	**d**	
		Permethrin	+	-	**d**	[135]
	New pesticides	Sulfonyl urea				
	Degradation products of pesticides	Desisopropylatrazine	-	+	**d**	[27]
		Desethylatrazine	-	+	**d**	[27,99]
Bio-cides	Biocides	Triclosan	+	+	**d**	[129,136]
		Methyltriclosan	+	+	**d**	[137]
Pharmaceuticals	Analgesic	Acetaminophen (paracetamol)	-	+	**d**	[129,138, 139]
		Codeine	-	+	p	
		Hydrocodone	-	+		
	Anorexic	Fenfluramine	-	+	p	
	Anthelmintic	Ivermectin	-	+	p	
	Antibacterial	Amoxicillin	-	+	p	
		Ampicillin	-	+	p	
		Azithromycin	-	+	**d**	[128,140]
		Chloramphenicol	-	+	p	
		Chlortetracycline	-	+	p	
		Ciprofloxacin	-	+	p	
		Clarithromycin	-	+	**d**	[95,141]
		Cloxacillin	-	+	p	
		Danofloxacin	-	+	p	
		Dicloxacillin	-	+	p	
		Doxycycline (anhydrous)	-	+	p	
		Doxycycline (monohydrate)	-	+	p	
		Enoxacin	-	+	p	
		Enrofloxacin	-	+	p	
		Erythromycin	-	+	**d**	[141]
		Flumequine	-	+	p	
		Josamycin	-	+	p	
		Lincomycin	-	+	p	

Category / class	Sub-class	Individual substances	Potential of non-polar samplers[a]	Potential of polar samplers[b]	Stage of develop-ment[c]	Sampler calibration data[d]
		Methicillin	-	+	p	
		Minocycline	-	+	p	
		Norfloxacin	-	+	p	
		Novobiocin	-	+	p	
		Ofloxacin	-	+	p	
		Oleandomycin	-	+	p	
		Oxacillin	-	+	p	
		Oxytetracycline	-	+	**d**	
		Penicillin G	-	+	p	
		Penicillin V	-	+	p	
		Roxithromycin	-	+	**d**	[141]
		Spiramycin	-	+	p	
		Sulfadiazine	-	+	**d**	
		Sulfamerazine	-	+	**d**	[128]
		Sulfamethazine	-	+	**d**	[141]
	Anticonvulsant	Sulfamethoxazole	-	+	**d**	[99,129]
		Sulfapyridine	-	+	**d**	[129,138, 141]
		Carbamazepine	-	+	**d**	[95,129, 138,141]
		Primidone	-	+		
	Antidepressant	Tetracycline	-	+	**d**	
		Tiamulin	-	+		
		Citalopram	-	+		[129]
		Escitalopram	-	+		
		Sertraline	-	+	**d**	[129]
		Fluoxetine	-	+	**d**	[129,141, 140]
		Fluvoxamine	-	+		
		Paroxetine	-	+	**d**	[129]
	Antidiabetic	Glyburide (glibenclamid; glybenzcyclamide)	-	+		
		Metformin	-	+	p	
	Antiemetic	Diphenhydramine	-	+	**d**	
	Antihistaminic	Loratadine	-	+		
	Antihyperten-sive	Nadolol	-	+		
		Verapamil	-	+		
	Anti-inflammatory	Aceclofenac	-	+		
		Acemetacin	-	+		
		Acetylsalicylic acid (aspirin)	-	+	**d**	[138]
		Alclofenac	-	+		
		Diclofenac	-	+	**d**	[99,138, 141]
		Fenoprofen	-	+	**d**	[141]
		Fenoprofen calcium salt dihydrate	-	+		

Category / class	Sub-class	Individual substances	Potential of non-polar samplers[a]	Potential of polar samplers[b]	Stage of develop-ment[c]	Sampler calibration data[d]
		Ibuprofen	-	+	**d**	[129,138]
		Indomethacin	-	+	**d**	
		Ketoprofen	-	+	**d**	[138,141]
		Meclofenamic acid	-	+		
		Mefenamic acid	-	+		
		Naproxen	-	+	**d**	[129,138, 141]
		Phenylbutazone	-	+		
		Phenazone	-	+		
		Propyphenazone	-	+		
		Tolfenamic acid	-	+		
	Antimicrobial agent	Clotrimazole	-	+		
	Antineoplastic	Cyclophosphamide	-	+	p	
		Cyclophosphamide (anhydrous form)	-	+		
		Daunorubicin	-	+		
		Doxorubicin	-	+		
		Epirubicin	-	+		
		Fluorouracil	-	+		
		Ifosfamide	-	+	p	
	Antiulcerative	Famotidine	-	+		
		Lansoprazole	-	+		
		Omeprazole	-	+	**d**	[141,140]
		Ranitidine	-	+	p	
	Anxiolytic	Alprazolam	-	+	**d**	
		Bromazepam	-	+	**d**	
		Diazepam	-	+	**d**	[138]
		Lorazepam	-	+	p	
		Medazepam	-	+	p	
		Meprobamate	-	+	p	
		Nordiazepam	-	+	p	[138]
		Oxazepam	-	+	p	
		Temazepam	-	+	**d**	[141]
	Beta-Blockers	Acebutolol	-	+	p	
		Atenolol	-	+	**d**	[129,141]
		Betaxolol	-	+	p	
		Bisoprolol	-	+	p	
		Carazolol	-	+	p	
		Metoprolol	-	+	p	[129]
		Oxprenolol	-	+	p	
		Pindolol	-	+	p	
		Propranolol	-	+	**d**	[129,141]
		Sotalol	-	+	p	[129]
		Timolol	-	+	p	

Category / class	Sub-class	Individual substances	Potential of non-polar samplers[a]	Potential of polar samplers[b]	Stage of develop-ment[c]	Sampler calibration data[d]
	Blood viscosity agents	Pentoxifylline	-	+		
	Bronchodilators	Albuterol	-	+		
		Albuterol sulfate	-	+		
		Clenbuterol	-	+	**d**	[138]
		Fenoterol	-	+		
		Salbutamol	-	+	**d**	[138]
		Terbutaline	-	+	**d**	[138]
	Diuretic	Caffeine	-	+	**d**	[128, 129,138]
		Furosemide	-	+	p	
		Hydrochlorothiazide	-	+	**d**	[141]
	Lipid regulators	Bezafibrate	-	+		
		Clofibric acid	-	+	**d**	[141]
		Etofibrate	-	+		
		Fenofibrate	-	+		
		Fenofibric acid	-	+		
		Gemfibrozil	-	+	**d**	[129,138,141]
		Lovastatin	-	+		
		Mevastatin	-	+		
		Pravastatin	-	+		
		Simvastatin	-	+	p	
	Sedatives, hypnotics	Acecarbromal	-	+		
		Allobarbital	-	+		
		Amobarbital	-	+		
		Butalbital	-	+		
		Hexobarbital	-	+		
		Pentobarbital	-	+		
		Aprobarbital	-	+		
		Secobarbital sodium	-	+		
	Steroids and hormones	17-alpha-Oestradiol	-	+	**d**	[25,128,129,142]
		17-alpha-Ethinyloestradiol	-	+	**d**	[25,128]
		17-beta-Oestradiol	-	+	**d**	[25,128,129, ,142]
		Beta-sitosterol	-	+	**d**	
		Cholesterol	-	+	**d**	
		Diethylstilbestrol	-	+	p	
		Oestriol	-	+	**d**	[142]
		Oestrone	-	+	**d**	[25,128,129]
		Oestrone 3-sulphate	-	+	p	
		Prednisolone	-	+	p	
		Dexamethasone	-	+	p	
		Bethametasone	-	+	p	
		Mestranol	-	+	**d**	

Category / class	Sub-class	Individual substances	Potential of non-polar samplers[a]	Potential of polar samplers[b]	Stage of develop-ment[c]	Sampler calibration data[d]
	Psychiatric drugs	Amitryptiline	-	+	**d**	[138]
		Doxepine	-	+	**d**	[138]
		Imapramine	-	+		
		Nordiazepam	-	+	**d**	[138]
		Zolpidem	-	+		
	X-ray contrast media	Diatrizoate	-	+		
		Iohexol	-	+		
		Iomeprol	-	+		
		Iopamidol	-	+		
		Iopromide	-	+		
Trace metals	Trace metals and their compounds	Tetramethyllead	+	-		
		Tetraethyllead	+	-		
	Benzotriazoles	4-Methyl-1H-benzotriazole	-	+	p	
		5-Methyl-1H-benzotriazole	-	+	**d**	
		5,6-Dimethyl-1-H-benzotriazole	-	+	p	
	Tolyltriazoles (TT)	Tolyltriazole				
		4-/5-Tolyltriazole (TTri)				
Wood preserva-tives	Phenols	para-Cresol	-	+	**d**	
Other	Drugs of abuse	Cocaine	-	+	p	
		Codeine	-	+	**d**	[141]
		Dihydrocodeine	-	+	p	
		Heroin	-	+	p	
		Hydrocodone	-	+	p	
		Morphine	-	+	p	
		Oxycodone	-	+	p	
	Benzothiazoles (BT)	Benzothiazole	-	+	**d**	
		2-Mercapto-benzothiazole	-	+	**d**	
		Benzothiazole sulfonic acid	-	+	p	
	Nicotine metabolite	Cotinine	-	+	**d**	[128]

The following considerations apply.

[a]potential of non-polar samplers: (e.g. SPMD, LDPE, silicone, non-polar Chemcatcher)

+ = log K_{ow} > 4; - = log K_{ow} < 3

[b]potential of hydrophilic samplers (POCIS, the hydrophilic version of Chemcatcher, Empore™ disks and others)

+ = log K_{ow} < 3 ; - = log K_{ow} >4

[c]stage of development:

d = performance has been demonstrated in the laboratory and/or in the field;

p = performance is likely to be good, but experimental evidence is not available.

[d]selected references are given to publications containing sampler calibration data

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NORMAN Association

Network of reference laboratories and related organisations for monitoring and bio-monitoring of emerging environmental substances

NORMAN Working Group on Prioritisation of Emerging Substances

Prioritisation framework for emerging substances: Discussion paper

DRAFT 2 – September 2010

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CONTENTS

I. Summary of the aims and conceptual basis of a prioritisation scheme for emerging substances

The list of emerging substances produced by the NORMAN network contains more than 700 substances that are frequently discussed in the literature as “emerging substances”.

Some substances have been discussed only recently and we know very little about them. Other substances are already at quite an advanced stage of assessment and are likely to become regulated substances soon.

It is not possible to deal with all these substances in the same degree of detail. We need to identify the substances of high priority for monitoring and/or risk assessment, but also for further research. However, if we apply the conventional prioritisation methodologies a large part (if not all) of these substances would be discarded or left on stand-by because of a lack of data / information: i.e. insufficient evidence of risk. On the other hand, because these substances are not prioritised by the conventional methodologies, they are monitored less or not at all: as a result, too few data are available to show evidence of risk. In other words, they are caught in a 'vicious circle'.

It is therefore important to decide how these individual substances should be dealt with in terms of actions to be taken to fill in the current data gaps (e.g. development of more powerful analytical methods, EQS development, new ecotoxicity tests, etc.).

The objective of this WG is therefore the development of a prioritisation scheme for emerging substances, using the existing prioritisation methodologies (e.g. Fraunhofer Institute (1999), OSPAR Commission (2000), INERIS (2008), UK Environment Agency (2007)) as a starting point.

As said above, however, the focus here is somewhat different from previous prioritisation schemes. For most of the existing prioritisation methodologies, the lack of knowledge / data / information, which is the most common situation for “Emerging Substances” and “Emerging Pollutants”, is used as a justification not to prioritise a substance, whereas for the NORMAN scheme, this lack of data may be the trigger for a high-priority for research. The NORMAN scheme should therefore go beyond the existing prioritisation methodologies to address the knowledge gaps and reflect what is 'emerging' or likely to emerge.

II. Scope and objectives

Protection target: the present prioritisation methodology addresses both environmental ecosystems and human health aspects.

The methodology aims to cover emerging substances in all environmental compartments.

However, in a first stage priority criteria will be developed for the aquatic compartment (water, sediment, SPM and biota) only.

NORMAN will extend the prioritisation methodology to the other compartments as part of the activities to be carried out after 2010.

III. Candidate substances to be dealt with in the prioritisation process

The current list of NORMAN emerging substances (update 2010) consists of more than 700 substances. These substances are selected by the NORMAN experts, based on citations in the scientific literature, and taking into account the definition of “emerging substances” and “emerging pollutants” given in the NORMAN Glossary of Terms (www.norman-network.net >> Glossary).

The candidate substances for this prioritisation exercise (reported in Annex I) represent a subset of the full list of emerging substances, given that, for example, nanoparticles have at this stage been excluded from the prioritisation methodology.

Nevertheless, it is important to keep in mind that a list of emerging substances is by definition a dynamic list. The NORMAN experts are in charge of regularly revising the list of emerging substances to be submitted to prioritisation.

IV. Prioritisation methodology

The methodology is based on two main steps:

I. A first **classification** of substances in a defined number of **action categories** (i.e. actions to be taken by the research community and public authorities and which will be part of the future NORMAN actions)
II. Subsequent **ranking** of the substances **within each action-category**.

I. Classification into action categories

This part of the process includes the following steps:

a) Definition of the different categories to group the substances according to the action(s) needed, based on the currently available information;
b) Definition of the criteria / indicators to be used for the categorisation process and derivation of a flowchart for the allocation of each substance to the correct category according to its known or predicted properties and identified knowledge gaps;
c) Data gathering, including identification of data sources, procedures for data validation (quality check) and data treatment;
d) Allocation of the substances to the identified categories (and review / adjustment of the criteria / indicators, improvement of supporting data).

II. Ranking of substances within each category

This part of the process includes the following steps:

a) Definition of (additional) parameters / indicators that should allow the evaluation of the level of priority within each action category;
b) Data gathering: additional data collection, analysis and validation;
c) Definition of the prioritisation algorithm (scoring system);
d) Application of the algorithm and expert review of the results.

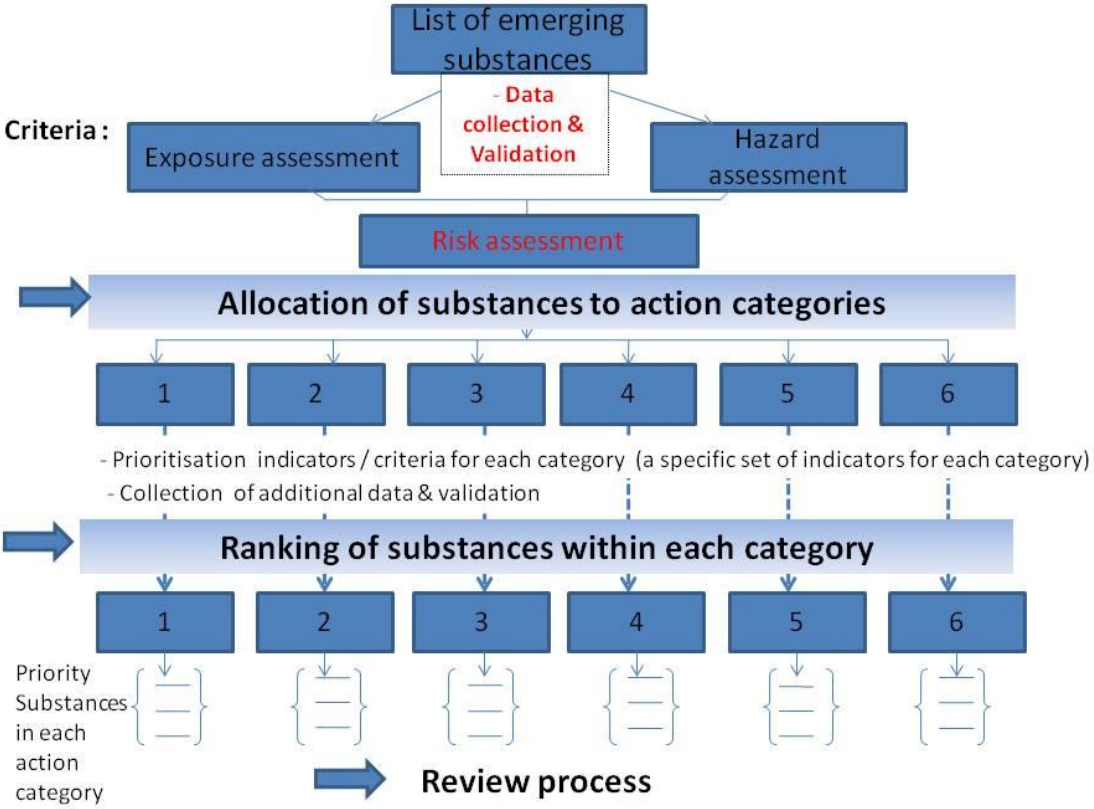

Figure 1: **Flow chart of the proposed approach for classification and prioritisation of emerging substances.**

IV.1.Classification into action categories

IV.1.1 Definition of categories for classification of emerging substances

Six categories are defined for classification of emerging substances by type of action needed.

IMPORTANT: ALL categories proposed below are intended to identify an action needed and not a level of priority among substances (e.g. substances in Category 2 are on the same level of priority as Category 3).

Category 1:	Compounds for which a legally binding EQS should be derived AND which should be considered for routine monitoring. For these emerging substances there is already sufficient evidence on exposure and effects to prioritise them. ***Action: these compounds should be included in regular monitoring programmes (e.g. substances relevant for submission to DG ENV WG-E – periodic revision of priority substances under WFD).***
Category 2:	Emerging substances with first evidence of occurrence in the environment and sufficient evidence of hazard from either laboratory studies or field studies that show effects in bioassays (EDA).

	Action: these compounds should be addressed in investigative monitoring (including NORMAN monitoring campaigns).
Category 3:	For these emerging substances there is sufficient evidence of environmental exposure, but further evidence (research) is needed concerning effects on ecosystems and human health (e.g. exceeding P-PNEC). ***Action: these compounds should be subjected to rigorous effect assessment (i.e. submitted to biological testing).***
Category 4:	For these emerging substances, there is hard evidence of hazard but observations in the environment are scarce (analytical capabilities not yet satisfactory). ***Action: these compounds should be addressed for development / validation / harmonisation of analytical methods (research on analytical methods).***
Category 5:	For these emerging substances there are no or few observations in the environment and there is no hard evidence on potential effects to ecosystem and human health. ***Action: for these compounds, both development of analytical methods AND rigorous effect assessment are required.***
Category 6:	For these emerging substances there is evidence that the exposure does not pose a risk to ecosystem and human health. These substances should be reconsidered to avoid excluding them incorrectly. A safety net can in this case be advised to consider in more detail: - Combined effects with other pollutants - Trends which may indicate increasing importance of the pollutant - Presence of pollutants with similar mode of toxic action and potentially additive / synergistic effects ***Action: these compounds should not be considered for first priority action. These compounds will be deselected from the list of NORMAN emerging substances and put on a clearly identified separate list with the justification for their deselection.***

Table 1: Overview of the six action categories

***NOTE*:** At this present stage of the development of the prioritisation methodology, the WG decided to carry out a run test on the list of NORMAN emerging substances based on the above listed categories. Further to the results of this test the number of categories may be revised / adjusted.

IV.1.2 Criteria and indicators for allocation of substances into the action categories

The criteria / indicators and threshold values which have been developed to classify the emerging substances into the six action categories are presented in this section, organised into three groups:

- *exposure assessment (incl. assessment of the analytical method performance and application of the results of fugacity models to identify the most suitable environmental compartment to be analysed for each of the candidate substances)*
- *hazard assessment*
- *risk assessment*.

The general principles behind the proposed criteria are described below. The flowchart for the classification of the substances into the action categories is presented at the end of this section.

⇒ *Exposure assessment*

Preliminary remarks:

1) Considered matrices: One prerequisite for the exposure assessment is that the compound should be detected in at least one matrix. However, which matrix is monitored often depends on the properties of the substance, and also on the purpose of the investigation. If there are any observations in the environment, this is a first clear trigger for the assessment of the substance. The following matrices are considered here for exposure assessment:

- surface water (both whole water and filtered water samples)
- sediment (both sediment traps and sediment cores)
- suspended matter
- biota
- water effluents
- sewage sludge
- ground water
- drinking water.

These matrices are different lines of evidence of the risk to or via the aquatic compartment.

2) *Assessment of exposure levels*: throughout the whole document three different indicators are used, all based on the maximum concentration observed at each site, referred to as Maximum Environmental Concentration (MEC):

- MEC_{site} - is the maximum reported concentration *in the most recent years* (i.e. after 2004) *at each site* and is used as an input for the calculation of the frequency of exceedance.
- $MEC_{95/a}$ - is the 95th percentile of the *annual* maximum concentrations of *all sites* with measurements *in the respective year* and is used for the time trend analysis.
- MEC_{95} - is the 95th percentile of the maximum concentrations *at each site* (most recent years, i.e. after 2004), taking into account that data with real concentrations for at least 20 sites are needed for a proper statistical analysis to derive a MEC_{95}.

The justification for considering the maximum concentrations for exposure assessment at each site, is to avoid underestimating the risks associated to substances released intermittently (e.g. pesticides), which have rather short term peaks. As the general sampling procedure consists of monthly grab samples, an annual average of these measurements can not be seen as a proper representation of the real exposure situation. Concentrations are known to fluctuate much more, which means that even the maximum annual grab sample is highly unlikely to represent the maximum exposure situation, expected to have effects on the aquatic communities.
Moreover, also for compounds with constant releases the maximum can be considered representative. With regard to the representativeness of effects, this could be easily illustrated by the example of ten very toxic compounds that affect the ecological status at about ten percent of the sampling sites each. When applying a somewhat lower percentile than the 95th (e.g. 90th), all sites affected by these compounds would be discarded from the calculation, and the impact of these compounds would be completely ignored. With the proposed approach, also compounds with clear local effects could be considered.

Questions to WG / comments

Do you agree with the proposed 95th percentile?

Do you agree with the proposal of requiring 20 sites with real concentration values as the minimum condition for a MEC_{95} to be derived?

Do you agree with the proposal of considering only the most recent data, i.e. data after 2004, for calculation of the MEC_{95} and MEC_{site} ?

The following parameters are proposed as indicators for *exposure assessment* in the categorisation process.

Number of countries with analyses The number of countries in which the substance was looked for is used as an indicator of the level of investigation of a given substance (well investigated substances *vs* not sufficiently investigated substances).

Consistency between investigated medium / matrix and the medium / matrix which is relevant for that substance (based on fugacity models) (YES / NO): This indicator describes the distribution of the substances among the different media as derived from fugacity models. A cut-off of 5% partitioning to a medium is considered here for a substance to have a "realistic presence" in that medium. If a substance has been looked for in a medium where there is little chance to find it, lack of positive detection cannot be used as a justification for absence of the substance in the environment / evidence of no exposure. This indicator is therefore used to check whether the available data are suitable to judge about the level of exposure to a given substance and to confirm the matrix(ces) in which the action needs to take place

Questions to WG / comments

Calculation of distribution between environmental compartments will be done using the fugacity concept developed by *MACKAY et al.* at 10°C. The details are given in Annex III. According to the complexity of the environment and the exchange between the compartments there are three different levels of fugacity calculations.

A test is currently under way. Based on the results of this test we can decide the MACKAY level that is most appropriate for our exercise. Do you agree with this proposal?

Number of sites with positive detections (>LOQ): The number of sites in which the substance was detected > LoQ indicates if the exposure is widespread or if it is only a "local problem", knowing that the actions of NORMAN might address both, compounds that are of concern at a river basin level and compounds that are of concern at the European level.

Max LOQ < lowest effect threshold (YES /NO): The max LOQ (from available data) allows us to confirm whether the analytical performance of the laboratories is sufficient. For example, if the substance is not detected above the LOQ and the LOQ is above the benchmark value (i.e. lowest value among EQS / PNEC / P-PNEC – see below or go to Annex III for detailed explanation of these terms) this should be used as an indication that the monitoring data available are not sufficient to exclude exposure to the given substance.

Questions to WG / comments

Shall we use Max LOQ or rather the 90th percentile of "all LOQs"? (meaning by "all LOQs", the LOQs for which we have found information in the databases or in the literature)

What is the influence of the year and how should we take this additional information into account? Shall we limit ourselves to the literature / data sources of the last five years?

⇒ *Hazard assessment*

Effect data allow EQS derivation (YES / NO): For the assessment of effects, the derivation of environmental thresholds is necessary. For this purpose, at least acute data for all three trophic levels should be available. Where data is insufficient, acute data will be predicted with respective QSAR models.

Non-toxic effects (including novel endpoints): Besides mortality, chemical substances may also have a number of other ecotoxicological effects on biota or human health. Respective toxicological endpoints are often tested with *in vitro* assays, e.g. (i) genotoxicity (umuC test), (ii) mutagenicity (Ames II), (iii) estrogenicity (ER-Calux, yeast estrogen screen (YES)) and (iv) androgen receptor agonism and antagonism (AR-CALUX, yeast androgen screen (YAS), (v) aryl hydrocarbon receptor (AhR) receptor mediated effects (DR-CALUX, EROD induction) or (vi) tumour promotion by inhibition of gap-junctional intercellular communication. Moreover, besides these more "established" endpoints, there might be a need also to consider new endpoints that are currently studied, such as nest holding, competition, egg production, heart rate, etc. (A. Boxall, 2008). There might also be a need to develop new endpoints to address certain effects of chemicals that mimic natural "substrates", such as info chemicals (e.g. artificial sweetener).

⇒ *Risk assessment*

Preliminary remarks:

For risk assessment, environmental thresholds below which no effects on the biota are expected are important indicators, referred to as Predicted No-Effect Concentrations (PNEC) or Environmental Quality Standards (EQS). These are usually based on eco-toxicological tests and the application of respective safety factors, which are dependent on the data availability. Chronic data should be preferred over acute data. The same holds for the Derived No-Effect Level (DNEL) to protect human health.

In this exercise we refer to four different types of environmental thresholds for risk assessment (see also Annex III):

- *Existing EQS*: environmental quality standards (EQS) already available at the national level in at least one country or at the European level.
- "*PNEC* $_{chronic}$": Predicted No-Effect Concentrations derived from available experimental data from chronic tests (e.g. PNECs derived directly by NORMAN or PNECs derived during the COMMPS or the INERIS prioritisation process for the revision of the list of Priority Substances under the WFD) with the application of safety factors in line with the EC requirements (see Annex III).

- *"PNEC $_{acute}$"*: PNEC $_{acute}$ can be derived using, in line with EC requirements, at least one short-term LC50 from each of three trophic levels, plus a safety factor of 1000 applied to the lowest value.
- *Provisional Predicted No-Effect Concentrations (P-PNEC):* Finally, if no or insufficient experimental acute toxicity data are available, Provisional Predicted No-Effect Concentrations (P-PNEC) can be calculated to provide an estimate of the hazard, based on appropriate QSAR models. These models make use of read-across methodologies and are based on a large database of acute standard toxicity tests for *Daphnia magna, Selenastrum capricornutum and Pimephales promelas*, covering all three BQE. This is in accordance with the EQS methodology and applies a safety factor of 1000 to the lowest acute value. The complete description of the process / methodology used to derive the QSAR is reported in Annex III.

NOTE: To avoid an underestimation of risks due to low assessment factors for chronic data, the respective EQS and "chronic PNEC" (which often exist only for insensitive lab organisms) will be compared to the "acute PNEC" and the P-PNEC and the lowest value will be taken as environmental threshold for risk assessment, as proposed below.

We suggest the following parameter as indicator for *risk assessment* in the categorisation process.

Exceedance of the lowest environmental threshold (i.e. MEC$_{95}$ > lowest effect threshold among EQS, PNEC$_{chronic}$, PNEC$_{acute}$, *P-PNEC):* For the calculation of the exceedance we suggest considering the MEC$_{95}$ (i.e. 95th percentile of the maximum concentrations at each site - see definition earlier). If only waste water concentration data are available, MEC$_{95}$ for surface water will be derived using concentration data available for waste water divided by a factor of 10.

Since the EQSs, PNECs and LC$_{50}$ mentioned here are all expressed as concentration in the water matrix, the exposure data in matrices other than water will be converted into water exposure (concentration) data, using the partitioning of Di Torre (1972).

*Bioavail. Concentration [µg/l] = Environ. Concentration [µg/kg] / (TOC/1000000000*Koc+1)*

Questions to WG / comments

Do you agree with the proposed approach for conversion of sediment concentrations into water concentrations?

Regarding the monitoring data in biota, do you agree with a conversion from biota concentration to water concentration, using the BCF of the respective compounds?

⇒ *Flowchart for classification of substances into action categories*

The decision tree for the classification of the substances into the earlier-described six action categories is presented here and can be illustrated with the help of the flowchart in *Figure 2*.

As a first step, compounds are assessed according to the availability of analytical data. The indicators used for this assessment are: the availability of analysis in more than 4 countries OR the availability of exposure data above the limit of quantification. In both cases, an additional condition must be met: the compound must be analysed in the correct matrix (based on fugacity modelling). By doing so, two groups are generated, which differentiate with regard to clear evidence of exposure: Group 1 (on the left side of the decision tree) lacks clear evidence, while Group 2 consists of compounds for which there are sufficient data to state about environmental exposure. This second group is then further split into new groups based on the availability of sufficient effect data for PNEC derivation. Those compounds which do not comply with this requirement fall in Category 3. For compounds in this category, a rigorous hazard assessment is recommended in view of the derivation of robust environmental theresholds.

The remainder group (1.1) is further separated into two categories (Category 1 and Category 6) based on the evidence of a risk, calculated as the ratio of the exposure level (MEC_{95}) and the effect level (lowest PNEC).

Compounds with MEC_{95}/PNEC ratios above 1 would trigger the substance's classification in Category 1: these compounds should be included in the list of river basin specific pollutants according to Article VIII of the WFD.

For compounds with MEC_{95}/PNEC ratios below 1, in turn, there is evidence that the exposure does not pose any harm to ecosystem and human health at the observed concentrations: they form Category 6. For these chemicals, monitoring efforts could be reduced, unless other non-toxic effects (e.g. endocrine disruption) are expected, in which case they would fall in Category 5.

An additional group of compounds is identified here, which consists of compounds that are always or most often below the LOQ. Keeping in mind that at least 20 positive data (above LOQ) are needed in order to derive MEC_{95} (see on page 7), if this condition is not met, then it will not be possible to calculate MEC_{95} out of the available data. It will therefore be necessary to verify that the analytical performance of the method is sufficient. If this is the case, then the compound will fall under Category 6 (sufficient evidence the there is no exposure). Otherwise, the substance will fall under Category 4 (development of more appropriate analytical methods).

Going back to Group 1 at the beginning of the decision tree, this group, which represents the compounds for which the set of available data is not sufficient to draw conclusion on the level of exposure, is submitted to further steps of evaluation of the knowledge gaps.

The first step consists in checking the availability of appropriate analytical methods.

Two groups are identified: those compounds that are always measured below the limit of quantification (LOQ) and for which the max LOQ exceeds the lowest PNEC, fall into Category 4: for these chemicals analytical methods have to be improved to assess the real risk of the substance. Further on, Group 1.1 – which consists of compounds with analytical methods of sufficient performance – is split into two groups (Category 2 and Category 5) based on the availability of sufficient effect data for the derivation of EQS.

Compounds with a comprehensive hazard assessment indicating a potential concern, but scarce monitoring data, fall under Category 2: for these compounds, a screening study should be performed to gain information about the current exposure situation.

For the remaining substances there are no or few observations in the environment and there is no hard evidence of potential effects to ecosystem. They comprise Category 5: for

these compounds, both the development of analytical methods and a rigorous effect assessment are required.

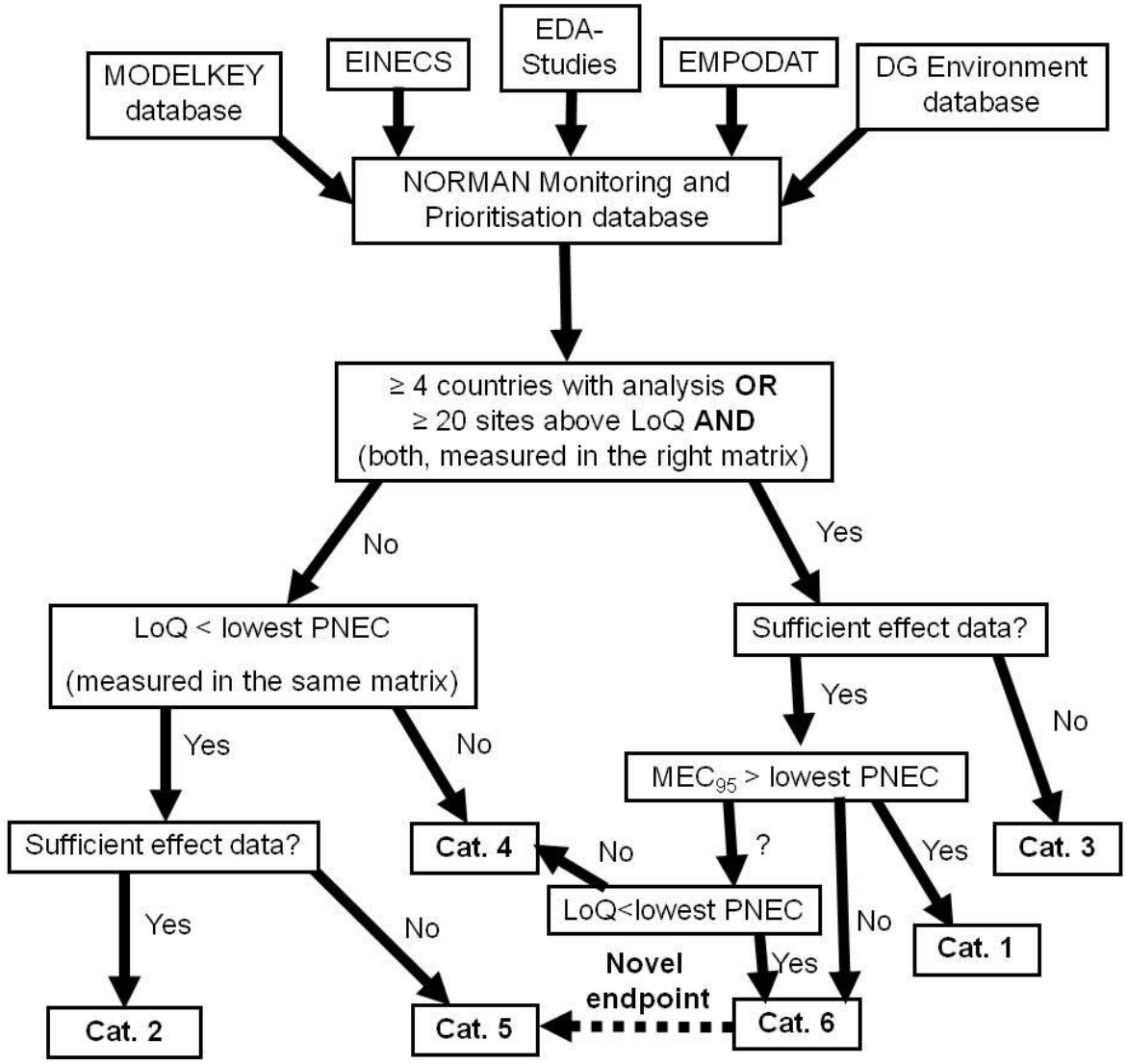

Figure 2 Flow chart of the proposed classification of emerging substances into 6 action categories (Cat.) For details about the 6 categories, please refer to table 1. The starting point is represented by the different sources of data from environmental observations.

IV.1.3 Data gathering, including identification of data sources, procedures for data validation / quality check and data treatment

For the purpose of classification into action categories, mainly aggregated data will be used (e.g. average and maximum concentration per country and year), as collected via literature review, questionnaires to the NORMAN network, expert judgement within the Working Group, etc. The rules for data validation for this step of the process can therefore be quite simple and limited to an assessment of (checking) the reliability of the sources of the data (e.g. “high confidence”, “satisfactory confidence”, “low confidence”, “not acceptable”).

On the other hand, we are aware that it will be difficult to obtain high-quality information for some of the substances. Hence, we propose to take into account data with a lower level of

reliability via a flagging system plus the application of a weighting factor later on in the prioritisation process. To this purpose the original source of the data will be systematically cited besides the data used for the classification step.

Questions to WG / comments

The prioritisation methodology needs to take into consideration the quality / reliability of the data used. This document does not yet indicate how this is to be done. What is your proposal?

The sources used for each type of data / indicator (e.g. exposure data, toxicity data, etc.) and the associated validation rules (data quality check) are provided in Annex IV.

Moreover, rules for data preference are defined in Annex V for each indicator, in order to deal with cases where experimental data are not available (replacement of experimental data by calculated data) and cases where more than one dataset is available for a given parameter (use of worst case data, use of the average value, etc.).

IV.1.4 Allocation of substances into the action categories

In this final step, the available information will be used together with the thresholds to classify the substances into one of the six action categories. We propose to do this "automatically", in order to allow for an objective evaluation, compiled in a NORMAN database. All entries are already in numerical form or should be transformed into numerical form. In this way, the addition of new substances is easily possible. If appropriate queries are programmed, classification and subsequent prioritisation (might change with additional data) could be done "on the fly", and the analysis does not have to be repeated manually. Of course, the results should be made transparent to allow for a critical expert review.

It is possible that some of the compounds might be classified into two different categories, based on the current threshold values. For this reason, we propose to make a first test before we decide on the final classification.

IV.2.Ranking of substances within each action category

IV.2.1 Definition of additional parameters / indicators that should allow the evaluation of the level of priority within each action category

Specific indicators and criteria are adopted for ranking of substances within each given category.

NOTE: Since the objective differs from one category to another, indicators and ranking criteria should differ from one category to another (e.g. category 4 identifies substances for which there is a need for improving analytical performance, while category 3 identifies substances for which there is a need for development of toxicity tests; the criteria for prioritisation within each category will need to be defined accordingly).

In addition to the simple indicators used for the previous classification into action categories, the indicators listed below are proposed. Moreover, as soon as data on novel indicators become available, they might be included in the methodology (based on a WG's decision).

Frequency of quantifications (i.e. frequency of observations > LOQ) : Besides the pure presence of a substance in one or more countries (or different matrices), the number of positive observations compared to the total number of measurements (samples) for each matrix is a good indicator for the assessment of the potential hazard with regard to temporal exposure.

Number of sites with positive observations (>LOQ): Similar to the frequency of observations, this indicator represents the spatial distribution of the potential hazard. Compounds that are found at many sites are in general of higher potential concern. However, caution should be taken in the interpretation of the results of this indicator. The fact that there are few observations might indicate the need for intensified monitoring. It might also indicate the present status of monitoring: i.e. some compounds are monitored with high frequency, but only at a few sites.

Production volume / Use: It is an obvious fact that substances that are produced, transported and used in very high quantities are more likely to end up in the environment (e.g. accidents) than those with low production volumes. If there are few environmental observations, this information can be used as a substitute to calculate a predicted PEC value (we are aware, though, that these data are often not available and many of the data available are old).

Questions to WG / comments

We need to know in more detail and with concrete examples whether or not we can have access to these data and, if so, how.

See also Annex IV on data sources: paragraph 2: "Production and usage data"

Usage pattern: Besides the information about production volumes, the way a substance is used might also be of importance for the potential hazard it might present. For example, pesticides that are deliberately put into the environment pose a high risk of diffuse input via run-off or spray-drift and get a high score. As a second example, pharmaceuticals are used in relatively lower quantities but they are often released via treatment plants, which results in local risks from point sources. The following types of patterns are proposed:

- "Controlled system" - isolated intermediate, no direct release to the environment (e.g. substances that are used in industry but in a controlled process without direct release in the environment)
- Industrial, non-dispersive use - small number of releases to the environment – e.g. used at industrial or other identifiable sites resulting in controlled point source emission, local releases to the environment;

- Wide dispersive use - many mainly diffuse source releases to the environment (e.g. substances present in personal care products, pharmaceuticals, etc. and which are regularly discharged in the environment via WWTP);
- Used in the environment - batch releases within the environment (e.g. pesticides).

Questions to WG / comments

The text above is taken from the UK EA Report "Prioritising chemicals for standard derivation under Annex VIII of the Water Framework Directive" - UK Environment Agency (2007).

Is there a table already available giving for each class of use (e.g. pesticide, personal care products, detergents, etc.) the usage pattern?

Availability of Analytical methods and level of validation: It is important to consider whether a substance can be analysed in environmental samples at the level of research lab / expert lab or on a routine level. Many of the emerging substances are of a polar nature and not detectable via routine GC-MS analysis. In this case, the absence of observations in the environment might be just because of the lack of appropriate analytical methods or the lack of validation / harmonisation of these methods. In line with the NORMAN protocol for methods validation the following types of validation levels are considered: Routine level (NORMAN V3), Expert (NORMAN V2), Research (NORMAN V1), Not available

Concentration trend: For some compounds that have been measured for a considerably long time (> 5 years), it might be possible to assess a trend (i.e. concentrations increase, stay the same or rather decrease). In the case of a significant increasing trend, a higher priority might be justified. For this purpose, for each compound we propose to calculate the **95 percentile of the maximum concentrations** (at each site) **per year** (MEC_{95a}) and analyse potential trends in the concentration development. By doing so, we want to make sure that compounds with intermittent release (i.e. pesticides) are appropriately considered. We also require that only sites which have data for at least five years are used for the calculation, in order to avoid that sites for which the compound has been rarely measured may bias the trend. To allow for a relatively representative average, at least 6 sites are required. The MEC_{95a} for each year are then used in a correlation, with the years as factors. Only significant correlations ($p < 0.05$) are considered to have a "real" trend and are used for the prioritisation. However, all correlation plots need to be inspected visually to account for outlier concentrations in certain years or single low concentrations in final years. By doing so, some additional compounds will become significant trends, while others will be removed.

Potential for Long Range Air Transport (LRAT): Substances that have the potential to be transported to remote areas of the globe are considered persistent. Evidence for long-range transport and deposition is taken into consideration in determining the persistence of substances. Key LRAT parameters are atmospheric oxidation (AO) t1/2 (>2 day) and air-water partition coefficient (log Kaw ≥5 and ≤ 1) (Canadian SDL).

Observations in groundwater (Yes / NO): If a compound is found in the groundwater, this would raise particular concern.

⇒ *Hazard Assessment*

EQS available (YES / NO): Availability of a legally binding (national) EQS in at least one country.

Lowest EQS / PNEC $_{chronic}$ / PNEC $_{acute}$ / P-PNEC / : In order to assess the potential hazards that stem from exposure to a certain substance, the lowest No-Effect threshold is proposed as an indicator. Substances with very low thresholds thereby pose higher potential hazards than those with very high thresholds. For each substance, besides existing EQS, $PNEC_{chronic}$ as well as $PNEC_{acute}$ or P-PNEC are calculated following the procedure described in Annex III. The lowest value among these will be used for this indicator.

PBT / vPvB criteria: Substances that are Persistent, Bioaccumulating and Toxic (PBT) or very Persistent and very Bioaccumulating (according to REACh) pose an additional risk to the environment. Beside their toxicity, which is already covered by other indicators, they can remain present for a long time in the environment and / or, once they are in the environment, they quickly accumulate in biota. For the allocation of a substance as PBT, vPvB we will check if the substance is classified as PBT or vPvB in the Stockholm convention, then in the Aarhus convention – UNICE and finally, classification under REACh - Annex XIII of the REACh Regulation No 1907/2006. Any new development / revision in the PBT criteria will be taken into account. In addition to this, for all compounds, the half-life in sediment and in water as well as the bioaccumulation potential (BCF) will be estimated using QSAR models. In the case in which there is data available, this will help to verify the existing classification, otherwise the estimated data will be used as a first indication of persistence or bioaccumulation potential. The QSAR models used in this study are described in Annex III.

Questions to WG / comments

For the substances for which classification of half-life and BCF is not available, they will be estimated using QSAR models. It is then necessary to define the criteria that should be applied for classification of the substances for their PBT properties. Shall we apply the REACh criteria / cut-off values for this classification purpose?

Human health toxicity: the following indicators are considered: T, T+, CMR, NOAEL < ??, (to be defined)

Questions to WG / comments

1. In the February 2010 WG meeting it was agreed that a proposal should be provided to introduce human health criteria / indicators in the prioritisation methodology. Two options were discussed: option 1) introduction of human health criteria already at the classification stage OR option 2) in the first phase only criteria associated with

environmental aspects should be considered for classification/prioritisation. When positive observations (i.e. for a limited number of prioritised substances) are identified the process should look at human health aspects as an additional criterion for prioritisation.
Based on this outcome, we propose to go for option 2 and introduce human health criteria only in this second phase (ranking phase). Do you agree?

2. What do you propose as indicators and thresholds / cut-off values to be taken into account?

⇒ *Risk Assessment*

Frequency of sites exceeding the environmental threshold: This indicator considers the spatial distribution of potential effects of a certain compound, i.e. the frequency of sites with observations above the lowest effect threshold (see above). For the calculation of this indicator, the maximum concentration per compound and site in the most recent years (MEC_{site}) is compared to the lowest environmental threshold. Subsequently, the number of sites where the threshold was exceeded for a given compound is divided by the total number of sites where the respective compound was measured. The resulting percentage indicates the relative percentage of sites where potential effects are expected. The results of this measure, scaled from 0 to 1, can be directly used for prioritisation (see below "Prioritisation algorithm). If the frequency for two compounds is the same, the compound with the higher number of sites will be given higher priority.

Exceedance of environmental thresholds: This indicator aims to rank compounds with regard to the extent of the expected effects. For the assessment of this indicator, the 95th percentile of the maximum concentrations at each site is first calculated for each compound (MEC_{95}). The MEC_{95} is then compared to the respective lowest effect threshold. In this way, compounds that have a somewhat lower spatial distribution might reveal their "local importance". In this way, one avoids overlooking compounds that might have substantial impact on the local Ecological Status despite a somewhat narrower distribution. The resulting ratio (MEC_{95} over PNEC) can again be directly used for prioritisation. Obviously, compounds whose ratio exceeds a value of 1 would be of much greater relevance compared to those with ratios far below 1, despite potentially similar or even lower concentration levels in the environment.

The selected indicators and score values are reported in Annex II for each of the different action categories.

IV.2.2 Additional data collection, analysis and validation

An additional data collection exercise will be necessary for the ranking process to be carried out. Whereas for the classification into the six action categories, it was possible to make use of aggregated data, for the prioritisation methodology more complex indicators are used. The calculation of these more sophisticated indicators (e.g. frequency of samples above the LOQ) requires the analysis of "raw data". For this purpose, we will create a dedicated tool linked with the NORMAN EMPODAT database, the MODELKEY BASIN database and other relevant databases, which would provide the values for the agreed indicator. Within this tool, simple validation queries for each parameter / indicator could be programmed (correct unit translation, etc.).

The original data sources should remain accessible.

As to the validation rules for the collected data, the considerations described in Annex IV also apply here.

IV.2.3 Definition of the prioritisation algorithm (scoring system)

In general, the indicators used could be seen as different lines of evidence of the hazard that a given substance poses to environmental and human health. For prioritisation purposes, we propose to use a specific, tailor-made set of indicators for each action category, in order to address the peculiarities of each category concerning differences in knowledge gaps / data availability, etc. In this way, indicators that might not be available for "most" substances do not bias the results.
Within a given action category, we propose to normalise the indicator values from 0 to 1 in order to give equal consideration to each of the indicators (each of them having different value ranges, with 1 as the maximum score). Afterwards, the scores of all indicators per substance could be simply added to an overall score. In this approach all indicators have the same weight. However, it would be also possible to increase the weight of one indicator by applying additional weighting factor(s) above 1.
Moreover, a weighting factor could be included for each indicator to address the reliability of the data (e.g. factor 0.5 for predicted values).

Questions to WG / comments

The algorithm for final ranking of the substances needs to be further discussed.

IV.2.4 Application of the algorithm and expert review of the results

As we proposed earlier, it would be most convenient to implement the calculation algorithm within a dedicated tool. All non-numerical information would have to be transformed into numerical values (as given in the table in Annex II) to calculate the scores. In this way, the prioritisation process would be as objective as possible and it would be easy to include new substances. The calculation could be done "on the fly" and the rank of the new substance could be seen immediately.

For the review, the indicator values for all substances could be exported in an Excel table, separately for each category, and checked "manually" by experts for plausibility.

V. Review process

If new evidence is available, the compound should get back into the process!

Questions to WG / comments

Do you agree to perform a review process and help in reviewing the results?

A protocol for: review of the information, substances to be submitted to the process, etc. should be defined and added in this Section.

ANNEX I - Candidate list of emerging substances

ADD final List here! (see separate Excel file)

ANNEX II - Indicators for the prioritisation of substances within each category

Exposure assessment

Indicator	Score value	C1	C2	C3	C4	C5	C6	WF
Frequency of observations above LOQ	% of samples above LOQ	X		X			X	1
Number of countries with analysis	# of countries	X		X			X	0.5
Number of sites with detections above LoQ	# of sites	X		X			X	1
Consistency between investigated matrix and the medium	Yes = 1 No = 0	X	X	X	X	X	X	1
Annual usage [t] 0-1 1-10 10-100 100-1000 >1000	 0 1 2 3 4		X		X	X		0.5
Use index - Controlled system (isolated intermediate) = 0.1 - Industrial (non-dispersive) use = 0.2 - Wide dispersive use (mainly diffuse sources) = 0.5 - Used in the environment = 1			X		X	X		0.5
Analytical methods available: Routine level (NORMAN V3) Expert (NORMAN V2) Research (NORMAN V1) Not available	 3 2 1 0		X		X	X		1
LOQ < lowest effect threshold (YES /NO)	Yes = 1 No = 0	-	-	-	-	-	-	-
Potential for Long Range Air Transport (LRAT):	Yes = 1 No = 0	X	X	X	X	X	X	0.5
Observations in groundwater	Yes = 1 No = 0	X		X	X	X	X	0.5

Effect assessment

Indicator	Score value	C1	C2	C3	C4	C5	C6	WF
EQS available (YES / NO):	Yes = 1 No = 0	-	-	-	-	-	-	-
Lowest PNEC	1 / PNEC µg/L	X	X	X	X	X	X	1
Human health toxicity:	T+ = 2 T = 1… To be completed	X	X	X	X	X	X	1
Non toxic endpoints: - Mutagenicity - Genotoxicity	 3 3	X	X	X	X	X	X	1

Indicator	Score value	C1	C2	C3	C4	C5	C6	WF
- Estrogenicity - Endocrine disruption - Aaryl hydrocarbon receptor - Tumor promotion - Inhibition of gap receptor	3 3 2 2 1							
PBT or vPvB like substances: P B vP vB PBT assessment under way PBT according to results from models	2 2 3 3 1 0.5	X	X	X	X	X	X	1

Risk assessment

Indicator	Score value	C1	C2	C3	C4	C5	C6	WF
Spatial frequency of exceedance of the lowest PNEC (based on MEC_{site})	# of sites showing exceedance of env. threshold / tot. # of sites	X	X	X	X	X	X	2
Exceedance of environmental threshold	MEC_{95} (95^{th} percentile of the max concentrations of all sites) / lowest PNEC	X		X			X	2

Questions to WG / comments

WG is asked to provide comments on the indicators that should be selected for each category. Do you agree with the given proposal?

The values of the Weighting factors (WF) to be assigned to each indicator need to be discussed by the WG.

ANNEX III - Procedure for derivation, validation and application of environmental thresholds

In general, chronic data should be preferred over acute data, which should be preferred over modelled data in the given order of preference for PNEC derivation, depending on their availability. However, to avoid an underestimation of risks due to low assessment factors for chronic data, the respective chronic PNEC will be compared to the acute PNEC and P-PNEC and the lowest value will be taken as environmental threshold.

The latter was decided because of evidence that acute based thresholds ($PNEC_{acute}$) are in good correspondence with observed effect levels in field communities, when considering benthic invertebrates (Fig. 2). Compliance with a respective threshold would ensure at least only minor departures from reference conditions. However, these results also indicate that the EQS that are higher than 1/1000 of the acute LC50 (corresponding to a log Toxic Unit of -3) are most likely not protective in all cases.

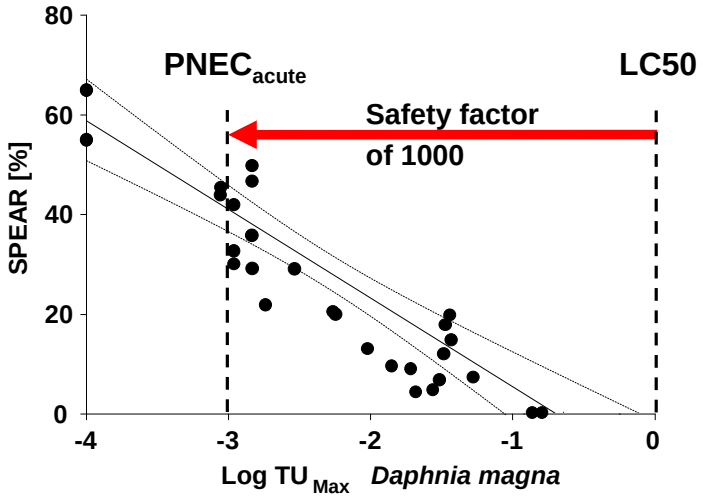

Figure 3 Acute-based Predicted No-effect Concentrations (P-PNEC) compared to a correlation of observed effects on the community structure of aquatic macroinvertebrate communities, expressed as SPEAR index and a measure of toxic stress, calculated as Toxic Units.

Description of the other modelled parameters (To be COMPLETED)

Procedure / methodology to derive P-PNEC

In this study, we use a novel read-across methodology to predict the acute toxicity to three standard test organisms, namely *Daphnia magna, Selenastrum capricornutum* and *Pimephales promelas*. The decision for choosing this method is based on the expected better performance of the method, compared to commonly recommended QSAR models, which are usually based on log K_{ow} and simple molecular descriptors. For the three test organisms, a rather huge number of chemicals are available for read across: about 1000 chemicals for *Daphnia*, about 550 for *Selenastrum* and about 700 for *Pimephales*. Moreover, this method allows to verify the applicability of the model (chemical domain of the training set), which is not given for all the other QSARs. Furthermore, also excess toxic

compounds can be predicted with reasonable accuracy, which is not possible with the commonly used baseline QSARs. In case sufficiently similar compounds were not available, the baseline toxicity estimated from the octanol-water partitioning coefficient (K_{ow}) was used, employing established QSAR models (USEPA, 2008; von der Ohe et al., 2005). If the predicted value was more than 10-fold higher than the expected baseline toxicity of the compound, the 10-fold baseline toxicity value was used. Compounds with a predicted toxicity 10-fold times higher than the estimated water solubility (USEPA, 2008) were excluded from the assessment.

LC50 Daphnia magna & Fathead minnow — Read-across (UFZ)

This method is not published yet and thus to be treated confidentially, and details will not be disclosed before publication. This method information will be updated as soon as a respective paper is accepted.

The read-across approach estimates the toxicity enhancement Te. LC50 is calculated from Te and from the baseline toxicity Tb by

log LC50 = log Tb - log Te

Log Tb is estimated from log Kow:

Log Tb = a • log Kow + b

The read-across set covers 1003 compounds for daphnia and 693 compounds for fathead minnow.

Read-across approach:

Structurally similar compounds in a reference set will be looked up via comparison of atom-centered fragments (ACF). The experimental values of the similar compounds will be weighted by their similarity.

The final result is a weighted average of different runs. Optionally, the results of the individual runs and a read-across code can be displayed (column “code” in the Excel sheets):

4 = compound found in training set and value used, no read-across necessary

3 = 1st order result equal to 2nd order result (no weighting required)

2 = full model - weighted average of 1st and 2nd order model applied

1 = 1st order model only, no sufficient 2nd order similarity

0 = no sufficient 1st order similarity - no valid read-across result

EC50 Algae — From DB/KNN (UFZ)

Acute toxicity (EC50) data towards algae will be provided. First, the database will be looked up. If no database hit is available, a k nearest neighbours approach with nearest neighbours selected by ACF similarity will be applied to estimate the toxicity.

Baseline Toxicity LC50 — Leeuwen et al

Acute (baseline) toxicity LC50 (96h) to the fathead minnow (Pimephales promelas) by van Leeuwen et al.

log LC50 = -0.85 • log Kow - 1.41

n = 68, r2 = 0.94, rms = 0.34

with LC50 in mol/L.

Actually, this equation is a simplification of the model of Veith et al. (1983). Most of the data seem to have been taken from there.

Baseline Toxicity LC50 — von der Ohe et al

Baseline EC50 (48h) estimation for Daphnia magna:

log EC50 = -0.857 • log Kow - 1.281

n = 36, r2 = 0.90, rms = 0.44

with EC50 in mol/L.

Baseline Toxicity LC50 — Algae (UFZ unpublished)

Baseline EC50 estimations for algae

Biomass

log EC50 = -1.0557 • log Kow - 0.4799

with EC50 in mol/L.

Growth rate

log EC50 = -0.9965 • log Kow - 1.2533

with EC50 in mol/L.

Procedure / methodology to derive physico-chemical parameters by QSAR

(TO BE COMPLETED)

Kow — Class-based model selection 25°C

ChemProp tries to get a result for each compound separately, by trying to apply the methods in the order listed below. The first valid result is accepted. However, the default order may be altered for certain compounds, compound classes or values. There are 24 rules implemented. In addition, the application domain of certain models (via atom-centred fragments) will be considered. Default order of using:

1 - Hou et al.
2 - Marrero and Gani
3 - Dubost et al.
4 - Wang et al.
5 - Broto, Moreau, Vandycke
6 - ALOGP [Ghose et al.]
7 - Klopman et al.
8 - Mannhold et al.

Water solubility (Sw) — ACF-based model selection

From the implemented estimation methods for water solubility, a subset of models not requiring the melting point input is considered. In consequence, the sub-cooled liquid solubility for solids is not available.

For each compound, the method with the lowest average error for the most similar compounds of a data set with known estimation errors is selected. The similarity is detected by structure comparison via atom centered fragments (Kühne 2006). Methods to be considered:

From Kow (either estimated or experimental)

1 - Meylan, Howard and Boethling

From structure (purely theoretical models)

2 - Hou et al.
3 - Tetko et al.
4 - Marrero and Gani
5 - Klopman and Zhu
6 - Huuskonen

From LSER descriptors (either estimated or experimental)

7 - Abraham et al.

Chemical Domain by ACFs (refers to all models were available, Kühne 2009):

3 = In: All ACFs are matching including the number of occurrences.
2 = Borderline in: Either the frequency of at least one substructure of the compound exceeds the range of occurrences in the training set, or one substructure is not in the training set at all.
1 = Borderline out: More than one substructures are not in the training set at all, but all 1st order ACFs are matching (without regard to the frequencies).
0 = Out: There is mismatch even with 1st order ACFs.

Koc — Decision tree model (Sabljic et al. 1995, Sabljic et al. 1996)

log Koc is estimated by a hierarchical decision tree, offering 20 different equations in total. The first equation applies to equation 1, while the other 19 equations correlate log Koc to log Kow.

For non-polar compounds, the more precise but also restricted model is Eq. 1 (the one with 1chi), if it cannot be applied, Eq. 2 (more general, less precise) is used.

For polar compounds, a 3-level scheme is applied:
First, there is an attempt to apply one of 14 models (Eq. 7-20) for particular compound classes. The usage is restricted by a log Kow domain, a chemical domain, and a substituent domain. Moreover, assignment must be unique, i.e., there must not be the formal applicability to more than one of them.
If assignment to Eq. 7-20 fails, a more general system of 3 equations (Eq. 4-6) will be tried to be used. Here, the three domains are defined less strictly.
If this still fails, the general equation for polar compounds (Eq. 3) will be tried. There is no substituent domain, the chemical domain is defined to be all compounds not classified as non-polar, and the Kow domain is larger.

Half-lives in air, water, soil and sediment (Kühne et al. 2007)

25°C data are estimated from 3 out of ca. 300 most similar compounds from the data base of half-life classes. Then, the weighted average is reclassified, and the result is the mean value of the respective class. Finally, a simple temperature dependence approach is applied.

Bioaccumulation

The EUSES model (EC 1996, Veit et al. 1979)

estimates the BCF for compounds up to log Kow of 6 by

- log BCF = 0.85 • log Kow -0.70

and for log Kow > 6 by

- log BCF = -0.20 • (log Kow)2 + 2.74 log Kow -4.72

The Dimitrov-Mekenyan (2002) model

log BCF = 3.321 exp (-[log Kow - 6.348]2 / 10.151) + 0.420

log BCFmax = 3.93 exp (-[log Kow - 6.61]2 / 11.9) + 0.931

Fugacity modelling

Calculation of distribution between environmental compartments by using the FUGACITY concept developed by MACKAY et al at 10°C.

According to the complexity of the environment and the exchange between the compartments there are different levels of fugacity calculations.

LEVEL I:

It is particularly useful for assessing the likely general fate in an evaluative environment. It calculates the equilibrium distribution of 1000kg of a chemical without consideration of emissions into special compartments, flow in or out of the environment, transport between the compartments at all, and reaction. It results in an overall fugacity.

LEVEL II:

This level introduces advection and reaction terms into the model. Advection as process of movement of chemical by virtue of its presence in a medium is possible into the main compartments air, water and sediment. Emission is handled as in level I as unspecified emission into the whole environment / region but can be determined by file input. Reactions are treated as first order processes. Reaction rates may be defined for all compartments. The basic concept behind the model is the assumption of the CSTR, the continuously stirred tank reactor thus the environmental media are assumed to be in equilibrium. It results in an overall fugacity.

LEVEL III:

To overcome the weakness of level II in that it assumes the environmental media to be in equilibrium the level III approach incorporates transport or transfer between the media. The processes may be non-diffusive as wet and dry deposition or diffusive as the interphase transfer. For a detailed introduction into the definition and handling of mass transfer coefficients cf. Mackay (1991).

The mass balance is formulated for all main compartments and the linear equation system is solved. It results in as many fugacities as main compartments exist. At the moment it is handled as a four (main) compartment model, which proves to be the best choice at the moment (Mackay (1991)). The resulting fugacities and the concentrations represent the steady state.

ANNEX IV - Data sources and procedures for data validation and data treatment

i. Exposure data

Three main databases will be considered as data sources on exposure for this prioritisation process:

- NORMAN EMPODAT database
- MODELKEY database
- DG ENV database

They contain data on emerging substances, they cover a wide number of countries in Europe and they allow retrieval of information via automatic queries.

The NORMAN database is especially focused on emerging substances and it is regularly upgraded with the data from national monitoring campaigns, results from research projects, etc.
The MODELKEY BASIN database comprises monitoring data for more than 600 substances in many countries.
The DG ENV database was developed for the process of revision of the list of Priority Substances, under the WFD (Art. 16). It represents the largest ever EU compilation of monitoring information for the aquatic environment, amounting to more than 14 million analyses of more than 1000 substances (including several emerging contaminants) in 27 countries.

All data in these databases are validated by the data owners and on this basis they are considered suitable for this prioritisation exercise. In addition, a scoring system is provided by NORMAN for classifying data according to the level of QA/QC information supporting the data (four categories are identified, with category 1 being assigned to “data adequately supported by QA/QC info”). The details of this scoring system are available in the NORMAN EMPODAT database (http://www.normandata.eu/empodat_index.php?menu_type=2) ….

Questions to WG / comments

The prioritisation methodology needs to take into consideration the quality / reliability of the data used. This is still not done in this document. What is your proposal?

However, there are still significant gaps in the collection of data on emerging substances. It is therefore important to stress that these databases cannot be considered as exhaustive in terms of substances or matrices covered.

As a result, where necessary, the above-listed data sources will be integrated with results from recent monitoring campaigns (investigative campaigns from research projects) and information from scientific literature.

As a general rule, official governmental information (monitoring data), if available, and peer-reviewed literature should be preferred over project data which were not quality checked. Expert judgement about data reliability without references could be accepted for the classification process only.

For concentration data, water solubility and original units will be checked.

ii. Production and usage data

To be COMPLETED

From [UK report]:
Where possible, data was obtained from peer-reviewed documents or reliable sources. These included:
- *Central Science Laboratory (CSL) pesticide usage statistics;*
- *Pesticide Safety Directorate database of approved pesticides; (national)*
- *Health and Safety Executive database of approved products; (national)*
- *Review documents such as ESR risk assessments and reviews undertaken by the Organisation for Economic Co-operation and Development (OECD), e.g. Substance Information Datasheets (SIDS);*
- *Environment Agency reviews on veterinary medicines and human pharmaceuticals.*

The scope of these data sources needs to be recognised when using the data. For example, the CSL data on pesticide usage relates to use on crops and would not therefore include data on use on hard standings. Therefore if a key use of a pesticide was to control vegetation on hard standings (e.g. amitrol) the tonnage data provided might underestimate the overall tonnage used.

Questions to WG / comments

The text above is taken from the UK EA Report "Prioritising chemicals for standard derivation under Annex VIII of the Water Framework Directive" - UK Environment Agency (2007)

Question to the WG: Is there an equivalent at EU level? Otherwise how can we make use of national statistics, inventories, etc.? What are the categories of substances for which it will be most relevant to look for production and usage data? (pesticides, pharmaceuticals ??)

iii. Analytical methods validation level:

To be COMPLETED

iv. Hazard data:

<u>PBT properties</u>
For the allocation of a substance as PBT or vPvB we will check if the substance is classified as PBT or vPvB in the Stockholm convention, then in the Aarhus convention – UNICE and finally, classification under REACh - Annex XIII of the REACh Regulation No 1907/2006.

Via this screening process we will be able to identify also substances such as siloxanes which are currently under discussion although they are not yet classified as PBT or vPvB. These substances will be flagged for PBT properties and this will be taken into account in the classification and in the ranking process.

Besides searching for PBT classification, primary data (i.e. half-life water, half-life soil, BCF) will be derived using respective QSAR models (see description above).

PBT properties [From the UK report]:
Where available, international review documents were used as the source of hazard data, as they have often been peer-reviewed. These included:

- *EU Plant Protection Product Directive (PPPD) assessments;*
- *Risk assessments undertaken under the Existing Substances Regulations;*
- *OECD Screening Information Datasheets (SIDS);*
- *WHO Environmental Health Criteria (EHC) reports.*

Where such reports were not available, readily available data sources were used. Key databases were the United States Environmental Protection Agency (USEPA) Ecotox database and the Hazardous Substances Database (HSDB).]

ED properties

Endocrine disrupting potential will be determined based on the review by the EU to identify substances of concern in relation to endocrine disrupters (*Endocrine Disruption classifications according to the BKH (2000)* report[1], *Grouping of substances according to SEC (2004) 1372*[2] and latest update (DHI final report to DG ENV *Study on enhancing the endocrine disrupter priority list with a focus on low production volume chemicals* (2007)) (http://ec.europa.eu/environment/endocrine/strategy/substances_en.htm).

Ecotoxicity data (experimental data)

The data sources for retrieval of experimental ecotoxicity data on aquatic species, for derivation of $PNEC_{water}$, will include the following.

Available *acute and chronic-based PNEC values* will be taken from the COMMPS follow-up report, performed by INERIS (James et al., 2009).

The *acute toxicity* data to *Daphnia magna* will be mainly extracted from a database from:

- von der Ohe et al. (von der Ohe et al., 2005),
- Pesticide Manual (Tomlin, 2003),
- the ECETOX database (USEPA, 2008),
- the RIVM e-toxbase database (De Zwart, 2002),
- the screening information data sets (IPCS, 2008),
- the footprint database (PPDB Management Team, 2009),

and from further open literature.

Data on toxicity tests with the *Green algae (S. capricornutum)* was solely derived from the above mentioned databases.

[1] http://ec.europa.eu/environment/endocrine/strategy/substances_en.htm#report3
[2] http://ec.europa.eu/environment/endocrine/documents/sec_2004_1372_en.pdf

For *P. Promelas*, the experimental toxicity data originated from the so-called Duluth database (Geiger et al., 1990) as well as from the above mentioned databases.

For the validation of the collected data

Questions to WG / comments
Procedure for validation of experimental toxicity and ecotoxicity data: TO BE DISCUSSED BY THE WG

Two-step approach from Environment Canada for the evaluation of the reliability of ecotoxicological data

This approach is based on the Klimisch (source: *H.-J Klimisch REGULATORY TOXICOLOGY AND PHARMACOLOGY 25, 1–5 (1997))*, IUCLID, and U.S. EPA approaches and uses an analogous coding system.

The first step of the evaluation is a general qualitative assessment of the entire study, taking into account the application of appropriate methods, the implementation of GLP principles, the usefulness of the data in the categorisation process, etc. (see table below).

Codes and categories used in the Experimental Toxicity and Ecotoxicity data quality evaluation

Codes and categories	Characteristics
1 (reliable without restrictions)	- Guideline study (OECD preferable) - Thoroughly validated and comparable to guideline study - Test procedures according to national standards followed - GLP principles implemented - All necessary data presented and documentation sufficient for assessment
2 (reliable with restrictions)	Not OECD study, but test procedure comparable to guidelines / standards with acceptable restrictions Study has met basic scientific principles All necessary data presented and documentation sufficient for assessment
3 (not reliable)	- Method not validated - Documentation insufficient for assessment - Important criteria of standard methods not met - Relevant methodological deficiencies

4 (not assignable)	- Only short abstract available - Only secondary literature (review, tables, books, etc.)
5 (not acceptable)	- Only short abstract available - - Only secondary literature (review, tables, books, - etc.)

If a study is considered to have high or satisfactory confidence, the evaluator should perform further assessment. The second step is a detailed evaluation of the information on physicochemical characteristics of the tested chemical, test conditions, data on the test organisms, endpoints, etc. [to be discussed]

ANNEX V - Rules for data preference and data aggregation

Only when experimental data are not available, should predicted values from QSAR be used. The top-five compounds (final ranking) in each category should be validated using experimental data

As a general rule, when more than one dataset is available for a given parameter (e.g. degradation time, or a toxicity endpoint) the average value will be taken in order to take variability into account.

However, for concentrations – level of occurrence – of a substance we will consider the maximum concentration per site for the calculation of the MECs.

TO BE COMPLETED (all situations in which we need to make a decision on data preference should be inventoried in this section in a transparent way).

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Workshop Report
River Basin-Specific Pollutants

Identification and Monitoring

Henna Piha, Valeria Dulio and Georg Hanke

A collaboration between NORMAN and JRC in support of the Water Framework Directive

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Contents

LIST OF ABBREVIATIONS

ACH	Acetylcholine
AMPS	Analysis and Monitoring of Priority Substances
CALUX	Chemical-activated luciferase expression
CIRCA	European Commission Communication and Information Resource Centre Administrator
CIS	Common Implementation Strategy
CMA	Chemical Monitoring Activity
DG ENV	Directorate General Environment
EAC	Environmental assessment criteria
EC	European Commission
EC 10	Effect concentration
ECHA	European Chemicals Agency
EDA	Effect-directed analysis
EEA	The European Environment Agency
Eionet	European Environment Information and Observation Network
E-PRTR	The European Pollutant Release and Transfer Register
EQS	Environmental quality standard(s)
ER-CALUX	Estrogen receptor-mediated chemical activated luciferase gene expression
EROD	Ethoxyresorufin-*O*-deethylase
GC-MS	Gas chromatography-mass spectrometry
JRC IES	Joint Research Centre, Institute for Environment and Sustainability
LC-MS	Liquid chromatography-mass spectrometry
LOD	Limit of detection
LOQ	Limit of quantification
MEDPOL	The Programme for the Assessment and Control of Marine Pollution in the Mediterranean region
MS	EU Member State(s)
MSFD	The Marine Strategy Framework Directive 2008/56/EC
NORMAN	Network of Reference Laboratories for the Monitoring of Emerging Environmental Substances
OSPAR	The Convention for the Protection of the Marine Environment of the North-East Atlantic
PCB	Polychlorinated biphenyl(s)
PNEC	Predicted no effect concentration
POP	Persistent organic pollutant(s)
QA/QC Directive	Commission Directive 2009/90/EC on technical specifications for chemical analysis and monitoring of water, sediment and biota
QA/QC	Quality assurance/quality control
QSAR	Quantitative structure activity relationship
RBSP	River Basin-Specific Pollutants
REACH	EU regulation for Registration, Evaluation, Authorisation and Restriction of Chemicals
SETAC	The Society of Environmental Toxicology and Chemistry
SPM	Suspended particulate matter

TEQ	Toxic equivalent
TU	Toxic unit(s)
WFD	The Water Framework Directive 2000/60/EC
WG	Working group
WISE	Water Information System for Europe

Country abbreviations

AT	Austria
BE	Belgium
BG	Bulgaria
CH	Switzerland
CY	Cyprus
CZ	Czech Republic
DE	Germany
DK	Denmark
EE	Estonia
EL	Greece
ES	Spain
FI	Finland
FR	France
HU	Hungary
IE	Ireland
IT	Italy
LT	Lithuania
MT	Malta
NL	the Netherlands
NO	Norway
PL	Poland
PT	Portugal
RO	Romania
SE	Sweden
SI	Slovenia
SK	Slovakia
UK	United Kingdom

1. INTRODUCTION

1.1. Background

Besides the set of Priority Substances laid down in Annex X of the Water Framework Directive 2000/60/EC (WFD), which are regulated and to be monitored at EU level, the EU Member States (MS) need to identify pollutants of regional or local importance (in particular substances listed in WFD, Annex VIII) and provide environmental quality standards (EQS), monitoring schemes, and regulatory measures for them. This means that MS need to decide which are the candidate substances for further investigation and which are the substances then to be declared as River Basin-Specific Pollutants (RBSP). This requires assessments of impacts as well as prioritisation efforts and strategic screening for substances possibly causing concern. While this is a matter of discretion for each of the MS of concern, there is as yet no harmonisation of the procedures involved.

1.2. Objective of the Workshop

The objective of the workshop was to provide a common forum for MS and interested groups for presenting, discussing and streamlining approaches for a harmonised selection and monitoring of RBSP in the WFD context. Particular attention was given to emerging contaminants, as their prioritisation and monitoring are particularly challenging. The workshop aimed to produce clear recommendations on how to proceed. The workshop was organised as a NORMAN (Network of Reference Laboratories for the Monitoring of Emerging Environmental Substances) annual workshop in collaboration with JRC IES (European Commission, Joint Research Centre, Institute for Environment and Sustainability).

The workshop was held in the same setting as the NORMAN–JRC Stresa workshop 'Emerging environmental pollutants: key issues and challenges' in 2006 - (JRC EU Workshop Report: http://publications.jrc.ec.europa.eu/repository/handle/111111111/846) and was a continuation of the very successful collaboration between NORMAN and JRC IES.

In order to allow a more interactive and constructive discussion during the workshop and in order to plan the workshop according to MS' needs, a questionnaire had been distributed to members of Working Group E on Chemical Aspects and the Chemical Monitoring group on 14.1.2010, both working under the umbrella of the Common Implementation Strategy (CIS) of the WFD. Additionally, MS had been asked to provide their (draft) RBSP lists. A set of working session questions largely based on MS questionnaire responses were also developed and sent to participants prior to the meeting.

2. CURRENT APPROACHES IN MEMBER STATES

2.1. Questionnaire

Responses to the questionnaire were received from 27 countries: 25 MS (except Latvia and Luxembourg), Norway and Switzerland. The following questions were asked:

1. Could you describe in brief (max. two pages to be enclosed with this questionnaire) the procedure applied in your country for the selection of RBSP?

2. Is there a reference document with the full description of the procedure? If yes, please attach it, even if in the national language.
3. What are the critical points/limitations of the procedure applied in your country that you think could be improved in the future? Please describe.
4. Have there been dedicated previous monitoring efforts in order to identify RBSP? If yes, please describe them (project title, duration) and attach/provide links to relevant reports if available.
5. Does your organisation intend to participate in this workshop? (Yes/No)
6. If yes, would you be available for a presentation about the experience in your country? (Yes/No)
7. Name, institution and contact details.

The main findings are set out below, in Sections 2.2 to 2.5. (The full MS responses are presented in Annex 1.)

2.2. Procedures applied by Member States for the selection of River Basin-Specific Pollutants

Although MS applied various procedures for the selection of RBSP, these could roughly be divided into 5 groups (Fig. 1). The majority of MS had used a two-tiered selection approach, in which the first tier involved the pre-selection of substances from the "universe of substances" according to existing legislation (such as the Dangerous Substances Directive 76/464/EEC and its "daughter directives" listed in Annex IX of the WFD, existing monitoring programmes, source identification, etc). The second tier involved the selection of specific substances from the candidate substances. This selection was based on the use of different approaches, the main ones being:

1. Comparisons with emission data, production volume/use
2. Comparisons with monitoring data (i.e. occurrence of contaminants) and toxicity data
3. Use of existing procedures, such as COMMPS (Combined Monitoring and Modelling Based Priority Setting Scheme)[1] or CIS Guidance no.3 Analyses of Pressures and Impacts[2].

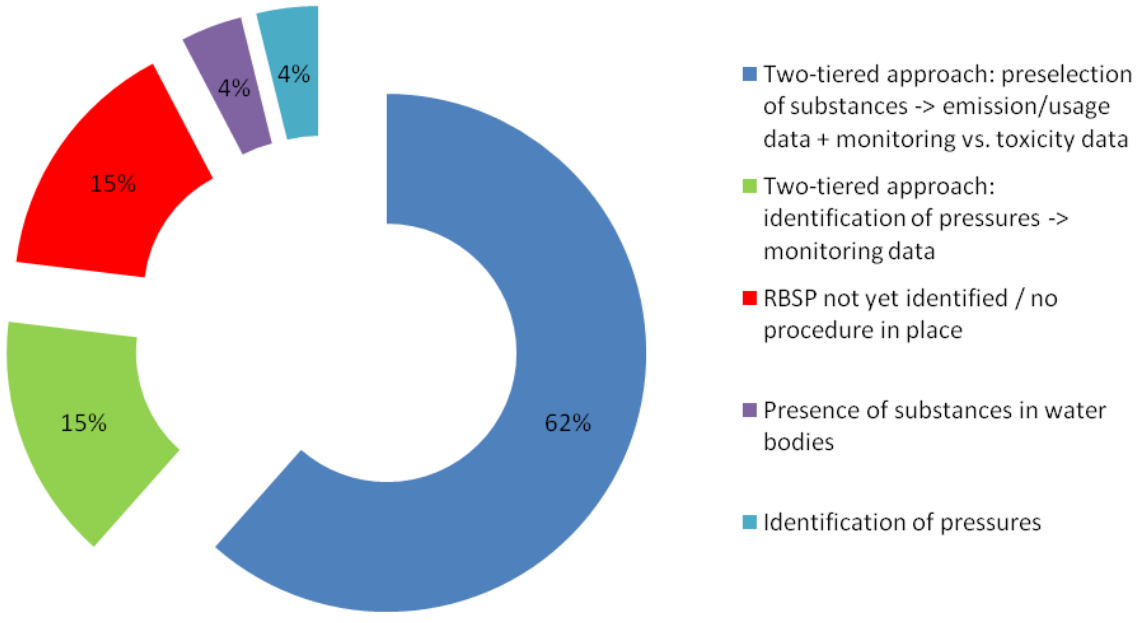

Figure 1. The main procedures applied by MS for the selection of RBSP.

[1] http://ec.europa.eu/environment/water/water-dangersub/lib_pri_substances.htm

[2] http://circa.europa.eu/Members/irc/env/wfd/library?l=/framework_directive/guidance_documents/guidancesnos3spressuress/_EN_1.0_&a=d

15% of MS had used another type of two-tiered approach, where the first step involved the identification of pressures and the use of inventories to produce a list of candidate substances (Fig. 1.). The second step included comparing this list to monitoring data followed by conservative selection of specific compounds.

Both those approaches are iterative, and include further adjustments to substance selections based on obtained results and new monitoring and/or ecotoxicological data.

In some cases, the selection of RBSP was based only on monitoring data (the presence of substances in water) or solely on pressure identification (Fig. 1.). In 15% of MS, RBSP had not yet been identified or there was no procedure yet in place.

2.2.1. Identification of River Basin-Specific Pollutants

From the questionnaire responses it was also possible to derive an estimation of the status of identification of RBSP in MS (additional update checks made with MS representatives in June–July 2010). Four types of situations occurred (Fig. 2.). In 21% of MS, RBSP had been selected, EQS had been developed for them, and they were already established as part of national legislation. In the majority of MS, the process of identifying RBSP or developing EQS was ongoing. In 32% of MS, RBSP had been identified and EQS had been developed/were being developed for them, but these proposals were still drafts or yet to be approved. Also in 29% of MS, only the RBSP had been identified but no EQS had yet been developed. For 18% of MS no RBSP had yet been identified.

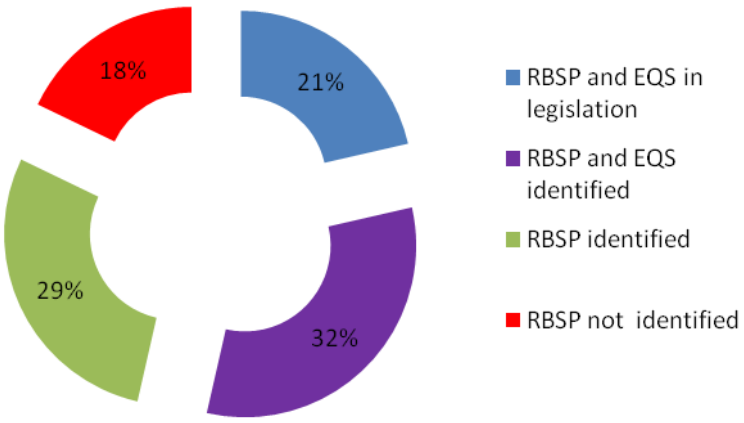

Figure 2. Status of RBSP identification in MS.

The number of substances for which national EQS had been derived ranged from 4 to 170. As requested by workshop participants, national RBSP lists have been compiled and made available to members on Circa:

(http://circa.europa.eu/Members/irc/env/wfd/library?l=/working_groups/priority_substances/specific_pollutants).
The content of the lists may differ between countries and they may include:

- A list of RBSP with corresponding EQS that are already included in the national legislation;
- A list of RBSP with corresponding EQS that are at draft/proposal stage;
- A list of RBSP without EQS;
- A list of substances that are currently monitored.

2.3. Reference documents for the selected procedures

The largest category of MS (37%) was those having referece documents describing the procedures used in identifying RBSP and in setting up EQS (Fig. 3.). For 30% of MS, documents were being drafted or at the

proposal stage, and were therefore still unofficial. For a third of MS the procedures had not been documented (Fig. 3.).

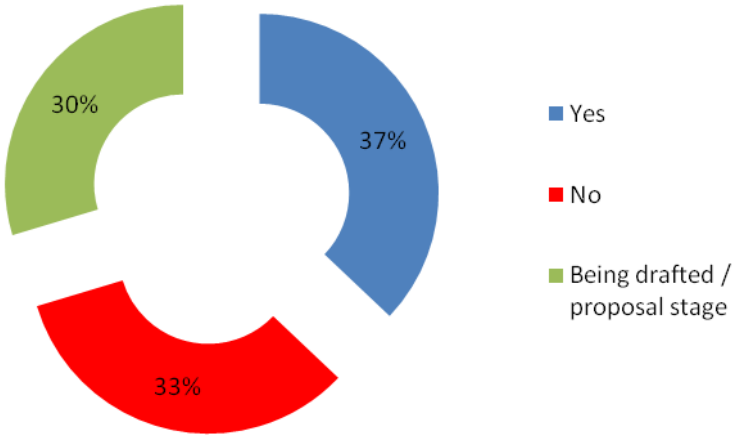

Figure 3. The availability of reference documents for RBSP selection procedures in MS.

The supporting documents received from MS as part of their response to the questionnaire are available via links provided in Annex 1, or as documents uploaded to CIRCA.

2.4. Critical points/limitations of the applied procedures and suggestions for improvements

Because MS identified a wide range of critical points and limitations, the reader is advised to read through the detailed MS responses presented in Annex 1. Some commonalities could, however, be found in the questionnaire responses, and they are grouped under the following themes: 1) general issues, 2) data quality and data gaps, and 3) emerging substances.

2.4.1. General issues

MS identified as a critical point the process of cutting down the potential candidate substances to a manageable number. Problems were also caused by a lack of consistency in the selection of RBSP, as different procedures were in some cases used for each river basin, and by insufficient co-operation between different authorities/stakeholders. The procedure was also seen as time-consuming and expensive. It was noted that a more precise definition of the criterion for the determination of "significant" quantities of pollutants discharged/released into water bodies would be needed.

2.4.2. Data quality and data gaps

The selection of RBSP was clearly affected by issues related to data quality and data gaps. Factors limiting the usability of data included the unreliability of monitoring results, and incomplete registers and databases. It was also seen that improvement of analytical methods is needed to achieve some of the EQS values established at EU level. There seems to be an overarching problem of uncertainty in the selection procedure caused by data gaps. These include:

- Lack of quality standards, emissions data, ecotoxicology and concentrations data
- Insufficient/inaccessible knowledge of sources and pathways (particularly diffuse sources)
- Use/production volumes and import data not available for all substance groups of concern, e.g. pharmaceuticals, cosmetics, pesticides.

2.4.3. Emerging substances

Many MS responses raised the issue of emerging substances receiving too little consideration. It was highlighted that the resources for setting up research programmes for emerging substances are often limited. Additionally, the use of screening methods is in many instances still rather limited.

2.5. Previous monitoring programmes for River Basin-Specific Pollutants

Overall, the pollutants were monitored in all MS under various programmes. It appeared, however, that there were seldom dedicated projects/programmes on the identification of RBSP. Sources used by MS in the identification of RBSP included national environmental monitoring programmes, specific projects and screening campaigns. Monitored matrices covered surface waters, biota, sediments and wastewaters.

3. RIVER BASIN-SPECIFIC POLLUTANTS WORKSHOP

3.1. Organisation

The workshop took place on 10–11 June 2010 in the Hotel La Palma in Stresa, Italy. As the main target group was the competent authorities in MS, invitations were issued through the relevant working groups in the WFD CIS (Chemical Monitoring Activity and Working Group E). The participation of high level scientists was ensured by also issuing invitations through the NORMAN network and by securing the presence of specific experts through direct invitation.

3.2. Working sessions

A main focus during the workshop was on interaction and direct information exchange between participants, achieved by a reduced number of longer presentations and the use of 5-minute flash presentations, introducing intense group work. The agenda of the workshop can be found in Annex 2.

Four different working sessions with specific topics were prepared:

- Data availability
- Identification of RBSP candidate substances
- Selection of RBSP
- Monitoring of RBSP

Workshop participants were divided into 6 working groups. Each of the groups tackled the same set of prepared questions and provided answers to them. In the following, the views of different groups are summarised by question. The answers received to the posed questions have been compiled here with editorial adjustments. They present a picture of the participants' views and are therefore a highly relevant compilation of opinions, needs and perceptions on the topic of RBSP across Europe, without interpretation by the authors of this report.

In Section 4, the key messages have been extracted from the group sessions and edited into a form where they can be transposed into a set of priorities for action within the WFD CIS.

3.2.1. Session 1 'Data availability'

Concentration data availability:

1. *Are data on concentrations of chemical compounds (conventional pollutants and less investigated / emerging contaminants) across Europe available and is the quality of the data sufficient for the purpose?*

    - It is not always easy to get access to data on specific pollutants from other countries, or from different regions within a country.
    - In general, the quality is sufficient but it depends on (the knowledge of) the single substance. Accepted rules are needed and these should be put into practice.

2. *Are databases accessible and practical to use (queries, interoperability, etc.)? If not, how could that be improved?*

   - An overview of existing databases (with links) is needed.
   - Often the screening data are not in databases; only the monitoring data are in databases but not always publicly available. For instance, SE has a specific database for screening data.
   - It would be nice to have easy access to screening data; NORMAN databases could be the way to handle the problem but then MS have to deliver their data to the databases.
   - In FI, for example, there is a central database containing various data, but there are also local databases. Now, these databases are being merged and the central database will be made available. The database is searchable upon request. In NL, a central monitoring database is in place. This database can be obtained upon request. However, in many MS no centralised databases exist.

3. *Are relevant metadata documented – e.g. information on data quality, general physico-chemical data of the water compartment, such as pH, DOC, hardness, etc.?*

   - No, metadata are not well documented. There is info on pH, DOC etc. available but it is often not connected to hazardous substances or not well documented and it is very difficult to link together physical and chemical info.
   - Habitat data are also missing.
   - It would be nice to have a common understanding on the description of the quality, and maybe a common format.
   - The minimum requirements should be added to reporting templates of WISE (Water Information System for Europe) and Eionet (European Environment Information and Observation Network), e.g. LOQ (limit of quantification), LOD (limit of detection), analytical method.

4. *Are reported limits of detection/quantification compatible with PNEC data?*

   - No, not necessarily. This depends on substance and the laboratory, and sometimes on how the LOD is calculated and how much effort there is put into this calculation. Sometimes this is due to insufficient performance of the analytical method. In some cases this can be solved by changing the matrix.
   - It is important to improve PNEC (predicted no effect concentration) first (more robust values) and then see whether a better method is needed.

5. *Is the spatial coverage of concentration data sufficient? Can neglected area types be identified (coastal zones, smaller river basins, etc.)?*

   - In general, there are quite a few measured data for certain systems like coastal waters, estuary data and seas. This again depends on the substance and on the country, and it should also be realised that open seas are marine systems and do not fall within the WFD.
   - MS identified data lacking from southern regions and small rivers (IT), sediment- biota- and small rivers (SK), coastal, biota and sediment (EL)
   - Spatial coverage of coastal zones is sufficient (MT, CY, AT, RO, LT).
   - Surveillance monitoring usually provides quite good coverage. Data are never enough but extrapolation is possible.

6. *Are data for the different environmental matrices available (according to the physical–chemical properties of the substances)?*

   - For some of the traditional pollutants like PCBs (polychlorinated biphenyls)this is not a problem as they have been measured in various matrices. For emerging substances, this is often not the case as most of the data are for water (and not for sediment and/or biota), despite the properties of the chemicals. On the other hand, MS have measurements in the relevant matrices, but water is a compartment that is easy to sample and analyse. In no country is “everything” measured.

- More high-quality monitoring data are needed. Many of the conventional substances are banned; monitoring has stopped for those that are no longer found and more effort is put into monitoring matrices other than water. The problem is that even at the EU level, the limits are set only for water, not for biota and sediment. Most of the data are on water, less on sediments, and least on biota.

7. *Do chemical concentration data need to be comparable at EU level?*

- The reporting should be comparable. Also, units need to be harmonized and laboratories need to participate in inter-laboratory comparisons/evaluations**.**
- It would be important to have comparable databases, and then we also need to have information about national EQS, since these might be different.
- Yes, data have to be comparable, in particular e.g. in the case of transboundary waters.

8. *Is the balance of efforts for monitoring of WFD Priority Substances versus non-listed compounds appropriate? If not, what are the consequences?*

- There is an obligation tomonitor priority substances but not clear obligations on specific pollutants, and for that reason there is an imbalance.
- Basic approach is “not on the list = not monitored on a regular basis”. For the other compounds, in reality there is less attention and only screening studies in combination with emission inventories are sometimes used to provide clues to the presence in the water basin: most attention goes to the regulated chemicals.
- Other compounds are mostly detected within EU projects or research (e.g. national or EU).
- Frequency of monitoring of old compounds could be reduced. Emerging compounds should be monitored more frequently.

9. *What are the major shortcomings in selection and prioritising compounds, caused by a lack of concentration data?*

- An obvious shortcoming is that possible relevant substances (as deduced by modelling on the basis of use and production) could be deselected/overlooked in the prioritisation process due to the absence of monitoring data. It can also work the other way round, in that a selected substance is not of relevance and does not pose a risk.
- Lack of fit-for-purpose monitoring data is also connected with high safety factors when setting EQS.
- Prioritisation based on monitoring requires more similar data for the different compounds.

Ecotoxicological data availability:

10. *Are ecotoxicological data for chemical compounds readily available? What are the sources of these data?*

- Not for most compounds; except for pesticides and biocides.
- There is a lack of chronic data.
- Sources are diverse: databases, general literature, grey literature, industry reports.
- An overview of databases needed: databases sometimes overlap and some databases are quality controlled (validated data), others are not.
- Ecotox data should be collected on a European level.
- An agreement (common quality assessment criteria) on the use of QSAR (quantitative structure activity relationship) data is needed.
- More support from the Commission is needed.

11. *Is the quality of the ecotoxicological data sufficient and documented? If not, what are the shortcomings?*

- Quality is often not sufficient, metadata missing, EC10 (effect concentration) values are needed.
- Not clear what databases can be trusted.

- It is inevitable to check the original publications when deriving EQS and make a Klimisch assessment of data validity. Especially whith respect to data on which the EQS are actually based.
- The main shortcoming is the lack of a standardised reporting format. It is recommended by the group to standardise the reporting of metadata as much as possible.

12. *Are ecotoxicological data for the different environmental matrices available according to needs?*

- No, most information is available for water, far less for benthic organisms. In deriving PNECs for sediment, it was for instance found that equilibrium partitioning had to be used most of the time to derive PNECs for sediment, as sediment data were lacking.
- Lack of bioassay data.
- The information should be provided by the producers via REACH (Regulation for Registration, Evaluation, Authorisation and Restriction of Chemicals) registration. It might not be the situation for "old" substances, and then the input must come from research.

13. *What are the major shortcomings in selection and prioritising compounds caused by a lack of ecotoxicological data?*

- It is currently not possible to decide if there is a potential problem, no (legal) instrument to generate more data. This is also the problem for setting EQS.
- It can have implications for analyses and interpretation of findings. Owing to lack of ecotox data, some standards become very low because of high assessment factors (lower than LOD), causing water bodies to be reported as failing the water quality requirements.
- Difficulty in establishing connections between chemical, ecotox and ecological studies.

3.2.2. Session 2 'Identification of River Basin-Specific Pollutants candidate substances'

1. *What is meant by a substance being discharged in "significant quantities" under Annex V WFD?*

- "Discharged": it would be better to use the term "occurring" rather than "discharged"
- Should be related to:
  - the (risk of) exceedance of a toxicity threshold,
  - risk of changing the status of a water body from "good" to "moderate"
  - what is important is to relate "significant quantity" to risk.
- Quantity, effect and use pattern are relevant information. BUT in reality (pragmatic approach) most MS define a threshold value for "concentration" and for "amount released", above which the substance is identified as candidate RBSP and then exceedance of toxicity thresholds is checked (concentration > EQS or x% EQS).

2. *One important step in the identification of the candidate RBSP is the evaluation of the available monitoring data (comparison with benchmark/target values). How are the existing monitoring data being used when EQS / PNEC are not available? Have you got experience with approaches such as: Toxic Units (TU) / Toxic Equivalent (TEQ) values/Estimation of provisional PNEC (P-PNECs) based on QSAR? What do you need in order to apply them?*

- There is a legal obligation to have a strategy for assessing the data because it is linked to the programme of measures.
- Use of QSAR: it is not yet recognised as an official methodology.
- Nevertheless, QSAR are used by some MS to derive provisional EQS (with high safety factors):
  - useful to estimate a level of concern and warrant whether or not a substance can be deleted from the list of chemicals to be monitored or further investigated/need to look for more info, but should not substitute experimental testing data.
  - QSAR are often used for pesticides: effect-based approach for assessment of total loads of pesticides.
- What is needed in order to apply QSARs:
  - knowledge of the backgrounds of QSAR models
  - some data about the toxicity and the chemistry of the compound

    - experience
    - validation of the models.
- It would be nice to have an exchange at European level of QSAR data used in the prioritisation of substances at river basin level.
- TU/TEQ values are useful for substances with similar mode of action. Less experience with TU/TEQs.

3. *At which spatial scale should the selections of candidate substances be done: local, river basin or national?*

- River basin scale would be the best, in reality in most MS it is done at national level, but should be checked at river basin level.
- In some MS the list of candidate substances from different sources is derived at national level and then the selection of specific substances recommended at river basin level.
- But EQS should be defined at the national level. And for international River Basins consensus should be sought at the river basin level (in particular for substances shared among different countries).

4. *Does the use of target monitoring neglect potentially relevant contaminants, including emerging contaminants as e.g. metabolites and degradation products?*

- Yes.

5. *What should MS do in order to identify relevant candidate contaminants which are not on the monitoring lists? Some possible approaches are:*

   Effect-directed analysis (EDA), use of biological methods (e.g. batteries of bioassays in vitro, in vivo tests, biomarkers), and non-target screening: to complement knowledge of organic contaminants actually appearing in river basin systems, and to orient monitoring programmes.

   Have you got experience with these approaches? What do you need to apply them? How can they be implemented in the monitoring programmes of MS?

- EDA can be a helpful tool to identify/prioritise locations for measures, but EDA needs experience and knowledge improvement.
- Gas chromatography-mass spectrometry (GC-MS) or liquid chromatography-mass spectrometry (LC-MS) screening are already used as a first TIER.
- Biomarkers (such as e.g. EROD (ethoxyresorufin-O-deethylase) activity and vitellogenin in fish) are used for screening purposes and to identify specific pressures in aquatic ecosystems (to be combined with chemical analysis).
- Bio-tests may not really be more costly, since it would hopefully target monitoring to the relevant substances of concern and causing the effects. Normally not enough money for effect studies to search for “unknown” substances.
- Overall, there is some experience with effects studies, but mostly at the project level.
- If it is necessary to use effect studies then clear rules on how to interpret the results will be needed.
- MS are not ready to implement effect studies in their monitoring programmes. But these techniques are seen as promising approaches.
- A need for more research at EU-wide level: pilot cases in different countries for testing before spreading (COHIBA project as an example).
- Guidelines and training are needed for this kind of screening monitoring.

6. *What could be ways for cost effective screening of compounds at Member State or EU-wide level?*

- Non-targeted screening like in Kleve/Bimmen (D/NL) is very helpful.
- A guidance/list of what to remember in order to harmonise the screening studies so that the result can be used by other countries in the future.

- Pan-European screening studies to identify the most relevant substances/less-investigated substances. However, there should be more harmonisation in the sampling strategy (choice of sites), sampling protocols, etc.
- Non-target screening OK: GC-MS less expensive but limited to non-polar compounds. LC-MS with accurate mass is the best choice. It is an investment but it works.
- Systematically reporting of new peaks which appear in the chromatograms. NORMAN role: coordination and dissemination, exchange info. Spectral database for identification of unknown.

Inventory of emissions as a tool for identification of candidate RBSP:

7. *Is the current status of developed inventories of emissions and their update frequency sufficient to identify river basin pressures?*

    - Inventories are not implemented everywhere, apart from the European Pollutant Release and Transfer Register (E-PRTR) which is mandatory.
    - Each MS shall submit national emission inventory data to Centre on Emission Inventories and Projections-CEIP (http://www.ceip.at/emission-data-webdab/submissions-under-clrtap/2009-submissions.
    - In principle it should be possible to use these inventories to identify pressures. It is questionable, however, whether there is sufficient information on emissions to allow for use of the database for monitoring purposes.
    - Emissions inventories are not used and not sufficient today to identify (new) candidate substances because most of the compounds listed are already regulated. Permits focus on substances that are discharged in 'significant' amounts.
    - They could be a useful tool if there are enough data. But the collection of data for new substances is very time consuming and therefore expensive.
    - An update frequency of 6 years is sufficient. Some countries have problems in keeping up with this frequency.

8. *Are diffuse and point sources being taken into account in an appropriate balance?*

    - The situation is very different in the several MS – in general there is no appropriate balance.
    - Data from point sources are normally available depending on the industry obligation to report. Data on diffuse sources are scarce or not included at all (a key problem!), but could be (depending on the substance and other information needed) modelled using point source emissions and monitoring concentrations. New modelling approaches in this direction are being developed, and could be helpful.

9. *What is the most critical aspect in emission inventories that should be improved? And how should it be done?*

    - There have been improvements made – but you have to live with inherently inaccurate and incomplete data.
    - Harmonisation of emission factors at European level, especially for diffuse sources.
    - The list of compounds to be included in the inventories (from discharge permits) should be enlarged.
    - Data are not measured data but just estimated data. There is a need for more measured data and then feed the data into the models.
    - Small enterprises are also not included.
    - Lack of supporting information in emission inventories. The only parameters that are so far provided are: concentration and volume.
    - In some countries: difficulties in exchanging information between different authorities. E.g. industrial permits are released by local authorities whereas monitoring is done at regional level.
    - Clarity on definition of what are: "emission", "discharge" and "losses" is important for correct implementation of inventory.

3.2.3. Session 3 'Selection of River Basin-Specific Pollutants'

1. *Are harmonised approaches available and useful for the selection of RBSP? At which level (river basin, EU, other) should that harmonisation occur?*
    - For general principles, EU-wide seems the most appropriate; details have to be addressed at the national level, and even more at river basin level.
    - EU guidelines are appreciated; harmonisation is needed, but should not be mandatory.
    - In many cases harmonisation is done on a national level: national lists are established. Subsequently, cross-border issues with regard to selection of RBSP are dealt with, making sure that for instance EQS-values do not differ between the two sides of the border.
2. *Does the analytical performance (LOD/LOQ) for a given substance influence the prioritisation process?*
    - Yes of course. If ecotox effect data are lower than the LOD/LOQ the substances can get on the list anyway if their toxicity is very high. However, if the LOD/LOQ is not low enough to detect ecotoxicologically-relevant concentrations, it is not possible to state the relevance of a substance as specific pollutant. Nonetheless, as soon as the substances are on the list, efforts will be made to sufficiently lower the LOD/LOQ.
    - Not only the analytical performance but also the national/local lab capacities on the substances they can analyse may influence the prioritisation.
    - If the process is based on modelling, in theory no influence in the first selection. But if you use monitoring data approach, yes.
3. *Do historical pollutants play a role as candidate substances in the prioritisation process?*
    - Yes, especially pesticides, PCBs, heavy metals from historical mining, military areas, where contaminated areas are identified, but also for substances no longer used in the country but in bordering countries.
    - If there is a danger of the chemicals still being used despite being banned and if the chemicals are persistent in the environment, then they will play a role. There is the danger of accumulation in the food chain, which warrants biomonitoring of these chemicals.
    - In FI, in the first round of priority setting, only intentionally produced compounds are considered for pragmatic reasons and historical pollutants are likely to be included in the second round of prioritisation. In CZ on the other hand, historical pollutants are fully included in prioritisation/monitoring.
    - Overall, if a compound is persistent and if there is evidence that they are still in the environment, then they should be monitored at least at a low frequency to show the long-term trends in the concentrations of these "old" pollutants.
4. *Are there criteria which should be harmonised in all countries for prioritisation methodologies?*
    - An international river basin should be one river body for which there is full harmonisation. The existing guidance is enough (see Guidance Document No. 3 Analysis of Pressures and Impacts *Impress*) at the EU level; there is no need for further harmonisation. At best, updating of the EU-wide guidance could be done.
    - Countries are well qualified to set their own criteria for RBSP. Cross-border issues can be dealt with on a bilateral basis, making sure that EQS are similar across a border.
    - Some relevant criteria are already harmonised (EQS-guidance, Commission Directive 2009/90/EC on technical specifications for chemical analysis and monitoring of water, sediment and biota (QA/QC Directive)), but the definition of "discharge/significant discharge" is an open question, which should be harmonised.
    - Endocrine disrupter criteria needed.
    - Guidance for prioritisation-based monitoring is needed: containing possible criteria for exceedence of thresholds, frequency of exceedence and tools for trends interpretation.
    - Minimum criteria for PNEC and MS could be more restrictive.
    - Harmonisation on safety factors for all compounds: same safety factors for all compounds.

5. *Is the selection of candidate substances done by the same authority for inland and marine environments?*

   - For some MS by the same authority (e.g. DK, FI, FR, IE, NL, SE), but not for all (e.g. MT, PT).
   - The methodological approach for the selection of candidate substances in inland and marine waters can be different to some extent even if they are managed by the same authority, e.g. for hydrocarbon spill related pollutants

6. *How is the guidance from marine conventions taken into account in the prioritisation process?*

   - Guidance and substance lists from marine conventions are taken into account but the final decision is at national level.

7. *Are specific EQS based on marine toxicological data being developed for the marine coastal environment?*

   - EQS derivation is costly and some countries use EQS already derived by other countries after having checked that these can be applied to their own situation. Other MS have specific marine EQS, e.g. FI, NO, and Environmental Assessment Criteria (EAC) in OSPAR.
   - For priority setting there is a lack of marine data (either on the effect or on the exposure site) – so limnic data have more weight. However, since it can be assumed that the main load of marine pollutants derives from freshwater water bodies this approach seems to be protective enough.

8. *Does the robustness of the EQS for a given substance influence the proritisation process?*

   - It is important to assess robustness to have correctly backed EQS: without ecotox data, the robustness is questionable and should thus be taken into account in the prioritisation.
   - Even when the EQS is not sufficiently robust and below the LOQ, the chemical can still be monitored and then there is still the legal obligation to meet the EQS: if the chemical is present and can affect good ecological status, it should be monitored.
   - An important issue is the relationship between EQS and LOQ. Two scenarios are possible:
     1 – LOQ<EQS: no problem
     2 – LOQ>EQS: then further action is needed:
     - When the assessment factors in deriving the EQS are very high, the preliminary EQS might be below the LOQ and then further refinement is needed. Two approaches are possible in this case:
       - 1 – Make the EQS more robust (e.g. by collection of additional toxicity data, or by generation of new data). This would in any case reduce the assessment factors, but it does not rule out that the intrinsic toxicity of a chemical is high.
       - 2 – Lower the LOQ by using the best available methodologies. This might involve development of new analytical methods for the chemical.
     - Another solution is to set an EQS for another compartment (mostly sediment) and make sure that the EQS for this compartment is not exceeded.
   - Not for the prioritisation but for the implementation process.

9. *What is done when concentration data are not available? Use of calculated data based on mathematical models?*

   - Yes, calculated data based on models are used. However, only as a first step; for the next steps measurements have to be done.
   - E.g. in CZ, passive samplers are used to screen for chemicals for which no data are available and screening is done for wide categories of chemicals. FR puts in place additional monitoring campaigns in order to improve monitoring data for less-investigated substances. In FI, modelling is applied on the basis of use amounts and use patterns and resulting emissions. Modelled PECs are derived and ranking of chemicals is performed. This approach still requires screening monitoring in addition. After that, monitoring is put in place taking into account chemicals ranked in the highest classes, and chemicals identified on the basis of screening monitoring.

- In the near future, it will be necessary to investigate what information exists in the European Chemicals Agency (ECHA) database.

10. *What is done if ecotoxicological data are not available? Use of calculated data based on mathematical models? (QSAR, etc.)*

- No use of models but look at other countries' experience and ecotox data. Such models require a lot of data not only on toxicity but on other aspects – and these data are also not easy to obtain – and also expertise to assess the results: resulting uncertainty is to be compared to uncertainty of selecting data or results from other countries.
- Ideally research is started, but it often depends on budgets. Joint efforts could be a solution. Joint databases on research projects would be useful.
- We need in the near future to see what ECHA database will give us.

11. What are the main difficulties in performing the prioritisation?

- Lack of data (monitoring data, ecotox data, emission and use quantities) and resources.
- Suggest gathering at EU level of all existing approaches in Member States or river basins and establishment of general principles.
- Deciding the starting list from pressure and available concentration data.

3.2.4. Session 4 'Monitoring of River Basin-Specific Pollutants'

1. *Are analytical methodologies for the monitoring of relevant substances available? Do they need to be harmonised?*

- Analytical methodologies are often available as a starting point. However, some need to be developed for specific chemicals. This is the case even for some priority substances.
- Harmonisation is not wished for, as there are harmonised performance criteria in the QA/QC Directive.
- Harmonisation of analytical methodologies is required only when the methodology is insufficiently reliable despite availability of standards.
- NORMAN can be used as a platform for info exchange.

2. *Are harmonised strategies for monitoring available and needed?*

- Yes, they are available and needed, but they are not used stringently. Balance between harmonisation and flexibility has to be ensured.
- Sharing of experience on sampling could also be relevant, either nationally or for on-site trials.
- Additional guidance and additional harmonisation are needed. In some cases only widely approved methods are used in monitoring, despite their being out of date. Harmonisation would minimise this problem and make sure that methods are up to date.

3. *Are levels of detection/quantification of analytical techniques for relevant compounds appropriate (e.g. in relation to EQS)?*

- Examples of EQS below LOQ are available and there is no good way of solving this problem. Two approaches are possible: refine the EQS on the basis of additional data, or lower the LOQ by means of technical method improvement.

4. *Could cost effective screening for compounds be organised at EU level?*

- Yes, MS are eagerly anticipating this. The question is to what extent countries are willing to make a contribution, but it is the general impression that countries are willing to make a contribution. It would reduce costs, make data more comparable, and in general it would be more efficient. From a political point of view, it would also make sense. Good planning, good sampling strategy and assessment of the main aims of EU-wide sampling campaigns would be essential elements to be considered explicitly.

- It is important that the cooperation of countries is "mandatory". OSPAR experience was not successful.
- A test of lab performance should be included.

5. *Are Gas Chromatography/Mass Spectrometry and Liquid Chromatography/ Mass Spectrometry non-target screening methods in (routine) use?*

- They are in use in many but not all MS. However, not widely/routinely applied.

6. Are other screening methods in use?

- Biological screening methods are in use as research programmes, although at a lower frequency and aimed at specific biota and/or endpoints. One of the aims is to do some monitoring for chemicals with very low EQS. On the other hand, biological monitoring is applied for specific classes of compounds only.
- Another screening method in use is ecotoxicity testing of effluents.
- Some biomarkers such as the CALUX (chemical-activated luciferase expression) assay are adopted in the monitoring plans for screening and classification.
- In NL for sediment classification after dredging.
- Biomarkers: Hydroxy pyrene (NL), passive sampling.
- Biological tests: ER-CALUX (estrogen receptor-mediated chemical activated luciferase gene expression) – endocrine (e.g. surface water for drinking water, NL), ACH (acetylcholine) tests are not applied any more (sensitivity is not very high).
- Antibiotics test (NL) – in-between regular monitoring and research.

7. Which biological effect methods for screening are in (routine) use?

- Biological early warning systems (e.g. daphnids) for operational process but not yet reported in the databases.
- Biomarkers for specific pollutants are generally used, usually on a project basis. A limited number of early warning on-line continuous monitoring systems are in use (like an early warning system based on daphnids). In some wastewater treatment plants some biological early warning systems are applied, as well as in drinking water production.
- Biomarkers in use are quite diverse and vary across a wide range of endpoints.
- EROD, yeast assay, CALUX. In marine there is an official action in OSPAR for biological effects monitoring.
- See also responses to previous question.
- There are three conditions for using biological tools: 1) guidelines (how to do it), 2) quality criteria, and 3) assessment criteria. OSPAR is developing assessment criteria for a set of tests and when the three conditions are fulfilled the test is implemented in routine monitoring.
- Biological effects-based monitoring will be the future because this route allows mixture effects to be taken into account. But data assessment has not been straightforward up to now. Need for managing tools for biological effects data.

8. *Are monitoring results from scientific projects/campaigns being considered?*

- Yes, but information exchange could be improved. Usually the information comes at conferences (e.g. The Society of Environmental Toxicology and Chemistry (SETAC)) and scientific literature. The existing databases should be used.
- In some cases (e.g. in biological monitoring) most results are derived from scientific projects instead of routine monitoring, e.g. Austrian programme run by Environmental Agencies for pesticides in groundwater was triggered by literature screening and field measurements.

9. *Which promising techniques for future assessments need further development?*

- Molecular biology "OMICs" – as biomarkers
- *In situ* sensors

- Passive sampling, including aspects of calibration (passive sampling has the advantage of obtaining time-averaged concentrations of chemicals)
- Sampling of biota and sediment
- Use of suspended particulate matter (SPM) as sampling matrix. This is especially attractive as it may be more sensitive than other techniques
- GC/ and LC/MS screening
- EDA
- Automated screening methods integrated with biological effects. More software tools needed for automation of identification of compounds from screening results
- High throughput bioassays (batteries of tests)
- Cost-effectiveness models for decision-making on which methods should be further developed
- Database on information on partition coefficients will be valuable.

4. WORKSHOP CONCLUSIONS

During the workshop itself, participants were given preliminary feedback on the outcomes of the working session discussions. While the discussions identified key priority areas, this could only be a starting point for further communication, harmonisation and interaction between stakeholders in RBSP identification and monitoring.

4.1. Key messages

Some key messages are provided here as they were presented at the end of the workshop, based on an initial analysis of the outcomes of the thematic sessions:

4.1.1. Accessibility/availability of monitoring data

Exchange/consultation of concentration data at EU level wanted

- Shared monitoring data through a database at EU level, NORMAN database for emerging pollutants wanted, in order to improve overview of status of contamination.

Common data format (concentration + metadata) needed to improve interoperability of databases and enhance exploitation of available monitoring data

- A common DG ENV-EEA data collection template is already available, used during DG ENV EU-wide data collection, also adopted by NORMAN. Implementation is needed at MS level.

4.1.2. Accessibility/availability of ecotox data

Exchange of ecotoxicological data at EU level needed

- A common exchange platform at EU level is needed to improve interoperability.
- There is a wish to have a list of databases for ecotoxicological endpoints, including meta information on data quality, effect modifying parameters, compartment, internet links, etc.

Common quality criteria for ecotoxicological data assessment are needed for improved data exchange

- These are under development (multilateral exchange – MS level), but action is needed at EU level.

Ecotoxicological data (chronic) missing for a great number of substances and the quality of available ecotoxicological data is not ensured

- Prioritisation of efforts is needed: alternative tools (e.g. QSAR) can help orient priorities (i.e. identify potential problem chemicals).
- It is necessary to improve the availability of quality-describing metatada.

4.1.3. Selection of River Basin-Specific Pollutants

More resources needed for investigative monitoring of RBSP candidates

- Collaboration at EU–level is useful for efficient use of resources in investigative monitoring.
- EU-wide monitoring programmes: useful exercises to improve use of resources in investigative monitoring. MS should be directly involved in planning and in the setting-up of EU-wide monitoring programmes. More harmonisation in selection of waters to be sampled is considered useful to help investigative campaigns (stricter guidance on selection of the water types, background vs affected areas, etc.): increasing effort in more harmonised sampling strategies and approaches.

No further guidance with rigid criteria is needed for RBSP identification/selection

- Exchange of experiences at EU level in WFD CIS is most welcome and useful.

Harmonisation is only needed in specific cases

- QA/QC (quality assurance/quality control) criteria have been established and should be implemented; harmonsation in WFD CIS should apply for new analytical methods.

4.1.4. Monitoring of River Basin-Specific Pollutants

Analytical methods not readily available for some substances

- QA/QC criteria have been established and should be the basis for method selection.

Improved screening techniques needed

- An exchange of experiences at EU level is wished by MS (activity will be launched by JRC and NORMAN in WFD chemical monitoring group).

Few specific approaches for marine environment

- Availability and use of marine toxicological data should be ensured, experience from marine conventions should be used.

4.1.5. Additional suggestions provided by a final discussion round

- There is a need to finalise the process which would guarantee that EQS for a certain substance are established based on the same approach and quality assessment criteria.
- Suggestion of setting a “threshold EQS” that would apply to all MS.
- There is a need to set up criteria to decide when a substance not present in the environment (values < LOD) should no longer be part of routine monitoring programmes.
- Data which should be shared among all MS:
  - EQS
  - Methodologies
  - Ecotox methodologies (bioassays, biomarkers)
- Strong support for harmonisation in order to ensure comparability between MS. Implemented performance criteria would guarantee this.
- Support for a workshop on sampling procedures.

4.2. Workshop follow-up

MS agreed during the workshop to start exchanging their (draft) RBSP and national (draft) EQS lists within CIRCA. The contributions have been collected by JRC IES and have been forwarded to DG ENV for publication on

the WFD CIRCA site. The further completion and continuation of this information exchange is suggested, utilising the WFD CIRCA platform.

Analytical screening methods, their availability, harmonisation and information exchange on their use for the identification of RBSP received much attention during the workshop. JRC and NORMAN are therefore planning a dedicated action in order to provide a platform at European level for discussion and practical intercomparison exercises.

4.3. Links

The workshop presentations together with other relevant documents are available on the public part of CIRCA (http://circa.europa.eu/Members/irc/env/wfd/library?l=/framework_directive/implementation_conventio/workshop_pollutants&vm=detailed&sb=Title).

National RBSP lists have been compiled and they are available to members on CIRCA (http://circa.europa.eu/Members/irc/env/wfd/library?l=/working_groups/priority_substances/specific_pollutants).

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ANNEX 1. QUESTIONNAIRE SUMMARY

Procedures applied by Member States for the selection of the River Basin-Specific Pollutants

Could you describe in brief the procedure applied in your country for the selection of the River Basin-Specific Pollutants (RBSP)?

AT

The Austrian Federal Ministry of Agriculture, Forestry, Environment and Water Management contracted the Federal Environment Agency (UBA) to draw up a list of the pollutants relevant for Austrian surface waters. These pollutants were selected as follows:

Selection of the relevant pollutants:

Pre-selection of a list of candidate substances from the following official lists and programmes:

- List of substances from the Communication from the EU Commission 1982
- List of the annex of Council Directive 76/464/EEC
- Priority substances pursuant to Decision No. 2455/2001/EC
- Substances from the emission inventory under Council Directive 96/61/EC
- Other individual substances from the annex of Council Directive 76/464/EEC
- Other substances which represent a potential danger to surface waters, selected by expert judgement
- Other dangerous substances with sufficient data from the Austrian Water Quality Survey ("Wassergüteerhebungsverordnung", WGEV) from 1995 onward.

This selection resulted in approximately 320 candidate substances. From these substances the subset of relevant substances was selected on the basis of the following rules. A substance was classified as relevant if it was identified as relevant either from emission data ("emission targeted relevance") or from ambient concentration data ("quality targeted relevance").

Assessment of emission targeted relevance:

Plant protection products

Plant protection products were selected if their annual use exceeded thresholds of 10 t/a (for herbicides and fungicides) or 1 t/a (for insecticides) and if the use of these pre-selected substances under worst-case scenarios would lead to a significant impact on the water quality (exceeding of the PNEC = predicted no-effect concentration).

Other pollutants

From among the other pollutants relevant substances were selected by the Institute for Industrial Ecology (as a subcontractor of the Austrian Federal Economic Chamber and the Federal Environment Agency). A substance was assessed as relevant if a local risk from point sources was identified on the basis of available information about the use of the substances in industry or trade. For this purpose a detailed assessment scheme was elaborated. For more information see study report.

Assessment of quality targeted relevance (ambient concentration targeted relevance):

For the purpose of testing the quality targeted relevance the data of the Austrian Water Quality Survey were assessed (including all data of the past five years). The assessment criterion was determined as follows:

- Where available, the PNEC (predicted no-effect concentration) from risk assessments was used.
- If no PNEC value from risk assessments was available, PNEC values were taken from the COMMPS study on the selection of priority substances.
- If no PNEC was available from the COMMPS study, the lowest value from a collection of national and international quality objectives was selected.
- The assessment criterion was reduced by a factor of ten for monitoring stations at the Danube River basin.
- If for a particular substance the assessment criterion was lower than the detection limit of the respective analytical method, the detection limit was used as the assessment criterion.

The assessment criterion was compared with the monitoring data as follows:

- For each monitoring site the arithmetic mean of all individual monitoring data was calculated. Values between the analytical detection limit and the limit of quantification (determination limit) were calculated with half of the limit of quantification. Measurements below the analytical detection limit were calculated with a value of 0.
- A substance was classified as relevant if the so-determined mean of the concentrations was above the assessment criterion at one monitoring site at least.

Individual substances for which no sufficient data were available to assess their relevance as described above, an expert judgement was carried out. More details on this assessment can be found in the final report of the study of the Austrian Environment Agency "Dangerous Substances in Surface Waters – technical basics in support of the Austrian programmes under article 7 of Council Directive 76/464/EEC" → see folder Austria on CIRCA**.**

BE **Setting EQS for specific pollutants**

Annex V of the WFD is asking member states to establish EQS for the specific pollutants, identified as being discharged in significant quantities into the waterbodies. Flanders, didn't actually make a selection of these substances but it established standards for a large amount of dangerous substances, still resulting from the Directive on Dangerous substances (76/464). This is also important because EQS for dangerous substances are relevant for the link with the permit system. So the situation in the Flemish Region is as follows: since 21st of May 2010 there exist official EQS for about 170 dangerous substances, covering the substances of the daughter directive 2008/105, but containing as well EQS for the so called "other pollutants". This was still necessary within the scope of the Directive on Dangerous Substances (76/464) for which Belgium underwent an infringement procedure at the Court of Justice in 1999, as a result of not adopting reduction programmes including EQS for the 99 listed dangerous substances.

In our reduction programme (2000) standards for about 170 dangerous substances were announced. This led to a decision by the European Commission that the Flemish Region was in line with Directive on Dangerous Substances. Implementation of this reduction programme leads now to this list of about 170 dangerous substances (41 of Directive 2008/105, 99 "black list substances" and the most important "grey list substances").

These EQS are set up as specified in Annex V (1.2.6) of the Water Framework Directive.

Within the next generation of River basin management plans, we will –based on this list of 170 substances - make a further selection of the relevant RBSP.

Screening for new substances

Besides this process of establishing standards, we are doing also some work on screening for new substances:

- pesticides

There is a screening programme for new pesticides on a limited number of locations and with a limited frequency. Based on these obtained measurements, sales figures, and PNEC- and MAC-values there 's decided which pesticides are relevant to be implemented in a larger monitoring programme, in order to obtain more information.

- endocrine disruptors

The Flemish Environment Agency measures in total a selection of about 40 substances from the EU-list that protruded from the EU-Strategy on Endocrine Disruptors, 1999.

A project is going on to monitor anti-androgenic substances because, from scientific literature, it is known that these compounds can play a role in the mechanism of endocrine disruption in surface water.

On the basis of these results the further approach and policy will be developed.

- ecotox

Effect based water quality tests are used to flag up effluents of concern (as a complementary tool to the substance- based approach). The whole effluent assessment includes tests for the determination of

persistency or biodegradability, acute and chronic ecotoxicity, genotoxicity/mutagenicity and endocrine disruption.

BG The process of identification of RBSP in Black sea basin area, West Aegean River Basin Directorate – Blagoevgrad, and East Aegean River Basin Directorate – centre Plovdiv has passed through two stages.

First stage was identification of possible specific pollutant within each river basin/water body by means of an overview of all possible sources of such substances. In this process was used information concerning point and diffuse source available within each basin/water body in particular:

- Information about types of industrial enterprises; raw products that are used; production processes and water purification processes;
- Information about enterprises connected to municipal waste water treatment plants/sewerage systems and information about water purification processes;
- Information about programs for elimination of old ecological damages;
- Information about substances that may be present due to widespread processes (like nonylphenols, octylphenols, PAHs);
- Information about substances that may present due to agricultural and forest management practices;
- Information about substances that may present due to influence of landfills.

The choice of substances is based on:

1. Methodological approach developed under SWIFT "**S**creening methods for **W**ater data **I**n**F**orma**T**ion in support of the implementation of the Water Framework Directive" guidance document;
2. Substances that are required to be monitored in the effluent water from IPPC and non-IPPC enterprises according to their permits;
3. Substances that are required to be monitored in the effluent water from WWTPs and sewerage systems according to their permits;
4. Information concerning applied pesticides and permitted for application pesticides within river basin district;
5. Substances that are detected in the effluent water and/or natural waters (river, lake) from previous monitoring programmes.

According to this approach applied during 2006 we have chosen the relevant pollutants to be included in the first monitoring programme under art. 8 of WFD.

Second stage is based on methodological approach developed and applied under topic 3 "Development of environmental quality standards for surface water", National project "Development of River Basin Management Plans" financed by Operational Programme "Environment 2007-2013".

A list with specific chemical pollutants for water environment is developed following the next steps:

1. Organic compounds identified as specific pollutants:

For identification of organic compounds was used Methodological approach COMMPS (Combined Monitoring-based and Modelling-based Priority setting Scheme) and EU IMPRESS (IMPacts and PRESSures)

After a review of:

- The used raw materials and products in industrial enterprises;
- A reference for published data for possible pollutants according to BREF;
- A choice of chemicals used in agricultural practice – on basis of permitted and banned products;

a combined approach is chosen for determination of organic compounds as specific substances, which include:

1. 1 Pollutants in relation with their environmental effects. For this aim Fraunhofer Institute data are used (represented as bioaccumulation, toxicity, carcinogenic / mutagenic effects). They are summed in order to get the total effect.

1.2. As a second step for the received values is prescribed a rank (as in IMPRESS) in order to be comparative with pollutants for which there are no data (the aim is to receive comparable data for all investigated pollutants).

1.3. In order to take into account the distribution of these pollutants and to use monitoring data a qualitative approach is used: value 1 is given to each positive result such as: a value at the method detection limit; usage; pollution etc. After a prioritization in the list are included all substances having a rank over 7,5.

A group of pesticides (nevertheless they are not classified according to the above mentioned approach) are included in the list of substances to be monitored in order to be assessed their presence in the water bodies:

- organophosphorous pesticides due to their big toxicity;
- triazin herbicides, MCPA, bentazon – due to their big solubility in water.

Some of them are already stopped from being offered at the market but still are persisting in water bodies and other media in the environment.

1. Metal ions identified as specific pollutants

A review of year reports made by the enterprises according to the IPPC permits is made. Data presented are reviewed and approach according to COMMPS is proposed as it is more suitable to rank toxic elements.

Thus the following elements were identified: Ag, Al, As, Co, Cr, Cu, Fe, Mn, Sb, Se, V, Zn.

In order these elements to be prioritized to those of them which cause carcinogenic, mutagenic and toxicity effects is given bigger weight, so at the end the following list was identified: Al, As, Cr, Cu, Fe, Mn, Zn (U, Ra).

For the Danube River Basin Directorate:

For a period of three years 2006-2009 a list of substances was monitored according to the programmeand schedule proposed from RBDR (river basin Danube region). The list of substances for this programmewas obtained taking into account main point sources for surface water pollution - industrial activities: small and medium enterprises discharging via waste water treatment plants, solid waste management, historical pollutions, stored banned products, large enterprises with their row materials, products, purification systems and degree of purification achieved, as well as the diffuse sources mainly agriculture activities, atmospheric depositions, transport and infrastucutre. The basic list under prioritization includes substances coming from List II of Dangerous Substances Directive, substances coming from permits for discharges, substances covered from existing legislation, widely used pesticides. In this way a kind of “Universe of chemicals” was defined. The process of prioritization was based on the method COMMPS (Combined Monitoring-based and Modelling-based Priority setting Scheme), Fraunhofer-Institut, Umweltchemie und Ökotoxikologie, Germany and ranking procedure used from UKTAG (UK). As it is recommended toxicity, persistence and bioaccumulation are main properties taken into account in ranking procedure. Positive results from monitoring programs, production quantities, well known historical pollutions were included with a kind of weight coefficients in ranking procedure. Additionally highly toxic pesticides (from the monitoring programs of Danube and other national projects) were included in the final list of substances.

CY For the selection of the RBSP in Cyprus, the analysis of anthropogenic pressures carried out for the WFD Art. 5 reporting was used. The pressures analyzed in this framework had been:

Surface waters:

- Urban waste water
- Industrial waste water
- Mines and quarries
- Storm water
- Solid waste (landfills)
- Agriculture runoff and infiltration
- Livestock waste

- Other types of pressures
  - hydromorphological pressures
  - aquaculture Climatic conditions

Groundwater:

- Saltwater intrusion
- Water abstractions (drinking water & agriculture)
- Agricultural activities (incl. livestock)
- Industrial activity
- Urban waste water (non-sewered)
- Solid wastes

Climatic conditions

The results of this analysis were reviewed for the WFD Art. 8 reporting, where a conservative approach was applied for the final selection of the substances to be monitored at each monitoring station. In addition, all available results of previous monitoring programmes were taken into account. The monitoring programme was reviewed in end-2009 and adjustments were made based on the knowledge and experience gained during 2007-2009 (substances systematically detected, etc.). The adjusted programme is in place since January 2010. It should also be kept in mind that heavy industries etc. do not exist in Cyprus, and therefore systematic releases of pollutants are very limited.

CZ There is no integrated procedure for selection of RBSP in the Czech Republic at this time.

DK Monitoring of hazardous substances is covered by the Danish national monitoring and assessment programme for the aquatic and terrestrial environment in the following subprogrammes:

- marine areas
- watercources
- lakes
- groundwater
- point sources.

The current monitoring programme, NOVANA is under revision, and the revised programme is scheduled to start 1 January 2011. The procedure described in the following has been used for selection of substances in the revision of the programme.

Surveillance monitoring

The selection of substances for surveillance monitoring is based on:

- obligations in directives, national legislation and international conventions (listed in prioritised order)
- knowledge about the occurrence of the substances from the monitoring up till now
- knowledge about the occurrence of the substances from screening studies
- availability of analyses of satisfactorily quality.

Initially, all substances which might be relevant for monitoring in each subprogramme/matrice have been listed (gross lists). The gross lists have besides the information mentioned above, also information on consumer pattern and the probable discharge. Weighting of the information have led to division of the gross list into three other lists:

- list of monitoring substances
- list of substances, which not will be monitored, because they have not been detected or been detected in very low concentrations with no environmental impact in previous monitoring, or due to an assessment that occurrence is not probable
- substances with insufficient data for the assessment of the relevance of monitoring. These substances are candidates for screening studies, which are a part of the monitoring programme. If the conclusion of the screening study is that monitoring of the concerned substance is relevant, the substance will be included in the monitoring programme.

The lists of monitoring substances are assessed across the subprogrammes in order the ensure

connection between the matrices. Besides, the lists are assessed in order to identify any substances of minor relevance with are not on the lists, and which without much effort (very cheap) can be included in the analysis, e.g. some pesticides or PAH.

Operational monitoring

In the operationel monitoring the lists of substances are based on the knowledge of potential source in the catchment areas which are responsible for the risk of failing to meet the environmental objective in each waterbody.

A list of substances which normally are relevant for specific sources, have been set up. The specific sources are:

- waste water treatment plants with advanced treatment
- waste water treatment plants with very simple treatment or sparsely built-up areas
- separate stormwater outfalls
- overflow from shared sewer
- factories
- fish farming
- maine dumping
- agriculture
- ship traffic
- soil pollution.

Locally other substances should be included due to knowledge about use in the catchment area, e.g. in a factory. The selection of pesticides is based on the growth of a certain crop.

EE For the selection of RBSPs inventories and investigative monitoring (screenings) activities are periodically carried out. In the frames of inventories mainly larger and most important wastewater and industrial wastewater discharges are chemically monitored. Investigative monitoring is focussed to the chemical quality of recipient waters and/or biota. Based on the results of those activities, the concentrations and pollution loads are clarified and relevant substances are introduced to the legislation and/or RB management plans.

FI **Selection of substances**

Substances covered in the selection were mainly intentionally produced substances.
The following substance groups were excluded:
- Process born substances
- Substances present only in imported articles (e.g. brominated flame retardants)
- Substances covered by other legislation than the Chemicals act and Pesticide act
Selection procedure consisted of three stages; initial candidate list, prioritisation of the initial list and final selection

1. Initial candidate list (279 substances)

1a. Previous work conducted in SYKE
- Johanna Peltola: "Proposal for Criteria for the Selection of Hazardous Substances for Environmental Monitoring"
- Sanna Koivisto: "Selection of hazardous substances for the risk management" (PBT-criteria, NSDB-database)
1b. International priority lists
- Water Framework Directive Annex X
- Dangerous Substances Directive (76/464) list I and II
- OSPAR and HELCOM
- EU candidate list of endocrine disrupters
- List of PBT & vPvB substances identified by QSAR-modelling
- Potential PBT & vPvB substances identifiend among HPV chemicals in IUCLID

2. Prioritisation of the initial list

- Use volumes (Finnish register of chemical products)
- Use pattern; Use Pattern Score, UPS = EF x number of activity sites

Substances that fulfilled the following criteria were selected for further assessment:
- Use volume > 100 tons or
- UPS > 500 and use volume > 10 tons or
- UPS > 6000

3. Final selection

- Evaluation of data
- Substances that fulfilled the following criteria are proposed:
  Toxic: (EC/LC50 $\leq$ 10 mg/l), and
  Persistent (degradation $\leq$ 70 % in ready test), and
  Bioaccumulable: (BCF $\geq$ 500 or logKow $\geq$ 4) and
  -very Toxic (EC/LC50 $\leq$ 1 mg/l) and Persistent or Bioaccumulable
- PESTICIDES; Expert Judgement and Pesticide Indicator
- METALS; monitoring data
- ORGANICS (excluding pesticides); risk assessment on aquatic environment (Finnish Environment Ministry 2005);
  - based on data on use volumes and use pattern type
  - modeling and measured data was utilized
  - information on relative importance of uses/sources $\rightarrow$ ranking into 3 categories

Nationally selected hazardous / harmful substances including industrial and consumer chemicals and pesticides in Finland are shown in Table 1. (see Annex and CIRCA)
The procedure for the nationally selected hazardous substances has been described in more detailed way in a separate SYKE publication (Londesborough 2003, in English).

EQS derivation

Environmental Quality Standards (EQS) were established for this set of substances in 2006. The EQS values were derived according to Annex V to the WFD, point 1.2.6. The methodology used is described in detail in the Fraunhofer report on EQS setting for Community Priority Substances (Lepper 2002) and the principals and methodology given in the Technical Guidance Document for the risk assessment of new and existing chemicals (TGD 2003). For pesticides the principles and methodology given under directive 91/414/EEC was taken into consideration. The EQS values are based on experimental ecotoxicological data. The derivation procedure has been reported in more detailed way in a separate SYKE publication (Londesborough 2005, in English).

FR Cf. 2.

DE The German list of the RBSP contains substances, which are not part of the Directive 2008/105/EC (EQSD) and which could contribute to pollution. The list contains substances which were part of the legislations of the federal states for the implementation of 2006/11/EG and WFD. For these substances national EQS will establish, in the last years in accordance to Annex V, No 1.2.6 WFD.The list of RBSP is regularly updated on the basis of new information.

With the next update new substances will be added, which were discharged in a significant amount in at least on German river basin in at least one year of 2005 – 2008. Before the inclusion there was a two-stage relevance check: First, an approximate assessment was done regarding REACH criteria on ecotoxicological and human toxicological relevance. This evaluation was done for substances, detected in surface waters. Only for substances, for which after these approximate assessment it will be probably, that these substances have concentrations about the expected EQS, a detailed EQS derivation in accordance to Annex V, No 1.2.6 WFD, was done. At least the “new” EQS were checked against actual monitoring data and relevant substances with low safety factors will go into the political and legislative process with the aim of adding these substances to the list of RBSP. For more information see background paper on CIRCA.

EL In the context of applying Water Framework Directive in Greece an extended National Monitoring Programme regarding chemical substances, has been conducted since 2006. This monitoring programme consists of sampling and analyzing for more than 155 chemical substances including all priority

substances (defined in EQS Directive 2008/105/EC) as well as 7 substances from List I and 115 substances from List II of Directive 76/464/EEC. According to the results of this survey for each river basin a specific pollutant catalogue has been determined that includes all substances that their annual concentrations exceed 20% of the respective National EQS. All these compounds have been considered as potential pressures and will be subjected to reevaluation after gathering more analytical results.

HU The complete territory of Hungary is within the Danube river basin, therefore the Hungarian principle for the selection of river basin-specific pollutants (RBSP) was the application of Danube river basin-specific pollutants. The "Convention on cooperation for the protection and sustainable use of the Danube River (Danube River Protection Convention)" specified a "Guiding list of hazardous substances and groups of substances" in Part 2 of Annex 2 of the Convention. Subsequently the Phare project "Strengthening sustainability of water quality management in the Danube basin" included a component (No. VI) on the identification of sources and amount of pollution for the substances on the EU list of priority chemicals.

The method used for identifying the list of hazardous substances which should be monitored in the surface waters of the Danube catchment to comply with the EU list of priority chemicals consisted the following activities:

- Review of the historical evolution of the EU Priority List and of the philosophy of the screening procedure.
- Assessment under the Initial Inventory of the quantity, quality and accessibility of the data on the priority substances presently available in the Danube Basin.
- Creation of the database.
- Compiling a preliminary list of substance of concern in the Danube Basin.
- Drawing up a strategic plan for developing a future ICPDR List of Priority Substances.

An output of the project was a proposed draft ICPDR list of hazardous substances harmonized with the EU WFD.

IE **Rationale**

In Ireland a National Expert group was established in 2003 to assist with developing candidate lists for specific pollutants in surface waters in Ireland and to design a substances screening monitoring programme as part of the implementation of the WFD. The starting point of the specific pollutant selection process entailed examination of the list of main pollutants as set out in Annex VIII of the WFD "universe of chemicals". Potentially all substances not identified as priority action substances (Annex IX & X) were to be considered as candidate pollutants. In the compilation of this list, the Dangerous Substances Directive was first looked at and substances previously identified as List I and II substances were added to the list as a starting point. The existing programmes were also identified for consideration in accordance with the IMPRESS guidance.

- Clean Technology Centre (CTC) project – 'Inventory and tracking of Dangerous Substances in Ireland and Development of Measures to Reduce their Emissions/Losses to the Environment'
- UNEP POPs –
- OSPAR -
- EPER - European Pollutant Emissions Register.

In addition to the main lists of substances identified by IMPRESS the expert group assessed the inclusion of other groups of pollutants associated with significant commercial activities in Ireland. These included substances associated with pesticides usage, aquaculture, forestry and weed control products. The expert group also considered findings of studies into endocrine disrupting substances. The expert group reviewed the datasets to screen the substances based on the output from existing registers and monitoring programmes in Ireland. The following rationale was applied:

• Substances which had been included in previous monitoring programmes and found to be consistently not detected at significant levels were dismissed from the candidate list.

• Substances which had been prohibited from distribution and use for over 10 years were also excluded from the candidate list.

• Alternatively, where there was no information from monitoring programmes or no ban on or lack of authorisation for the substance, a precautionary principle approach was adopted and substances remained on the candidate list.

The total number of substances on the candidate relevant pollutants list is **161.**

Summary of Substances added to Candidate Relevant Pollutants List	
DSD List II	91
CTC Project	3
UNEP POPs	2
OSPAR	3
EPER	2
Pesticides of possible relevance	42
Control Products Introduced to the Aquatic Environment	2
Endocrine disrupting substances - BKH report	8
Endocrine disrupting substances – usage reviews	8
Total Number of Substances /Groups	**161**

Survey and Screening

A water quality survey, to establish whether they were present in significant concentrations, was then carried out. A total of 23 Monitoring sites were selected downstream of areas where these substances were most likely to be found, comprising 17 surface water, 4 ground water one large waste water facility and a landfill effluent site.

Monthly samples were taken over a 12-month period, in 2005-06, allowing the calculation of annual average concentrations. Although at the time of the survey, no WFD compliant environmental quality standards were yet established for these substances, benchmark values were available for most substances from the scientific literature or from standards in use in other Member States (including a number of standards previously set at a national level under existing Irish legislation). A substance was judged to be present at a significant concentration where the **annual average concentration was found to exceed one quarter of the benchmark value used for that substance.**

Using these tests, 25 specific relevant pollutants were identified for inclusion in the national WFD monitoring programme for more widespread evaluation. The substances Toluene, Xylenes and Cyanide were added to this list on the basis that standards had already been established for these substances in the Irish Dangerous Substances Regulations (S.I. No. 12 of 2001) even though they were not detected in significant concentrations in the national screening survey for dangerous substances. The final list of 28 relevant pollutants included in the monitoring programme comprises 12 Metals, 11 Pesticides and 5 other substances.

Eleven additional specific relevant pollutants have been added to a Supplementary Monitoring List where information indicated that they might pose a risk to the aquatic environment due to particular uses or because they were of cross-border concern. It is proposed that these substances will initially come under the investigative monitoring programme. These include 7 Pesticides and 4 other substances.

Standards

EQS have been developed and are now included in National WFD Regulations for 16 of the above substances (including two chromium species), see folder Ireland on Circa. Standards will be brought forward for the other substances at a later stage, if deemed necessary, taking into account *inter alia* the findings of the national dangerous substances monitoring programme which is being undertaken by the EPA. Because of the complexity of the procedure for derivation of EQS for these substances, the process of identifying substances and developing environmental quality standards is ongoing, as in most other Member States, in keeping with the iterative approach of the Water Framework Directive.All proposed standards will be kept under review *inter alia* in the event of technical or scientific progress.

IT In Italy, with the publication of the ministerial decree n.56/2009, has been selected a list of national specific pollutants in support of the classification of the ecological status. For all the specific pollutants included in the DM have been derived EQS in the water column (51 substances included total pesticides) and in the sediment for transitional and marine coastal-waters (e.g. PCB and Dioxins).

The national list of specific pollutants included in the DM has been derived on the basis of the

monitoring data collected in different Italian regions, from data derived in the framework of a national monitoring programme of pesticides and, in particular for sediment, from data derived in the national programme of remediation of highly contaminated sites. Many of these substances are the same included in the list II of dangerous substances directive 76/464/EEC. The primary criterion for the inclusion in the list has been the presence of the substances in the waterbodies, in the case of pesticides also the production has been considered.

This list is provisional and will be amended (in terms of addiction or deletion of substances) on the basis of new recent monitoring data and on the analysis of pressures and impact.

In the national decree is clarified that the selection of specific pollutants (Annex VIII of WFD) should be based on the analysis of pressures and impacts, on the basis of the existing and new monitoring data (compared with EQS derived at national level) and on the basis of ecotoxicological effects on the ecosystem.

LT Inventory. Nacional legal act for wastewater „Nuotekų tvarkymo reglamentas“ („Wastewater Management Regulation “) MoE 2009 07 03 oder No. D1-386 requires an inventory of hazardous substances in the wastewater and effluent in the cases when operator (company, client) wishes to obtain an IPPC permit. Inventory schould be done not for all 74 (in our legal acts we have such list with 74) hazardous substances. Not for each operator. The operator must conduct an inventory of its industry-related hazardous substances. Only wastewater treatment plant must check all 74 hazardous substances in their effluents

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MT In order to select River Basin-Specific Pollutants (RBSP) of relevance to Malta, it has been considered appropriate to assess other pollutants which are not included in Annex II of the Priority Substances Directive (2008/105/EC). In this process, the following groups of substances have been considered:

- List II families and group of substances included as Annex I of the Dangerous Substances Directive (2006/11/EC - Codified version); and
- Substances indicated as relevant for the Strategic Action Programme (SAP) to address pollution from Land-based Activities as per requirements under the revised Protocol for the Protection of the Mediterranean Sea against Pollution from Land-Based Sources and Activities (LBS Protocol[3]).

During this assessment, the presence and nature of the point sources and diffuse sources of pollution in the local water bodies have been considered; the assessment also included a review of existing scientific data for local waters. The scientific data has been collected on an *ad hoc* basis through studies carried out principally as part of research work and as part of environment impact assessments.

Substances were identified on the basis of the level of importation of the chemicals or class of chemicals by the National Statistics Office for the period 2000-2004 and on the level of occurrence in local discharges and/or environment of the respective chemicals. All substances identified as having significant loads in the LBS Protocol National Baseline Budget (NBB) were also identified as RBSP.

NL Water management in the Netherlands and in Europe did not start with the coming of the WFD. Several basis lists of substances have been developed in the past based on monitoring results (what can be analysed in a practicable way) and based on information in terms of what kind of specific discharges of polluting substances result from which activities. (e.g. oil is discharged by crude oil refineries, heavy metals are discharged as a result of surface treatment of metals, PAH are discharged as a result of coke production etc.) In addition to that specific activities result is diffuse discharges such as agricultural activities (discharge of nutrients and plant production products, shipping result in the discharge (leaching) of anti fouling agents (e.g. TBT or Cu) etc.)

In the past iterations between “what can we monitor” and “what are significant discharges resulting

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[3] As a contracting party to the Barcelona Convention, Malta signed and ratified the LBS Protocol and has submitted to the United Nations Environment Programme, Coordinating Unit for the Mediterranean Action Plan (MAP/UNEP) in 2004 a National Baseline Budget (NBB) of emissions and released of the SAP targeted pollutants.

from man made activities" resulted in "lists" of substances as a basis for our monitoring programme.

So in fact we followed the DPSIR-approach (in principle also applied when preparing the IMPRESS-guidance) which was fine tuned via the "monitoring cycle approach" (explain in advance what should be monitored (define the question to be answered); than execute the monitoring, check the monitoring results with standards or references, conclude whether the monitoring activity has resulted in "answering the question").

At international level cross seeding took place with activities in which production volumes of certain substances times a "toxicity of such a substance" (resulting in a potential toxicity equivalent) resulted in ranking lists. E.g. the International Rhine Commission prepared, many years ago, a list of approximately 70 substances of relevance for the catchment area of the river Rhine. A EU-wide equivalent is the well known list of 129 substances (in a later stage expanded to 132 substances) in connection with the implementation of Directive 76/464/EC (1976) (new number: 2006/11/EC).

At this moment our general list of substances, relevant for the WFD, is included in a ministerial decree (in preparation) comprising i.a. a general list of substances that may be relevant for our river 4 (international) basin districts. Taking account of this list it is decided at water body level which of these RBSP are not meeting the water chemical quality standard.

NO In Norway we have not yet included the RBSP in our legislation. However we (The Norwegian climate and pollution agency) are in short time proposing a list of substances to be included in our legislation as RBSP. The list includes substances on our national priority list. Norway's national targets are to eliminate or substantially reduce emissions of the substances on the list by 2010. The priority list includes about 30 substances and groups of substances (Prop. 1S 2009-2010, Ministry of the Environment). See http://www.environment.no/Tema/Kjemikalier/Kjemikalielister/Prioritetslisten/ for more information.

At first this national list was based on existing chemical list eg. OSPAR and other conventions. In later time the revisions of the list has been based on a list of criteria and monitoring data (mostly emerging substances).

Criteria for the selection of Priority Substances

Substances that fulfill one or more of the following five sets of criteria are included in the national target to achieve substantial reductions in emissions by the year 2010 (Prop. 1S 2009-2010, Ministry of the Environment). The criteria and the values that are presented below are mainly based on international work in the EU and OSPAR.

1	2	3	4
P+B+T	**vP+vB**	**Additional criterion**	**Additional criterion**
Substances that are persistent, bioaccumulative and have serious long-term effects on health (including carcinogenic, mutagenic or toxic for reproduction) or are highly toxic for the environment	Very persistent, and very bioaccumulative substances (documentation of toxicity is not required)	Substances that are detected in the food chain at levels which give rise to an eqvivalent reason for concern	Substances that give rise to an equivalent level of concern as substances that meet the criteria 1-3, such as certain metals and substances that have endocrine disrupting effects

For these sets of criteria the following definitions are used:

Criterion		Defined by

Persistent	**P**	**One of the following:** 1) Fresh water: half-life □ 40 days 2) Marine water: half-life □ 60 days 3) Sediment, fresh water: half-life □ 120 days 4) Sediment, marine: half-life □ 180 days 5) Soil: half-life □ 120 days Other relevant information may be used if test results are lacking.1)
Bioaccumulative	**B**	Bioconcentration factor (BCF) □ 2000 Other rele□ant information may b□ used if test results are lacking.1)
Serious long-term effects on health	**T**	**One of the following:** 1) Carcinogenic (Category 1 or 2 according to Directive 67/548/EEC), i.e. classified as T; R45 or T; R49 2) Mutagenic (Categori 1 or 2 according to Directive 67/548/EEC), i.e. classified as T; R46 3) Toxic for reproduction (Category 1, 2 or 3 according to Directive 67/548/EEC), i.e. classified as T; R60,T; R61, Xn; R62, Xn; R63 or R64. 2) 4) Chronic toxicity: i.e. classified as T; R48 or Xn; R48
Highly toxic for the environment	**T**	**One of the following:** 1) Very high chronic toxicity for aquatic organisms: NOEC (aquatic, chronic) □□0,01 mg/l 2) Very high chronic toxicity for terrestric organisms: NOEC (bird, chronic) □ 30 mg/kg 3) Substances that are sufficiently documented in internationally accepted tests as causing endocrine disrupting effects Other relevant information may be used if test results are lacking.1)
Very persistent	**vP**	**One of the following:** 1) Fresh water and marine water: half-life □□60 days 2) Sediment, fresh water or marine: half-life □ 180 days 3) Soil: half-life □ 180 days Other relevant information may be used if test results are lacking.1)
Very bioaccumulative	**vB**	Biocentration factor (BCF) □ 5000 Other relevant information m□y be used □f test results are lacking.1)
Additional critierion		**One of the following:** 1) Metals that may cause serious long-term effects. 2) Substances that are traced in the food chain or in mother's milk at levels that may represent a risk to health or the environment. 3) Substances that are sufficiently documented in internationally accepted tests as causing endocrine disrupting effects at low levels. 4) Other substances that are shown to represent risks to health or the environment at similar levels as PBT- or vPvB-substances.

1) Test results that show potential for persistency, toxicity and bioaccumulation may be used if tests of higher quality are lacking: a) potentially high persistency: does not fulfil the criteria for ready or inherent persistency (OECD 301,302 or 306), b) potentially high chronic aquatic toxicity: L(E)C50 in acute test £ 0,1 mg/l. This is most relevant with regard to persistency, as half-life test has recently been internationally accepted and little test data therefore exists today.

PL No specified procedure. The main research is screening and monitoring for sources of pollutions, used materials in technology, imported materials, etc.

PT

- The procedures that Portugal adopted to assess and select RBSP were:
- Assessment of substances used in the several activities (agriculture, trade and industrial) present in Portugal;

- Appraisal of types of activities presented in each region/basin;
- The drawn up of an inventory of installations (industrial and trade activities) that potentially used and/or produced dangerous and/or priority substances, based on the previous results. The installations were inventoried by region and basin;
- Selection of installations for specific characterization (selection criteria: IPPC installations, installations with voluntary environmental agreements, installations with a discharge permit and other installations that demonstrate interest to the region/basin);
- Development of:
    - Characterization studies from the selected facilities;
    - Other works related with specific pollutants for basin (e.g. studies that are being developed or had been prepared for Algarve basin: "Impact Assessment of Roads in Water Quality", "Definition of guidelines for water pollution prevention from chemical accidents with dangerous substances", "Prevention pollution control from dangerous substances by diffuse sources" and "Risk assessment related with the dangerous substances discharged into water resources").

RO The procedure has 3 components :

1. an inventory of the possible substances in discharges (based on some criteria, attached, in Romanian) – this procedure normally reveal substances not known up to that moment to be possible present in discharged. This procedure takes into consideration the data and declarations of point sources about the raw substances, used intermediary products and final products handled in their industrial unit. Also, new substances used for new technological process for new industries are included in the list of specific substances at basin level whe such a industry is licenced for the first time. Up to now, these procedures were not largely applied because of big quantity of collected data, necessary to be processed later.

2. analysis of emmisions (substances and quantities of discharged industrial waste waters from the licenced point sources); this analysis confirm or not certain substances which normally are present in the list of authorised substances to be discharged. It is an easier process and is dedicated mainly to revision of the water management licences and to the check of compliance with pollution reduction/elimination programs with dangerous/priority substances.

3. analysis of immisions – analysis of surface waters in the monitoring sections, established according to ''pressures'' criteria ; the analysis was developed based on the so-called ''screening'' of waters using the following criteria '' if a substance if found as having a concentration bigger than the national EQS is at risk ; if a substance is found as having a concentration of 80% from the national EQS is considered as being at a possible risk ; in both cases that substance is introduced in the monitoring of that water body. It is worth mentioning that this rule is applied at the so-called ''list II substances'' for which national EQS is established in national legislation (see folder Romania on CIRCA); it is not applicable at substances not present in national legislation

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SK In 2004, 59 relevant substances were selected in the Slovak Republic. The basic selection criteria were production volume or use of substance and results of monitoring. Part of work was done by Twinning project SK02/IB/EN/01-"Implementation and enforcement of Council Directive on discharges of dangerous substances into the aquatic environment.

SI The procedure for selecting RBSP in Slovenia is described in research project (b) CRP: *Preparing environmental standards for chemical substances in water environment. November 2006.* In the first stage of project the list of substances relevant for water environment was gathered in such a way that the data from the previous project (a) were methodological assessed and supplemented on the basis of unified criteria (COMMPS procedure, based on the environmental concentrations, toxicity, bioaccumulation and long-term effects). In the second stage , the proposal for environmental quality standards as annual average and maximum admisable concentration for chemical substances from the list was prepared.

The proposal for environmental quality standards as annual average and maximum admisable concentration are based upon the toxicological data for water organisms. The toxicological data from several data bases were used (RIVM, EPA, database accessible in internet..). For overcoming the problem of unknown effects due to lack of data the safety factor was applied.Environmental quality

standards were proposed for water and sediment. For some naturaly occurring substances background concentrations were determined and take into consideration in determination of environmental quality standard.

ES At a river basin level there are two approaches to select the RBSP:

A) INVENTORY OF EMISSIONS: all the substances discharged in significant amounts are analysed. The inventories consulted are: IMPRESS analysis, PRTR inventory, register of discharge permissions, and declaration of hazardous substances discharged in the sewage system to obtain the urban wastewater discharge permission.

B) MONITORING RESULTS: all the substances detected in water bodies or in wastewater discharges, are included in the monitoring programs. An Investigative Monitoring is implemented, as part of the Monitoring Program, to detect new pollutants in the water bodies. The aim of the investigative monitoring is to detect new substances present in the water bodies but not included in the routine control. This new substances are detected using screening techniques applying mass spectrometry as main technique. By this way are selected new pesticides to be included in the Operational Monitoring Programs

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SE Swedish Environmental Protection Agency has in a handbook from 2007 a suggestion in broad outline on how the Water Authorities (WA) could proceed in order to identify RBSP. The very short text is copied in italics below. In practice however the methods used have varied amongst WA and not always followed this suggestion. In general regional monitoring data was gathered and compared to the national list of potential specific pollutants (see response to question 2 below). In addition, as far as possible, the national candidate list was also checked against inventories of contaminated sites and emission data as well as substances handled/imported.

Status, potential and quality requirements for lakes, watercourses, coastal and transitional waters *- A handbook on how quality requirements in bodies of surface water can be determined and monitored, Swedish Environmental Protection Agency, Handbook 2007:4, Chapter 16.5*

Choice of specific pollutants

What is meant by a substance being discharged in significant quantities? In the EU Guidance no 3 (Analysis of pressures and impacts)[4] the concept of discharge is interpreted in a broad sense. It covers discharges from point sources in the river basin, leakage from diffuse sources and e.g. atmospheric deposition from other areas. One should therefore consider all the possible pathways by which the pollutant can reach the water body. The Swedish EPA interprets “significant quantity” as a quantity of a substance that can prevent the biological status/potential from being fulfilled by 2015.

The water authorities shall classify the specific pollutants discharged into the water body. Discharged substances are identified with the help of the supporting data produced when assessing impact (See the Handbook for Typology and Analysis). The EU Guidance describes the procedure for selecting the specific pollutants in each river basin and in particular water bodies. Here is a summary of the most important steps.

1. Starting-point

The indicative list of the main pollutants set out in Annex VIII of the WFD can be the starting-point of the selection process.

2. Screening of information

A screening of all available information on pollution sources, impacts of pollution and production and usage of pollutants in order to identify those pollutants that are being discharged into water bodies in the river basin district.

2a. Collation of data/information

Data from:

- Sources - Production, industrial processes, usage, treatment, emissions
- Impacts - Change in the occurrence of pollutants in the water body (water quality monitoring

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[4] Common Implementation Strategy for the Water Framework Directive (2000/60/EC) Guidance no 3 Analysis of pressures and impacts, produced by working group 2.1 – IPRESS, 2003

data)
- Pollutants - Intrinsic properties of the pollutants affecting their likely pathways into the water environment.

Information from existing programmes/registers, e.g.:

- Swedish Pollutant Release and Transfer Register (PRTR)
- C-EMIR (emissions from point sources)
- MIFO (contaminated areas)

2b. List of pollutants

Assessment of information collated under Step 2a will result in a list of those pollutants identified as being discharged into water bodies in the river basin district. Pollutants for which there is adequate confidence that they are not being discharged into water bodies in the river basin district may be excluded from further considerations.

3. Assessment for relevance

All the pollutants being discharged in the river basin district have been identified in Step 2. Step 3 tests which of these are relevant. In other words, those pollutants that are likely to cause, or are already causing, harm to the water environment. This will depend on the intrinsic properties of the pollutants, their fate and behaviour in the environment and the magnitude and form of their discharges. Selection should ideally be based on an assessment of the ecological relevance of the concentrations estimated for the pollutant or its metabolites in the water body. However, effect data or a modelling of critical loads may also be relevant in the selection process.

3a. Data on concentrations and loads

Obtaining data through monitoring and/or modelling.

3b. Comparing concentrations with threshold values

Pollutants identified under Step 2 may be excluded where their concentrations are estimated to be lower than the most relevant critical value such as estimated LC_{50}, NOEC, PNEC, EQS or model estimations for e.g. critical load.

Natural background concentrations of non-synthetic pollutants (mostly metals) may exceed EQS without them necessarily being considered relevant.

Potential bioaccumulations of the pollutant in sediment or biota should be considered.

4. Safety net

A safety net is needed to ensure that pollutants that may be environmentally significant are not incorrectly excluded from the list of specific pollutants during Step 3. For example, the safety net should consider;

- whether a number of small (individually minor) pollution sources may be expected to have a significant combined effect,
- whether there is a trend indicating the increasing importance of a pollutant, even though the EQS is not currently exceeded, and
- whether pollutants are present that have similar toxic effects and hence via additive or synergetic effects may cause significant impacts.

5. Final outcome

The final outcome is a list of specific pollutants relevant to a river basin district or to particular water bodies within a river basin district. It is therefore the water authorities that select the relevant specific pollutants for each water body. Class boundaries should be established for these pollutants in accordance with Annex V of the WFD so that the status of the specific pollutants quality element can be established.

CH The procedure is work in progress. It is planned to apply a procedure that would be leaned on the one described in the following:

- The first step for the selection of organic substances was to develop a candidate substance list.

The candidate substance list of potential MCs was based on three criteria. The compounds (a) were listed in the EU WFD, (b) were listed in the list of relevant substances for the river Rhine, or (c) had been measured in Swiss surface waters (Götz et al 2010, see folder Switzerland on CIRCA).

- As a second step, the candidate substance list was categorized for prioritisation of mobile organic compounds that are mainly found in the water phase of surface waters. In total, seven exposure categories are distinguished: (I) highly persistent chemicals that are continuously released into surface waters, (II) highly persistent chemicals with a complex input dynamic, (III) moderately persistent chemicals with a continuous input, (IV) moderately persistent chemicals with a complex input dynamic, (V) volatile and strongly sorbing chemicals, (VI) rapidly degradable chemicals, and (VII) unclassifiable chemicals. The seven exposure categories are discussed in detail in the Results section. The categorization procedure is given in the Figure 1 in Götz et al 2010, folder Switzerland on CIRCA. The compounds are categorized using three filters: (a) distribution behaviour between different environmental media, (b) compound degradability, and (c) input dynamics. If the required chemical property data are not available, the selected compound properties are estimated with publicly available QSPRs, such as EPI SuiteTM (Götz et al. 2010, folder Switzerland on CIRCA).

For the first part of the work, which deals with compounds from urban areas, some compounds from the categorized candidate list were selected: So called “Swiss relevant compounds from urban systems”

The following additional criteria are planned to apply for the selection of the “Swiss relevant compounds from urban systems”:

- Substances have to be from exposure categories I - IV (mobile, persistent)
- Substances have to be approved by current legislation
- Substances have to fulfil one of the following criteria:
    - Widely detected in Switzerland (more than 20% of the investigated samples have to be positive)
    - Measured in high concentrations (more than 100 ng/L)
    - Substance is specifically toxic

UK Annex VIII of the Water Framework Directive (WFD) requires Member States to identify ‘Specific Pollutants’, ie those discharged to water in ‘significant quantities’, and derive Environmental Quality Standards (EQS) for these chemicals in order to help achieve the objective of Good Surface Water Status. A collaborative project between the Environment Agency and the Scotland and Northern Ireland Forum for Environmental Research (SNIFFER) was commissioned in 2004 to develop a robust and transparent methodology for identifying and prioritising Annex VIII chemicals in the UK, and to develop standards for the first tranche of Specific Pollutants. This report outlines the work that has been undertaken to meet the former objective. It details the development of a list of chemicals of concern and a prioritisation methodology, and summarises the results of the subsequent prioritisation exercise.

It was agreed by the UK Technical Advisory Group (TAG) Chemistry Team that the approach used to identify and prioritise chemicals should be consistent with the guidance produced by the EU IMPRESS (IMPacts and PRESSures) working group,which was set up to identify pressures and assess impacts on water bodies in relation to the WFD. The guidance outlined a generic approach that could be used to select a list of Specific Pollutants. In line with the IMPRESS guidance, candidate chemicals were identified from a range of existing drivers. These included existing monitoring and legislative requirements, e.g. the National Marine Monitoring Programme and the Dangerous Substance Directive (76/464/EEC) as well as national initiatives such as the UK pesticide usage surveys. The initial list was reviewed to remove duplicates, those chemicals already being considered by the EU under Annex X of the WFD and substances for which the prioritisation process is not appropriate, such as metals and other inorganic substances. This process resulted in a list of approximately 300 candidate chemicals which was termed the ‘Universe of Chemicals’.

The Environment Agency’s Chemicals Screening and Prioritisation method was chosen as the basis of the prioritisation approach, as it met the requirements of the IMPRESS guidance and was a method with which we already had some experience. The screening tool was developed to consider impacts on terrestrial and aquatic life as well as human health considerations. As the WFD standards only need to consider the protection of aquatic life, the tool was modified for this exercise, to only consider hazards related to the aquatic environment (water column, sediment and secondary poisoning).

The prioritisation process ranks substances based on their potential exposure in the aquatic environment and hazard to aquatic life. Exposure is assessed according to available monitoring and use

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(tonnage and use scenario) data and hazard is assessed based on persistence, bioaccumulation and toxicity. A score is then assigned for both exposure and hazard based on the available data. These scores are combined to give an overall priority ranking of 1 to 5 with 1 indicating highest priority and 5 the lowest.

There are minimum data requirements for an assessment to be made and if these are not met the substance will be assigned a final ranking of 'Insufficient Information'. The prioritisation approach also incorporates a review of the priority rankings. This does not involve detailed discussion of the data used to determine the priority ranking, but:

- enables a check on the score assigned and flags any anomalies

Prioritising chemicals for standard derivation under Annex VIII of the WFD

- provides an opportunity for highlighting further data sources
- enables discussion about how particular substances should be dealt with, for example should they be taken forward for EQS development, should additional data be obtained, are other controls in place which reduce the need for an EQS.

Due to time constraints not all substances could be reviewed and therefore we focused attention on those substances assigned a priority ranking of either 1 or 2. The review exercise concluded that not all the substances identified as high priority (ranked 1 or 2) should be put forward for consideration for EQS development at this stage. This was for a number of reasons including a need for further information (such as additional data on use), existing controls (such as restrictions on use which may influence the need for an EQS) and on-going reviews (such as reviews under the Plant Protection Products Direcive the outcomes of which may affect the need for an EQS).

The latter, for example, may result in a pesticide not being approved for use in the EU. At this stage a total of 32 substances have been identified for EQS development as a result of the prioritisation exercise undertaken on the 'Universe of Chemicals' (including the List 2 chemicals) and the review of discharge permits. EQS are currently being derived for 30 of these chemicals. A number of other substances were identified as of high priority based on the prioritisation process but were not put forward for EQS development at this stage due to a need for further information. They will need to be reconsidered as additional data become available. In addition, due to time constraints, the review process focused on those substances that were ranked as Priority 1 or 2.

The other substances need to be reviewed before any decisions are made on these chemicals. The exercise has highlighted a number of issues that need consideration when using the prioritisation process. These include limited availability of usage data and the need to consider data on persistence and bioaccumulation more broadly. Many of these issues have been addressed at the review stage and this supports the need for inclusion of this within the overall prioritisation process. However others will need to be addressed before further prioritisation exercises. This includes use and interpretation of fugacity modelling. This was included as a tool to help assess potential exposure in the aquatic environment but due to data limitations it provided limited benefit during this particular exercise. The use of this approach in future exercises needs to be considered.

Reference documents of the selection procedures

Is there a reference document with the full description of the procedure? If yes, please attach, even if in the national language.

AT	„Gefährliche Stoffe in Oberflächengewässern – Fachgrundlagen für österreichische Programme nach Artikel 7 der RL 76/464/EWG“ (2002). Please see folder Austria on CIRCA or http://publikationen.lebensministerium.at/filemanager/download/21972
BE	*There is no reference document.*
BG	Methodological approach developed under SWIFT “**S**creening methods for **W**ater data **I**n**F**orma**T**ion in support of the implementation of the Water Framework Directive” (see folder Bulgaria on CIRCA) First Interim Report on topic 3 “Development of environmental quality standards for surface water”, National project “Development of River Basin Management Plans” financed by Operational Programme Environment 2007-2013” (see folder Bulgaria on CIRCA)
CY	*There is no reference document.* Attached the report on the pressure analysis (see folder Cyprus on CIRCA)
CZ	*There is no reference document. The proposal of this document is currently being drafted.*
DK	See folder Denmark on CIRCA. However, the procedure is not implemented yet. (Overordnet strategi for overvågning af miljøfremmede stoffer og tungmetaller af 7. maj 2009).
EE	*There is no reference document.*
FI	Please find the following documents in English: Selection of specific pollutants: see folder Finland on CIRCA or http://www.ymparisto.fi/default.asp?contentid=92296&lan=en Environmental Quality Standards: see folder Finland on CIRCA or http://www.ymparisto.fi/default.asp?contentid=143511&lan=en Finnish National Decree: see folder Finland on CIRCA or http://www.finlex.fi/fi/laki/kaannokset/2006/en20061022.pdf
FR	Please see folder France on CIRCA for a short description of the procedure. The document is validated by the French water director but can’t be considered as the French reference document. It can be completed by: • the 2005 national action plan against pollution caused by dangerous substances to the aquatic ecosystem[5] implementing the requirements of D76/464/CEE. • The French regulation fixing and implementing the national monitoring programmeunder the WFD (circulaire DCE 2006/16[6]).
DE	Yes, but only as a draft (see folder Germany on CIRCA).
EL	*There is no reference document.*
HU	The reference document of the description of the procedure mentioned in point 1 of the questionnaire is the project report “Strengthening sustainability of water quality management in the Danube basin. Component VI: Identification of sources and amount of pollution for the substances on the EU list of

[5] Arrêté du 30/06/05 relatif au programme national d'action contre la pollution des milieux aquatiques par certaines substances dangereuses

[6] Circulaire DCE 2006/16 : document de cadrage pour la constitution et la mise en œuvre du programme de surveillance (contrôle de surveillance, contrôles opérationnels, contrôles d’enquête et contrôles additionnels) pour les eaux douces de surface (cours d’eau, canaux et plans d’eau).

priority chemicals" Final report, October 2000, WRc Medmenham.

IE	This document best describes the procedure (see folder Ireland on CIRCA or http://www.wfdireland.ie/docs/19_DangerousSubstances/Dangerous_Substances_Summary_Screening_Programme_Final.pdf) Further background documents may be found using this link http://www.wfdireland.ie/docs/19_DangerousSubstances/
IT	In the National Decree "decreto 14 aprile 2009, n. 56 Regolamento recante «Criteri tecnici per il monitoraggio dei corpi idrici e l'identificazione delle condizioni di riferimento per la modifica delle norme tecniche del decreto legislativo 3 aprile 2006, n. 152, recante Norme in materia ambientale, predisposto ai sensi dell'articolo 75, comma 3, del decreto legislativo medesimo» is included briefly the procedure. **Selezione degli elementi di qualità** "La selezione delle sostanze chimiche da controllare nell'ambito del monitoraggio di sorveglianza si basa sulle conoscenze acquisite attraverso l'analisi delle pressioni e degli impatti. Inoltre la selezione è guidata anche da informazioni sullo stato ecologico laddove risultino effetti tossici o evidenze di effetti ecotossicologici. Quest'ultima ipotesi consente di identificare quelle situazioni in cui vengono introdotti nell'ambiente prodotti chimici non evidenziati dall'analisi degli impatti e per i quali è pertanto necessario un monitoraggio d'indagine. Anche i dati di monitoraggio pregressi costituiscono un supporto per la selezione delle sostanze chimiche da monitorare"
LT	IPPC permits; Regulation act "Nuotekų tvarkymo reglamentas" („Wastewater Management Regulation ") MoE 2009 07 03 oder No. D1-386; Lietuvos Respublikos vyriausybės nutarimas dėl valstybinės aplinkos monitoringo 2005-2010 metų programos patvirtinimo, 2005 m. vasario 7 Nr. 130 (Republic of Lithuania Government Resolution for approval on the state environmental monitoring programme for 2005-2010, 2005 m. February 7 No. 130).
MT	The national procedure adopted in selecting the RBSP has been based on unpublished expert assistance on the design of surveillance and operational monitoring networks for local surface waters. The preliminary list of national identified RBSP includes: Copper, Chromium, Manganese, Zinc, Barium, Beryllium, Boron, Cobalt and Fluorides. However, it is being envisaged that the finalised list will be made available during the implementation of the 1st Water Catchment Management Plan.
NL	*There is no reference document.* The process has been summarised under item 1 of this questionnaire.
NO	*There is no reference document.*
PL	*There is no reference document.*
PT	*There is no reference document.* The procedures were developed based on general guidance notes, therefore there is no document with the full description of them.
RO	No, there is not such a document; there are different pieces of articles in different national legislations, as mentioned in answer nr. 1 and some of them are present in folder Romania on CIRCA. The relevant pieces of legislation are: • Ministerial Order 31/2006 with the reorganisation of national integrated monitoring system of waters in Romania; • Ministerial Order nr. 662/2006 with inventory of industrial discharges and revision of water licences; • Governmental Decision 351/2005 with the national EQS for ''List I'' and ''List II'' substances.
SK	In 2004 approach for pollution reduction has been elaborated. At present updated version is under preparation, including substances relevant for the Slovak Republic (country´s specific substances). Reference to document: http://www.enviro.gov.sk/servlets/page/868?c_id=2348
SI	http://www.mop.gov.si/si/delovna_podrocja/direktorat_za_okolje/sektor_za_vode/ekolosko_stanje_pov

rsinskih_voda/

(a) (Kemijski inštitut, Identifikacija nevarnih snovi na področju RS z namenom priprave programov zmanjševanja onesnaževanja vodnega okolja, Ljubljana, september 2003)

(b) ZZV MB, Priprava okoljskih standardov kakovosti za kemijske snovi v vodnem okolju, CRP projekt, Maribor, september 2006: (linki na dokumente s temi imeni, ki so na I/SKUPNO/CRP_projekt_ZZVMB)

- Zaključno poročilo projekta
- Poročilo I faze projekta
- Poročilo II faze projekta
- Priloga 1
- Priloga 2
- Priloga 2a

ZZV MB, Nadgradnja predloga okoljskih standardov kakovosti za nekatere kemijske snovi v vodnem okolju, Maribor, januar 2009:

- kobalt in njegove spojine
- dibutilkositrove spojine
- S-metolaklor
- terbutilazin

ES	*There is no reference document.*The document is a draft not approved yet.
SE	To support the regional Water Authorities (WA) when performing the classification for specific pollutants the Swedish Chemical Agency, by order of the Swedish Environmental Protection Agency (Swedish EPA), has derived proposals for environmental quality standards (EQS) for a number of pollutants that may be problematic in certain parts of Sweden. This is done in a EPA-report no 5799 (see Attachement 16 on CIRCA or http://www.naturvardsverket.se/Documents/publikationer/620-5799-2.pdf). The report is in Swedish with only a very short summary (1/2 page) in English.
CH	As this work is still in progress, there is no official document available that shows the whole procedure. The applied prioritisation procedure is documented in the article of Götz et al 2010 (in folder Switzerland on CIRCA). The whole procedure is still subject to discussion with different stakeholders.
UK	The process has been documented in the UK Environment Agency Report SC040038/SR (see Attachemnt 17 on CIRCA). This report was in turn used as the basis for the modelling based approach for the review of Priority Substances.

Critical points / limitations of the applied procedures and suggestions for improvements

What are the critical points/limitations of the procedure applied in your country that you think could be improved in the future? Please, describe.

AT The most important critical points of the selection procedure were:

- restriction of the number of potential candidates out of the universe of chemicals to a manageable list,
- uncertainty in assessment due to data gaps

Regarding the list of potential candidates, Austria used existing EU-lists (e.g. List of substances from the Communication from the EU Commission 1982), existing monitoring data and expert judgement. For the future the use of ecotoxicological studies for the selection of hot spots where a detailed chemical analysis should follow could be an interesting possibility to identify RBSP.

BE Implementing the WFD-monitoring requirements on biological and chemical elements as well as other obligations use a large part of the available monitoring budget. Little financial room is left to set up research programmes concerning emerging substances. Since monitoring of new emerging pollutants is highly time- and money consuming, we believe that the work of the Commission in this area is very important.

Points to be improved in the procedure applied in Flanders:

- specific screening in effluent of waste water treatment plants
- improve the knowledge on sources of dangerous substances and the pathways in which pollution occurs
- which metabolites are being formed and how to treat them

BG The second procedure (First Interim Report on topic 3 “Development of environmental quality standards for surface water”, National project “Development of River Basin Management Plans” financed by Operational Programme Environment 2007-2013”) for determination of specific pollutants is newly developed. It was developed as response to the need of basin directorates in Bulgaria to improve methodology for identification of specific pollutants that has to be monitored: in order to be able make cost effective monitoring and to put efforts in substances that are relevant. This approach is based on a broad base: experiences of foreign countries, methodologies, scientific investigations and relevant legislations have been investigated, so the contemporary knowledge for the choice of specific pollutants is taken into account in the developed methodology.

We think that there is still need to get more experience in its practical application in order to assess all possible areas of further improvement. Nevertheless we think that there are at least these possible areas for improvement of the procedure:

1. A good practice would be the possibility to apply analytical screening (i.e. detection of emerging substances or substances that are released from unidentified sources) before final formulation of the list of substances to be monitored under regular monitoring.
2. Determination of a criterion for “significant” quantities of pollutants discharged/released into water bodies.
3. Assessment of the contribution of atmospheric pollution to the water pollution and to the list of specific pollutants
4. Development of a methodology for identification of a list of substances to be monitored in sediments.
5. Applied research projects.

The main disadvantage is that monitoring data were not well present and included in the developed procedure. That is way the list of specific pollutants achieved is relatively theoretical and quite long. However the main reason is unreliability of monitoring data. Additional information for the identified pollutants from industrial activities, solid wastes, atmospheric depositions is required in future prioritization process. Therefore future improvement of the procedure should include more representative, real positive results from monitoring as well as newly identified pollutants.

CY	Cyprus has used an extensive pressure analysis and all available data for the initial selection of RBSP, has reviewed this selection based on results of the WFD Art. 8 monitoring programme and adjusted the RBSP selection accordingly. We believe this approach worked and works well; however there is always room for improvement, like more detailed pressure analysis.
CZ	The critical point of the procedure is disunity for selection of the RBSP. The procedure is different in each river basin.
DK	In the procedure the selection of substances in operational monitoring is based on knowledge about sources in the catchment area which are responsible for failing to meet environmental objectives. It is a critical point if the knowledge about sources in the catchment area is insufficient or not accessible.
EE	Main problem - co-operation is insufficient between different authorities/stakeholders (eg shared databases). Incomplete registers or databases (eg on chemicals import, use, discharges) don't provide sufficient information for decision-making and/or water management activities. Possible improvments could be achieved if proceduers and duties or task of differents institutions would be more clear. Also, environmental permits of enterprises are too general and do not include all relevant substances. To improve the problem - the training of issuers of those permits is essential. Lack of finances breaks the monitoring of RBSPs, resulting in insufficient environmental data and basic information for the decision making, incl selecting RBSP. Also laboratorial measurement methods must be improved to fulfill the EQS and chemical monitoring directives requirements (2008/105/EU and 2009/90/EU respectively).
FI	The exposure estimation is largely based on use and production volumes that have been reported to the national product register. It covers data only on chemical products classified hazardous and imported or produced in Finland. Some substance groups, e.g. pharmaceuticals, chemicals in imported articles, cosmetics are not covered.
FR	• Quality of the monitoring results either in surface waters or discharges: at that time, the laboratories where not prepared to analyse such substances at low detection limits. • Availability of quality standards and quality of the data • Number of pesticides and need for a global standard.
DE	• Less availability of data, e.g. real application amount from pesticides • Procedure needs a lot of time and money, especially if you need toxicological data • Danger of less consideration of emerging substances
EL	Improvement of analytical methods: Although the limit of quantification has been reduced since 2008, it remains greater than the respective National EQS for some chemicals and some laboratories. This necessitates an additional improvement of analytical methods employed up to now (following requirements of Directive 2009/90/EC). Verification of the RBSP: A more thorough analysis of pressures at each river basin is required in order RBSP catalogues to be verified.
HU	In Hungary the critical limitation of the RBSP selection procedure is that the ICPDR list of RBSPs is not verified thoroughly by sufficient monitoring data of surface water bodies and data of point and diffuse sources of pollution.
IE	• Further guidance/information exchange would be useful. We do already maintain close links with our UK colleagues especially in view of cross-border issues. It would appear that this project is intended to improve co-operation etc. at a broader EU level • Further development of analytical methods to achieve the required EQS values, where needed, would be an advantage. We understand that some work is being undertaken at European level through CEN.
IT	We think that the procedure suggested by the national decree should be applied in Italy; at the moment the selection of specific pollutants has been based mainly on the bases of monitoring data. The new

	approach takes into account of the real situation that occur in the waterbodies and is not more based on a defined list of pollutants for which there is an obligation of monitoring.
LT	Inventory specific substances in wastewater and effluent. Source tracking of hazardous substances. We have no limit values for hazardous substances in sediments and sludge.
MT	The procedure that has been applied is based on chemicals importations data and on a review of the existing scientific literature. Limitations may be accounted to data gaps to some extent in the importations data and to the unknown uncertainties of the limited scientific studies, where in most cases have been carried out on an *ad hoc* basis. As a first step, the quantitative chemical monitoring of 2010 will be used to review the status of the water bodies. During this surveillance and operational monitoring programme it will be ensured that the methods employed in sampling and analysis will conform to standard methods. In the years to come, it is intended that the implementation of the Priority Substances Directive (2008/105/EC), requiring the establishment of an inventory of emissions, discharges and losses will be streamlined as much as possible with the current and planned processes related to environmental permitting.
NL	In a number of cases “pragmatic choices” had to be made. E.g. PCB’s. In principle, PCB’s are by definition a diverse mixture resulting from a “wild chlorination” of biphenyls in an industrial process. From an analytical point of view pragmatic choices have been made in focussing on e.g. 7 PCB’s which are easy to analyse, but may not necessarily reflect the correct set of PCB’s in an aquatic ecosystem. For PAH a more or less comparable discussion exist. In a number of cases the analytical level of quantification is not low enough to determine whether a toxicity level of a certain substance is met or not.
NO	The limitation in the procedure is lack in knowledge when it comes to substances of concern. Better data on properties, use, exposure and environmental monitoring, would increase the possibility to select the most hazardous substances.
PL	-
PT	The main limitations are: • The development and the updating of the inventories of the emissions and losses from point sources of pollution. Therefore, it would be helpful the development/implementation procedures or tools that allowed these actions, in particular for the non IPPC/PRTR installations; • The assessment of diffuse sources, including the pathways appraisal, in particular for non agriculture activities.
RO	It is necessary the procedure for identification of unknown substances in water resources to be improved; it is especially necessary new and more practical criteria for such identification to be developed; it is necessary to extend the attention to polar and very polar substances (medicines, anti-inflammatory products, endocrine disruptors, etc.), almost not known in Romania as polluters of waters. It should be also necessary to develop a project, maybe at European level, (including participation of Romania also) for setting up a common methodology for identification of relevant specific substances al basins level.
SK	Critical point is lack of data concerning substances in discharged wastewater, in surface water and sediments. Improvement : to manage appropriate monitoring.
SI	The greatest problem to define environmental quality standards for individual parts of water environment is lack of several ecotoxicology data. There is also lack of data on emissions.
ES	-

SE	Monitoring, including screening on a local level, and inspection needs to be integrated better in the future, for both active and contaminated sites.
CH	The accuracy of the prioritisation procedure is limited by a lack of data about organic chemicals: The procedure could be improved with better physical-chemical property data and specifically with ecotoxicological data. Available consumption data of organic chemicals would help too to identify potentially critical compounds.
UK	The principle problem encountered in the UK was a lack of data. Which in turn meant that a number of substances were effectively left “on hold” pending the acquisition of sufficient data to proceed.

Previous monitoring programmes for River Basin-Specific Pollutants identification

Have there been dedicated previous monitoring efforts in order to identify RBSP? If yes, please describe them (project title, duration) and attach/provide links to relevant reports if available.

AT	The procedure to identify RBSP (details see 1.) includes the evaluation of all previous monitoring programs since 1995. Since 1992 Austria runs a national network (WGEV, GZÜV) which includes different special programs concerning the detection of hazardous substances – please see details in folder Austria on Circa and http://publikationen.lebensministerium.at/filemanager/download/21973
BE	See 1.b
BG	• Project ”Bulgaria, Arda river basin, field survey“, 2003-2007; • “Support to the Black sea Basin Directorate for the implementation of the WFD concerning coastal water monitoring.” 2005-2007 • Topic 3 “Development of environmental quality standards for surface water”, National project “Development of River Basin Management Plans” financed by Operational Programme “Environment 2007-2013” – ongoing; 2009-2010.
CY	There were no such dedicated programmes.
CZ	VaV/650/3/00 Výskyt a pohyb nebezpečných látek v hydrosféře ČR (Occurrence of dangerous substances in hydrosphere of the Czech Republic – in Czech only) http://voda.chmi.cz/ojv2/htm/pdf/VaV650300.pdf Duration: august 2000 – February 2003 The main aim of this project were specification of dangerous substances with relevance for the Czech republic, survey of their possible occurrence in hydrosphere and specification of quality objectives for ground water and surface water which are affected by discharge of contaminated waters.
DK	Previous national monitoring programmes: NOVA-2003 and NOVANA, and screening studies on specific substances.
EE	In the frames of the state environmental monitoring programme the groundwater bodies were monitored in 2007-2009 with respect to directive 2006/118/EU annex 2 part B substances. The results of "Põhjavee tugivõrgu seire" (Monitoring of groundwater basic network) and other environmental monitoring activities are available only in Estonian on the website of the state environmental monitoring programme http://eelis.ic.envir.ee:88/seireveeb/. Based on former investigations and monitoring data the RBSP for groundwater bodies are given in the Regulation No 75 of the minister of the Environment. For surface waters several inventories have been carried out during last decade. However, RBSPs with respect to surface waters haven't been identified. Only phenols are well-known RBSPs in North-East Estonian oil-shale minig areas, falling into East-Estonian RB District. However, limit values and EQS's for phenols are set for whole territory of Estonia, ie they are not only river basin-specific.
FI	Not solely dedicated on this purpose, but both National and Nordic screening campaigns have been utilized in assessing the relevance of the selected specific pollutants. National screening: http://www.ymparisto.fi/default.asp?contentid=180531&lan=en http://www.ymparisto.fi/download.asp?contentid=82118&lan=en Nordic screening: www.nordicscreening.org

FR In 2005, France has carried out a special monitoring campaign of more than 200 hundred substances in surface waters, referred as "campagne exceptionnelle[7]" (2 monitoring campains in 2005 on 222 monitoring stations).

An inventory of 106 substances (from the D76/464/CEE list of dangerous substances and the 33 PS WFD) in more than 2800 urban and industrial discharges was also carried out from 2002 to 2007, referred as "action nationale de recherche et de réduction des rejets de substances dangereuses dans les eaux - RSDE[8]" (one monitoring campain at each site through one 24h sampling, when possible).

The results of these 2 inventories were combined in order to identify "relevant" substances to monitor in French surface waters, using criteria of presence in surface waters and/or discharges. These substances (91 substances from D76/464/CEE and 89 pesticides) were listed in the regulation 2006/16 implementing the monitoring programme under the WFD.

Those "national relevant" substances have been monitored at 25% of the WFD surveillance monitoring sites. Data collected through this monitoring gave material for the selection of RBSP.

DE There are a lot of activities from several federal states, e.g.:

Common Information, example NRW and Saxony-Anhalt

http://www.umwelt.nrw.de/ministerium/presse/presse_aktuell/presse091124.php
http://www.sachsen-anhalt.de/LPSA/index.php?id=39644
Workshop „ Monitoring priority substances and other pollutants, Northern Germany"

http://www.lung.mv-regierung.de/insite/cms/publikation_download_includes/publikation_download_gewaessersymp.htm
Real-time Monitoring of surface waters, example NRW

http://www.lanuv.nrw.de/veroeffentlichungen/fachberichte/fabe8/fabe8start.htm
http://www.lanuv.nrw.de/veroeffentlichungen/fachberichte/fabe13/fabe13start.htm
Bericht "Pflanzenschutz- und Arzneimittelbefunde in Oberflächengewässern und im Grundwasser M-V im Frühjahr 2008" Juli 2008 http://www.lung.mv-regierung.de//insite/cms/publikation_download_includes/publikation_download_wasser.htm
Example PFOA/ PFOS

http://www.lanuv.nrw.de/pft/pft-bewertung.htm
http://www.umweltbundesamt.de/wasser-und-gewaesserschutz/dokumente/fgpfc/gesamtueberblick_ueber_pfc-untersuchungen_in_nrw-bergmann.pdf
http://www.umweltbundesamt.de/wasser-und-gewaesserschutz/veranstaltungen.htm
http://www.lanuv.nrw.de/veroeffentlichungen/jahresberichte/jabe2007/jabe2007S25S33.pdf
Pharmaceuticals

http://www.blac.de/servlet/is/2255/
http://www.blac.de/servlet/is/2146/P-2b.pdf
http://www.lanuv.nrw.de/veroeffentlichungen/fachberichte/fabe2/fabe2.pdf
http://www.sachsen-anhalt.de/LPSA/fileadmin/Elementbibliothek/Master-Bibliothek/Landesbetriebe/LHW/neu_PDF/5.1/Dokumente_GLD/Bericht_2_Arznei_2004-2005.pdf
http://www.blac.de/servlet/is/2146/P-2c.pdf

EL Previous monitoring efforts have been dedicated. These are described as follows:

- Identification of the pollution status of the surface waters from substances belonging to Catalogue I of Directive 76/464/EEC. Duration: From February 1995 to May 1995.
- Identification of the pollution status of the surface waters from substances belonging to Catalogue II, candidates for Catalogue I of Directive 76/464/EEC and organization-function of

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[7] INERIS - DRC - 06 - 66026 - CHEN - BLe - 06.0087 « Etat des lieux de la contamination des milieux aquatiques par les substances dangereuses, campagne exceptionnelle 2005 (2006) » (http://www.ineris.fr/)

[8] http://rsde.ineris.fr/

	Monitoring Network for the quality of surface waters according to the substances identified. Duration: From March 1998 to January 2000. • Evaluation of domestic and industrial wastewater discharges in the river basins that include Pagasitikos Golf and Vegoritida Lake from substances belonging to Catalogues I and II of Directive 76/464/EEC According to the above-mentioned Studies the substances for monitoring were selected as follows: • 7 substances belonging to Catalogue I of Directive 76/464/EEC • 115 substances belonging to Catalogue II of Directive 76/464/EEC • Furthermore, 33 priority substances defined in Directive 2008/105/EC
HU	References of considerable survey efforts: • Vom Rhein zur ungarischen Donau (1999). Booklet Vol. I-II. Ministry of Environment and Forestry Rhineland-Palatinate, Mainz, Germany • Joint Danube Survey. Technical Report of the International Commission for the Protection of the Danube River. September 2002, ICPDR Joint Danube Survey 2. Final Scientific Report. 2008, ICPDR
IE	Dangerous Substances Screening Programme 2005-6. Please see item 2 for references
IT	
LT	Case study (project) "Screening of dangerous substances in the aquatic environment of Lithuania" 2005-2007. The whole project report posted on our website: http://gamta.lt/cms/index?rubricId=3286b5eb-7eeB-413c-8f84-fc2d613de35a
MT	No previous dedicated monitoring efforts have been carried out to identify the national RBSP.
NL	No. We used the information as described under item 1 of this questionnaire (national level) and existing monitoring programmes agreed at international level for the river districts Rhine, Meuse, Scheldt and Ems.
NO	The Norwegian Climate and Pollution Agency conducts each year a screening exercise monitoring emerging substances in the Norwegian environment. This exercise has been and will be used in the revision of the national list.
PL	As I heard only small few projects, not only for identify RBSP. One of them was made by expert group here in Chief Inspectorate of Environmental Protection (GIOS), but basically for establishing system of chemical monitoring.
PT	1. In the last decade some monitoring efforts have been developed for surface waters and groundwaters, related with: • Implementation of the Directives 76/464/EEC and 80/68/EEC. The monitoring points were selected according the results of the inventory mentioned above and the existing discharge permits (wastewater); • Existent monitoring networks (metals and pesticides, according to the annual list reported by Ministry for Agriculture); New monitoring programmes that aim to establish the status of water bodies.
RO	No, there is not any relevant project at national level. Still, we can mention the JDS – 2 (Joint Danube Survey – 2) developed in 2007by ICPDR (International Commission for the Protection of Danube River). This project was a multinational project – an expedition on Danube - including all riparian countries and all main tributaries and was dedicated to identification and quantification of priority substances and other relevant pollutants in Danube catchment area. The main results are presented on site www.icpdr.org.

SK	Survey in years 2002-2004 focused on occurrence of dangerous substances in discharged wastewater, in surface water and sediments, eco-toxicological tests and screening had been done. During surveys 189 target compounds and screening analysis of unknown organic pollutants have been analysed by mass spectrometry techniques.
SI	Same of the NRS were included at selected sampling points in the frame of river quality monitoring in past (2006 and earlier)
ES	At a National level we already have a list of Relevant Substances approved by Royal decree since 2000. Each substance has a water EQS. Besides, it is obliged to monitor trends in sediments and biota. The selected substances are relevant for each River Basin District.
SE	Activities aiming to identify "new" or less known pollutants outside regular monitoring are in Sweden denoted as screening. Screening surveys are a first step in identifying chemical substances which may cause problems for the environment and/or human health. The screening programme, which was introduced on a small scale in 1996–97 and has increased in scope over time, is run nationally by the Swedish EPA. In recent years though, also the county administrative boards are able to enhance these surveys with regional sampling and analysis. Sometimes this can therefore be equal to identify so called RBSP. For a more detailed description of screening and how it is conducted; its purposes; how substances are chosen and also examples of substances that have been screened can be found in the following fact sheet (in English): http://www.naturvardsverket.se/Documents/publikationer/620-8322-9.pdf Also, individual screening reports are listed under the Swedish EPA´s web site at the following link http://www.naturvardsverket.se/sv/Tillstandet-i-miljon/Miljoovervakning/Rapporter-och-nyhetsbrev/Rapporter---Miljogiftssamordning/
CH	There are ongoing activities of monitoring relevant organic compound in natural water bodies. Currently a monitoring campaign in 14 wastewater treatment plants (WWTP) over whole Switzerland and downstream connected natural surface waters is going on. Data from cantonal authorities are gathered by the Swiss federal institute for the environment (FOEN) in a national database. This database can be used as a basis for an overview of measurements in Switzerland. In combination with a national mass flow model, measurements in WWTP and surface water have been conducted (in folder Switzerland on CIRCA).
UK	The Environment Agency has a Targeted Risk Based Monitoring Programme (TRBM) that has been used to identify the risks posed by a range of substances that have not been picked up under normal monitoring drivers. Unfortunately I do not believe that the findings from this programme has ever been published

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ANNEX 2. WORKSHOP AGENDA

EUROPEAN COMMISSION
DIRECTORATE-GENERAL
Joint Research Centre
Institute for Environment and Sustainability
Rural, Water and Ecosystem Resources

JRC - NORMAN
Water Framework Directive
Workshop on
River Basin-Specific Pollutants
Selection and Monitoring
STRESA, ITALY
10-11 JUNE 2010

AGENDA

Workshop venue Hotel La Palma, Stresa, Italy

Thursday, 10.6.2010

Time	*Issue*
9:00	**Welcome** L. Hordijk, JRC IES Director
9:15	**Member States' reporting on water quality: focus on river basin-specific pollutants** M. David, DG ENV
9:35	**Emerging pollutants and river basin-specific pollutants – Scope of the workshop** V. Dulio NORMAN Association, G.Hanke JRC IES
10:00	**MS approaches – Questionnaire outcome overview** H. Piha JRC IES Presentation of overall results from the questionnaire addressed to the Member States, followed by questions from the floor.
10:15	**COFFEE BREAK**
10:45	**MS approaches – Questionnaire outcome** An overview on responses by Member States, with short presentations (15 min each) by selected MS on their particular experiences followed by questions from the floor. Alfred Rauchbüchl, Austria: Danube case Beate Zedler, Germany: Rhine case John Batty, United Kingdom: United Kingdom case Lauriane Greaud, France: France screening case
12:30	**LUNCH BREAK**
	Thematic working sessions on selected RBSP topics Each thematic working session will consist of short introductory presentations followed by a facilitated discussion in (table) groups on a prepared set of questions. Each table will collect the group's responses to the questions and an overall feedback on each topic will then be presented to all participants in a short wrap-up session.
14:00	***Thematic working session 'Data Availability'*** Availability and quality of data on environmental occurrence and (eco)toxicological properties of chemicals Flash presentations (5 min) : Benoit Fribourg –Blanc: EU Data collection exercise Jaroslav Slobodnik: NORMAN databases Bernd Gawlik: JRC FATE EU-wide campaigns Willie Peijnenbourg: Availability of ecotoxicological data
15:15	**COFFEE BREAK**

Time	*Issue*
15:45	***Thematic working session 'Identification of RBSP candidate substances'***
	Identification of 'candidate substances' for the selection of RBSP: Assessing pressures in the river basins and use of screening analysis Flash presentations (5 min) : Werner Brack: Field based approaches for identification of RBSP Robin Law: Identification and prioritisation of hazardous substances within OSPAR: the DYNAMEC process
17:00	**Wrap-up of thematic working sessions and proposed list of actions**
17:30	*End*

20:00 Workshop Dinner at Hotel La Palma, Invitation by JRC

Friday, 11.6.10

Time	*Issue*
9:00	**Thematic sessions on selected RBSP topics (continued)** ***Thematic working session 'Selection of RBSP'*** The process of prioritisation for the definition of the RBSP and compounds currently listed in Member States Flash presentations (5 min) : Madalina David: EU WFD Prioritisation process Willie Pejinenburg: Prioritisation of substances: tools in the light of general lack of data
10:30	**COFFEE BREAK**
11:00	***Thematic working session 'Monitoring of RBSP'*** Monitoring programs for RBSP and applied monitoring methodologies Flash presentations (5 min) : Mario Carere: WFD Chemical Monitoring Georg Hanke: JRC Chemical Monitoring on-site Stefano Polesello: Multiresidue analytical methods
12:30	**LUNCH BREAK**
13:45	**Wrap-up of thematic working sessions**
14:45	**COFFEE BREAK**
15:00	**Drafting of outcome – Identification of follow-up actions**
16:00	End

European Commission

EUR 24613 EN – Joint Research Centre – Institute for Environment and Sustainability

Title: Workshop Report: River Basin-Specific Pollutants - Identification and Monitoring

Author(s): Henna Piha, Valeria Dulio and Georg Hanke

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Abstract

Besides the set of Priority Substances laid down in Annex X of the Water Framework Directive 2000/60/EC (WFD), which are regulated and to be monitored at EU level, the EU Member States (MS) need to identify pollutants of regional or local importance (in particular substances listed in WFD, Annex VIII) and provide environmental quality standards (EQS), monitoring schemes, and regulatory measures for them. This means that MS need to decide which are the candidate substances for further investigation and which are the substances then to be declared as River Basin-Specific Pollutants (RBSP). This requires assessments of impacts as well as prioritisation efforts and strategic screening for substances possibly causing concern. While this is a matter of discretion for each of the MS of concern, there is as yet no harmonization of the procedures involved.

Therefore, JRC (European Commission, Joint Research Centre)and NORMAN (Network of Reference Laboratories for the Monitoring of Emerging Environmental Substances) organized a workshop in order to support MS. The objective of the workshop was to provide a common forum for MS and interested groups for presenting, discussing and streamlining approaches for a harmonised selection and monitoring of RBSP in the WFD context. Particular attention was given to emerging contaminants, as their prioritisation and monitoring are particularly challenging. The workshop aimed to produce clear recommendations on how to proceed.

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TransCon2010 – Environmental Transformation of organic compounds: Towards a joint perspective on the importance of transformation products as environmental contaminants

12. - 17. September, 2010, Ascona, Switzerland

Organizers: Juliane Hollender (Eawag, CH), Kathrin Fenner (Eawag, CH), John Sumpter (Brunel University, CH)

Transformation products of organic contaminants formed in the environment might and in some cases are known to be more persistent, bioaccumulative and/or toxic than their parent compounds. They are therefore considered an emerging issue in environmental chemistry and toxicology. Since consistent methodologies for their assessment are missing and environmental toxicology and chemistry data on transformation products are in most cases sparse, an international conference on the topic, TransCon2010, was convened on Monte Verità, Ascona, Switzerland, in September of this year. The conference brought together about 75 academic, regulatory and industry participants from different countries to develop a common understanding of how much transformation products contribute to the overall chemical risk in the environment and of how to deal with transformation products in chemical risk assessment and environmental quality assessment.

Defining the scientific state-of-the-art

In the opening keynote lecture John Sumpter (Brunel University) set the basis for discussing the importance of transformation products by pointing out that the overall goal of our research should be to protect the environment and that therefore our focus should be on those transformation products that are of most ecotoxicological concern. Over the course of the conference, several cases of known, problematic transformation products were presented including well-known cases such as the transformation of DDT to its toxic and persistent transformation product DDE, but also some more recently discovered issues such as the photodegradation of triclosan to toxic products (Kris McNeill, ETH Zurich) or formation of drinking water disinfection by-products linked to carcinogenic effects in humans (Susan Richardson, U.S. EPA).

Sessions on Monday and Tuesday on analytical tools for the identification of transformation products, reconnaissance and field studies and laboratory-based studies on the chemical and biological formation of transformation products demonstrated that current research on transformation products is heavily focused on assessing exposure to transformation products. Specifically, analytical approaches to identify transformation products including high-resolution mass spectrometry, and 1- and 2-dimensional NMR techniques were pointed out by Thomas Ternes (BAFG). Juliane Hollender (Eawag) presented an overview of quantitative analyses of transformation products present in the aquatic environment in trace concentrations, thus demonstrating that highly sensitive and temporally and spatially resolved monitoring of transformation products is possible and ongoing at different institutions. Further, sessions on Wednesday discussed models to predict environmental exposure to transformation products (Kathrin Fenner, Eawag) and structure-based approaches to predict rates and pathways of different transformation processes (Gerrit Schüürmann, UFZ Leipzig), thus emphasizing the diversity of ongoing exposure-related research. Presentations on attempts to predict biotransformation pathways of micropollutants were nicely contrasted by Perry

McCarty's (Stanford University) historical perspective on microbial transformations of chlorinated solvents, which also enumerated some challenges in predicting these transformations considering general principles of microbiology.
Sessions on Thursday were dedicated to effect- and risk assessment and featured experimental and model-based approaches to assess ecotoxicologial and human health effects of transformation products relative to their parent compounds (Beate Escher, University of Queensland). These sessions clearly demonstrated the large data gaps on the effect side, and also emphasized the uncertainties concerning transformation product data and the resulting difficulties in their inclusion in chemical risk assessment that regulatory authorities (Mark Bonnell, Environment Canada) and chemical and pharmaceutical industry (Jason Snape, Astra Zeneca) are confronted with. Finally, ongoing research on the transformation of nanoparticles in the environment was presented by Joel Pedersen (University of Wisconsin-Madison) and identified as another very complex scientific field that is only just started being investigated in a systematic manner.

Research opportunities
Besides the keynotes and regular conference contributions as poster or platform presentations, there were four concurrently run workshops aimed at deepening the discussion on specific topics and particularly pointing out promising new research opportunities. The four groups addressed novel analytical tools, opportunities to predict transformation products and rates, effect assessment, and risk assessment of transformation products. They were chaired by Michael Radke (University of Bayreuth), Christian Zwiener (University of Tübingen), Martin Hansen (University of Copenhagen), and Carla Ng (ETH Zürich). The three most important visions that came out of the working groups were (i) establishing a closer link between exposure and effect assessment of transformation products through the concept effect-driven transformation studies, (ii) a more extensive usage of a number of databases to develop tools that predict the probability and likely routes of chemical and biological transformations through cooperation of those who use the data (regulators), those who own it (industry) and the researchers developing the models, and (iii) developing methods to read across from existing experimental data on the parent compound to facilitate property prediction for the transformation products.

Workshop

Engineered Nanoparticles in the Environment

Analysis, Occurrence and Impacts

19-20 October 2010 at BfG in Koblenz

Introduction

Nanotechnology has become an important part of our everyday life and nanoparticles, i.e. particles with dimensions smaller than 100 nm, are already used today in a large number of consumer products such as personal care products, clothing or sports equipment. Furthermore, their use and application is expected to strongly increase with nanotechnology being on of the most promising future technologies. However, there are still many uncertainties about the potential adverse effects of nanoparticles, especially when considering that these particles, owing to their size, even have the potential to penetrate into living cells or to cross the blood-brain barrier. Also with regard to the environmental behaviour there are still major gaps in our current knowledge. Due to the high production amounts (~2 Mio. t TiO_2 in 2009) as well as their wide spectrum of application, nanoparticles are discussed as a new emerging group of environmental pollutants.

The NORMAN workshop 'Engineered Nanoparticles in the Environment – Analysis, Occurrence and Impacts' addressed, amongst others, issues related to analytical techniques for nanoparticles in environmental matrices, the fate of engineered nanoparticles in the aquatic environment and during wastewater treatment, their interactions with inorganic and organic pollutants as well as their potential ecotoxicological impacts on biota. The main objective of the meeting was to discuss and evaluate the future requirements with regard to a profound environmental assessment of engineered nanoparticles.

The following central questions have been discussed during the workshop:

Analysis: Are there appropriate analytical methods for environmental matrices?

For specific questions appropriate analytical methods are available, especially for laboratory systems with a limited number of substances. However, for complex environmental matrices with high quantities of natural particles it is still a challenge and comprehensive methods to quantify engineered nano particles (ENPs) are lacking to date. It is therefore absolutely crucial to use several independent analytical methods for the determination of ENPs in the environment. However, there is the still an enormous need for concepts and analytical developments enabling to determine ENPs in environmental matrices.

Behaviour of ENPs in the environment: To what extent they are modified in the environment? Do they pass "natural and technical" barriers?

Already the ENPs which are discharged into the environment are modified by chemical, physical and biological processes. For instance, ENP tend to agglomerate with each other and with naturally occurring particles, forming particles with larger sizes in the µm- or even in the mm-range. Furthermore, chemical processes such as oxidation or hydrolysis are likely to alter their surfaces which have been specifically designed for certain applications. Others may completely dissolve and precipitate again as is the case for Ag^0-ENP which transform mainly into Ag_2S. Finally, the formation of biofilms at the ENP surfaces might alter the properties of ENPs. The interaction of the surface of the ENP, which can be functionalized at will, with the surrounding media will largely control the fate of the ENP in the environment.

All these factors have to be considered when assessing and determining the potential of ENPs to pass natural barriers (e.g. hyporheic zones, soil) and technical barriers (e.g. bank filtration, wastewater treatment processes). Based on the current knowledge the barriers are passed only under special conditions and to a limited extent. However, the knowledge gaps with respect to that topic are huge.

Pollutant carriers: are NPs expected to be relevant carriers for inorganic/organic pollutants?

ENPs are prone to adsorb or absorb organic and inorganic pollutants due to the extended surfaces of their small sizes and due to their specific surface properties. However, is the portion of ENPs high enough to compete as sorbent with natural particles which are already present in environmental samples, is one crucial question for the relevance of ENPs as carriers for pollutants. Preferential flow might have a major impact, although it is difficult to assess. On the other hand there are pollutants which might be sorbed to ENPs already during their application such as in sunscreens. Since the desorption of pollutants is frequently a rather slow process, ENPs might carry at least these pollutants, since during application the competition of other sorbents might be much lower than under environmental conditions.

Ecotoxicity: Do ENPs have severe impacts on biota?

The number of ecotoxicological studies is increasing in literature. However, the design of these studies is extremely challenging due to the rapid chemical, physical and biological modification of their surfaces which might significantly differ between laboratory and environmental conditions. These modifications have a significant influence on the ecotoxicological results. Furthermore, there is frequently a lack of a proper characterization of nanoparticles, both before and during the tests applied. However, there are already a few scientifically sound ecotoxicological studies indicating that sever impacts are likely to occur, even though the knowledge gaps are much higher than the number of available studies. There is a crucial need to put much more efforts on the reproducibility and the validation of the results as well as on the proper selection of test organisms and end points. Furthermore, it will be very challenging to transfer the results from lab-scale to environmental relevant conditions. Also the size effect has to be investigated in greater detail: It is crucial to assess whether the observed effects are caused by the size-related physico-chemical properties (e.g. higher specific surface area) or whether there is a real ‘nano-effect’ which can not be explained just by the increased surface of the equivalent mass of smaller particles compare to larger ones.

Overall conclusions

In total, 70 participants from all over Europe and US attended the Workshop. All participants agreed that a NORMAN working group on ‘Nanoparticles in the aquatic environment’ should be initiated, with regular meetings every year and an extended workshop every two years. The primary goal of this working group will be to design the future directions of research in the exciting and emerging field of the environmental impacts of nanoparticles on an European level.

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