

COMMON IMPLEMENTATION STRATEGY FOR THE WATER FRAMEWORK DIRECTIVE (2000/60/EC)



Guidance Document No. 19

GUIDANCE ON SURFACE WATER CHEMICAL
MONITORING
UNDER THE WATER FRAMEWORK DIRECTIVE

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This technical document has been developed through a collaborative programme involving the European Commission, all the Member States, the Accession Countries, Norway and other stakeholders and Non-Governmental Organisations. The document should be regarded as presenting an informal consensus position on best practice agreed by all partners. However, the document does not necessarily represent the official, formal position of any of the partners. Hence, the views expressed in the document do not necessarily represent the views of the European Commission.

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FOREWORD

The Water Directors of the European Union (EU), Acceding Countries, Candidate Countries and EFTA Countries have jointly developed a common strategy for supporting the implementation of the Directive 2000/60/EC, "establishing a framework for Community action in the field of water policy" (the Water Framework Directive). The main aim of this strategy is to allow a coherent and harmonious implementation of the Directive. Focus is on methodological questions related to a common understanding of the technical and scientific implications of the Water Framework Directive. In particular, one of the objectives of the strategy is the development of non-legally binding and practical Guidance Documents on various technical issues of the Directive. These Guidance Documents are targeted to those experts who are directly or indirectly implementing the Water Framework Directive in river basins. The structure, presentation and terminology are therefore adapted to the needs of these experts and formal, legalistic language is avoided wherever possible.

In the context of the above-mentioned strategy, a range of guidance documents have been developed and endorsed by the Water Directors during the period 2002-2008 (18 documents in total). They provide Member States with guidance on e.g. the identification of water bodies (CIS Guidance No. 2), the analysis of pressures and impacts (CIS Guidance No. 3), monitoring (CIS Guidance No. 7) etc. in the broad context of the development of integrated river basin management plans as required by the WFD.

As a follow-up, and in the context of the development of the new Priority Substances Directive (2008/105/EC) developed under Article 16 of the Water Framework Directive, Member States have expressed the need to clarify chemical monitoring issues concerning priority substances and other chemical substances covered by the WFD. This has resulted in the decision to develop a new guidance document which would complement the existing series (in particular the Monitoring CIS Guidance No. 7 and the Groundwater Monitoring CIS Guidance No. 15). For this purpose, an informal drafting group has been established under the umbrella of the CIS Chemical Monitoring Activity (CMA). This drafting group has been coordinated by Germany and the EC Joint Research Centre, and involved a range of experts from other Member States and from stakeholder organisations

The present Guidance Document is the outcome of this drafting group. It contains the synthesis of the output of discussions that have taken place since December 2006. It builds on the input and feedback from a wide range of experts and stakeholders that have been involved throughout the procedure of Guidance development through meetings, workshops, conferences and electronic media, without binding them in any way to this content. It also contains inputs from the AMPS (Analysis and Monitoring of Priority Substances) Report, as well as from the EAQC-WISE (European Analytical Quality Control in support of WISE) funded under the 6th Framework Programme.

"We, the water directors of the European Union, Norway, Switzerland and the countries applying for accession to the European Union, have examined and endorsed this Guidance during our informal meeting under the French Presidency in Paris (24-25 November 2008). We would like to thank the participants of the Chemical Monitoring Activity and, in particular, the leaders of the inputs drafting group for preparing this high quality document. We strongly believe that this and other Guidance Documents developed under the Common Implementation Strategy will play a key role in the process of implementing the Water Framework Directive and its daughter Priority Substances Directive.

This Guidance Document is a living document that will need continuous input and improvements as application and experience build up in all countries of the European Union and beyond. We agree, however, that this document will be made publicly available in its current form in order to present it to a wider public as a basis for carrying forward ongoing implementation work.

We also commit ourselves to assess and decide upon the necessity for reviewing this document in the light of scientific and technical progress and experiences gained in implementing the Water Framework Directive and Priority Substances Directive'.

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1. PURPOSE OF THIS GUIDANCE DOCUMENT

A strategy for dealing with pollution of water from chemicals is set out in Article 16 of the Water Framework Directive 2000/60/EC (WFD). As a first step of this strategy, a list of priority substances was adopted (Decision 2455/2001/EC) identifying 33 substances of priority concern at Community level. The proposal of a Directive of the European Parliament and of the Council on environmental quality standards in the field of water policy (developed under Article 16 of Directive 2000/60/EC) has the objective to ensure a high level of protection against risks to or via the aquatic environment arising from these 33 priority substances by setting European environmental quality standards. In addition, the WFD requires Member States to identify specific pollutants in the River Basins and to include them in the monitoring programmes. Monitoring of both WFD priority substances and other pollutants for the purpose of determination of the chemical and ecological status shall be performed according to Article 8 and Annex V of the WFD.

Member States have expressed the need for more guidance on implementation details of the monitoring for chemical substances. In-line with previous documents under the WFD Common Implementation Strategy (WFD CIS) this guidance document has, therefore, been developed as mandated through the Chemical Monitoring Activity (Mandate of Chemical Monitoring Activity 2005-2006). While not being legally-binding, it presents the common view of EU Member States on how to monitor chemical substances in the aquatic environment. This document should present best practices, complement existing CIS guidance and give links to relevant guidance and international standards or procedures already in practice. Guidance on groundwater monitoring is given in a separate document elaborated by CIS Working Group C¹.

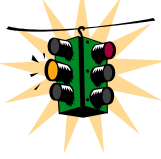
This guidance includes the monitoring of the WFD priority substances, other specific pollutants and all other chemical parameters relevant in the assessment of the ecological or chemical status of a water body or in the assessment of programmes of measures. The guidance focuses on monitoring including sampling and laboratory analyses, it covers also in-situ field monitoring of physico-chemical quality elements, but not the monitoring of hydromorphological elements.

This document represents the current state of technical development in a field that is undergoing continuous changes through ongoing scientific research. This denotes that the guidance is open to continuous improvements according to the boundary conditions set in the WFD with possible updates along the 6 years river basin management cycle of the Directive. Since there is an overlap between WFD and the Marine Strategy Framework Directive (Directive 2008/56/EC) as regards chemical pollutants in territorial waters a link between monitoring activities for both Directives has to be established. However, this guidance refers to monitoring of inland, transitional and coastal water bodies under the WFD, and includes some areas of territorial waters also covered by the MSFD. It does not cover some specific aspects of marine monitoring.

Member States will have the opportunity to adjust their monitoring programmes starting in 2007 according to technical progress and the outcome of discussions on the proposal of a

¹ CIS Guidance document No. 15 'Groundwater Monitoring', European Commission, 2006


Directive on environmental quality standards in the field of water policy, amending Directive 2000/60/EC.

	<p>Look out! Issues of compliance, statistical treatment and reporting of monitoring data are not within the mandate of this guidance document</p>
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2. BACKGROUND

The Water Framework Directive, including its amendments and existing guidance, provides the background for this guidance document. Links with these documents are indicated and sections of these documents of specific importance are provided for easier reading.

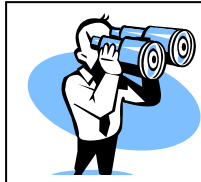
In the Water Framework Directive provisions regarding monitoring of chemical substances in surface waters are laid down in Article 8 and the Annex V.

	<p>Look in: Water Framework Directive 2000/60/EC Article 8 and Annex V</p> <p><i>1. Member States shall ensure the establishment of programmes for the monitoring of water status in order to establish a coherent and comprehensive overview of water status within each river basin district.</i></p>
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The Directive sets the Environmental Quality Standards and the basic provisions for compliance checking.

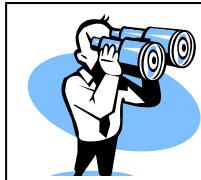
	<p>Look in: European Parliament legislative resolution of 17 June 2008 on the Council common position with a view to the adoption of a directive of the European Parliament and of the Council on environmental quality standards in the field of water policy and amending Directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/491/EEC, 86/280/EEC and 2000/60/EC (11486/3/2007 – C6-0055/2008 – 2006/0129(COD))</p>
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General guidance on monitoring water quality elements can be found in the guidance document No. 7 MONITORING UNDER THE WATER FRAMEWORK DIRECTIVE produced by Working Group 2.7 - Monitoring. The document deals with both chemical and biological parameters, but specific requirements on guidance for chemical monitoring under the WFD like, e.g., sampling, analytical methods and quality assurance have not been covered completely.

**Look in:**

Guidance document No. 7 - MONITORING UNDER THE WATER FRAMEWORK DIRECTIVE

The monitoring requirements depend to a large extent on the pressures and impacts that have been identified for the specific water body. Monitoring requirements can, therefore, change with ongoing assessments and changes in anthropogenic pressures and impacts.

**Look in:**

Guidance document No. 3 - ANALYSIS OF PRESSURES AND IMPACTS

The Final Draft of the “Commission Directive laying down, pursuant to Directive 2000/60/EC of the European Parliament and of the Council, technical specifications for chemical analysis and monitoring of water status” specifies minimum performance criteria for analytical methods used by laboratories mandated by competent authorities of the Member States for chemical monitoring of water status as well as rules for demonstrating the quality of analytical results.

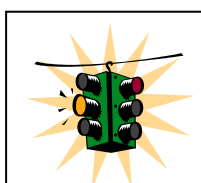
**Look in:**

Final Draft of the “Commission Directive laying down, pursuant to Directive 2000/60/EC of the European Parliament and of the Council, technical specifications for chemical analysis and monitoring of water status”

The content of this document has been based on the activities of the Expert Group on Analysis and Monitoring of Priority Substances (AMPS), the Chemical Monitoring Activity (CMA) and discussions throughout the ongoing WFD implementation process.

**Look in:**

EU REPORT CONTRIBUTIONS OF THE EXPERT GROUP ON ANALYSIS AND MONITORING OF PRIORITY SUBSTANCES AMPS to the Water Framework Directive Expert Advisory Forum on Priority Substances and Pollution Control (EUR 21587 EN)

**Look out!**

The guidance for chemical monitoring will have to be adapted to regional and local circumstances keeping in mind that the development in water status should be monitored by Member States on a systematic and comparable basis throughout the Community.

3. TERMS AND DEFINITIONS

Selected terms and definitions of specific importance for the chemical monitoring according to WFD are listed here. In addition, some terms of utmost importance are given here using the exact wording from WFD, daughter directives and the CIS guidance documents to assist clarity. All other terms, which have already been agreed upon and defined elsewhere in WFD and associated documents, are not listed here, but are used without amendment.



Look in:

Water Framework Directive 2000/60/EC Article 2

1. Surface water means inland waters, except groundwater; transitional waters and coastal waters, except in respect of chemical status for which it shall also include territorial waters.

3. Inland water means all standing or flowing water on the surface of the land, and all groundwater on the landward side of the baseline from which the breadth of territorial waters is measured.

7. Coastal water means surface water on the landward side of a line, every point of which is at a distance of one nautical mile on the seaward side from the nearest point of the baseline from which the breadth of territorial waters is measured, extending where appropriate up to the outer limit of transitional waters.

24. Good surface water chemical status means the chemical status required to meet the environmental objectives for surface waters established in Article 4(1)(a), that is the chemical status achieved by a body of surface water in which concentrations of pollutants do not exceed the environmental quality standards established in Annex IX and under Article 16(7), and under other relevant Community legislation setting environmental quality standards at Community level.

**Look in:**

Guidance document No. 7 - MONITORING UNDER THE WATER FRAMEWORK DIRECTIVE

“Significant quantities”

2.7.3 Selection of quality elements

...Those priority list substances discharged into the river basin or sub-basins must be monitored. Other pollutants also need to be monitored if they are discharged in significant quantities in the river basin or sub-basin. No definition of ‘significance’ is given but quantities that could compromise the achievement of one of the Directive’s objectives are clearly significant, and as examples, one might assume that a discharge that impacted a Protected Area, or caused exceedance of any national standard set under Annex V 1.2.6 of the Directive or caused a biological or ecotoxicological effect in a water body would be expected to be significant.

Specific Terms and Definitions for the Guidance of Chemical Monitoring**Whole water:**

“Whole water” is synonym for the original water sample and shall mean the water sample when solid matter and the liquid phase have not been separated.

Liquid (dissolved) fraction:

“Liquid (dissolved) fraction” shall mean an operationally defined fraction of whole water from which suspended particulate matter has been removed by an appropriate methodology.

Suspended particulate matter:

“Suspended particulate matter (SPM)” shall mean the particulate matter fraction of the whole water sample after separation with an appropriate methodology.

Total concentration of the analyte:

“Total concentration of the analyte” shall mean the total concentration of the analyte in the whole water sample, reflecting both dissolved and particle bound concentrations of the analyte.

Dissolved concentration of the analyte:

“Dissolved concentration of the analyte” shall mean the concentration of the analyte in the liquid (dissolved) fraction of a whole water sample.

Particle bound concentration of the analyte:

“Particle bound concentration of the analyte” shall mean the concentration of the analyte bound to SPM.

Discharged:

A substance is considered being discharged into a river basin when it is being introduced via point or diffuse sources or accidental releases.

4. MONITORING DESIGN RELATED TO SURVEILLANCE, OPERATIONAL AND INVESTIGATIVE MONITORING

4.1. General – Monitoring Design

The surface water monitoring network shall be established in accordance with the requirements of Article 8 of the Water Framework Directive (WFD). The monitoring network shall be designed so as to provide a coherent and comprehensive overview of ecological and chemical status within each river basin.

On the basis of the characterisation and impact assessment carried out in accordance with Article 5 and Annex II of the WFD, Member States shall establish for each river basin management plan period three types of monitoring programmes:

- surveillance monitoring programme,
- operational monitoring programme and,
- if necessary, an investigative monitoring programme.

Designing Surveillance/Operational Monitoring Programmes

All available information about chemical pressures and impacts should be used for setting up the monitoring strategy. Such information would include substance properties, pressure and impact assessments and additional information on sources, e.g., emission data, data on where and for what a substance is used, and existing monitoring data collected in the past.

In many cases, it will be relevant to use a stepwise screening approach to identify non-problem areas, problem areas, major sources etc. This approach may for instance start with providing an overview of expected hot spots and sources to receive a first impression of the scale of the problem. Thereafter, a more focused monitoring can be performed directed to relevant problem areas and sites. For many substances, screening of the levels in water as well as in biota with limited mobility and in sediment will be the best way to get the optimum information within a given amount of resources. When the problem areas are identified, analysis of a limited number of water samples can be performed.

The monitoring programmes will need to take account of variability in time and space (including depth) within a water body. Sufficient samples should be taken and analysed to adequately characterise such variability and to generate meaningful results with proper confidence.

The use of numerical models with a sufficient level of confidence and precision for designing the monitoring programmes can also be helpful.

The documentation of progressive reduction in concentrations of priority substances and other pollutants, and the principle of no deterioration are key elements of WFD and require appropriate trend monitoring. Member states should consider this when designing their monitoring programmes. Data obtained in surveillance and operational monitoring may be used for this purpose.

4.2. Sampling Strategy

Important principles of sampling strategy have been described in the CIS guidance document No.7 (e.g., 2.4., 2.7.2, 5.2.5). Depending on the objective of the monitoring, the physico-chemical properties of the substance to be monitored and the properties of the water body under study water, sediment and/or biota samples have to be taken.

The set-up of the monitoring strategy includes decisions on the sampling locations, sampling frequencies and methods. This selection is a compromise between a sufficient coverage of samples in time and space to generate meaningful results with proper confidence and limiting the monitoring costs.

As the establishment of environmental quality standards (EQS) has been limited for the majority of priority substances to water only, the principle matrix for assessing compliance² with respect to EQS is whole water, or for metals, the liquid fraction obtained by filtration of the whole water sample. EQSs referring to concentrations in biota have been established only for mercury, hexachlorobenzene, and hexachlorobutadiene at Community level. In order to allow Member States flexibility depending on their monitoring strategy, they may either monitor and apply the EQSs for biota, or introduce stricter EQS for water in order to provide the same level of protection as the EQS for biota. Furthermore, Member States may opt to establish and apply EQSs for sediment and/or biota for other substances listed in the proposed Directive. These EQSs shall offer at least the same level of protection as the EQS for water.

For other pollutants, the matrix for analysis should be in line with the matrix for which national EQS have been derived.

Water/SPM


WFD chemical status is generally assessed from analyses of water samples for substances with stated chemical water quality criteria. However, supporting parameters for the assessments of the ecological and chemical status may have to be analysed in water or other matrices.

The type of water sample to be taken at each site is part of the strategy for the monitoring programme. For most water bodies spot samples are likely to be appropriate. In specific situations, where pollutant concentrations are heavily influenced by flow conditions and temporal variation and if pollution load assessments are to be performed, other more representative types of samples may be beneficial. Flow-proportional or time-proportional samples may be better in such cases. In stratified water bodies such as lakes, some estuaries and coastal areas, water samples may be taken in different depths to give a better representation of the water column compared to a single sampling depth. For example, multiparameter probes (e.g., CTD-probes) can be employed to detect stratifications.

² For the purpose of this guidance document the term compliance means that

- a) reported annual average concentrations or reported concentrations of priority substances/other pollutants do not exceed the EQS laid down in Directive on Environmental quality standards in the Field of water policy and amending Directive 2000/60/EC.
- b) environmental objectives specified in the WFD such as no deterioration of the status of a water body, good chemical status of a water body, or trend reversal have been achieved.

In general, reliable data on emission sources reduce monitoring costs because they give a good basis for choosing proper sampling locations, and optimising the number of sampling sites and the appropriate sampling frequencies.

	<p>Look in: Water Framework Directive 2000/60/EC Article 16(7)</p> <p><i>The Commission shall submit proposals for quality standards applicable to the concentrations of the priority substances in surface water, sediments or biota.</i></p>
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Whole water data may be generated by analysis of the whole water sample, or by separate determinations on liquid and SPM fractions. If it can be justified – for example by considerations of expected contaminant partitioning – it may be argued that there is not a need to analyse a particular fraction. If a sampling strategy is selected involving only liquid or SPM fractions, then, Member States shall justify the choice with measurements, calculations, etc.

However, demonstrating compliance with EQS in water may be problematic in some cases. Examples include:

- available analytical methods are not sufficiently sensitive or accurate for quantification of substances at the required concentration level (see 6.1),
- water bodies with high and fluctuating SPM content and varying properties (sampling representative water sample is problematic).

Sediment and Biota³

To check compliance with biota EQS values, the most appropriate indicator species among fish, molluscs, crustaceans and other biota should be monitored (this will be dealt with in a separate guidance document, see footnote 3).

In addition to chemical and ecological status assessment, the prevention of further deterioration of the status of aquatic ecosystems is another important objective of the WFD. Monitoring of contaminants in sediment and biota may be used to assess the long-term impacts of anthropogenic activity and thus, to assess the achievement of the above mentioned objective. It includes the determination of the extent and rate of changes in levels of environmental contamination.

Hydrophobic and lipophilic substances that tend to accumulate in sediment and biota may be monitored in these matrices for resource effective trend monitoring in order to:

- assess compliance with the no deterioration objective (concentrations of substances are below detection limits, declining or stable and there is no obvious risk of increase) of the WFD,
- assess long-term changes in natural conditions and those resulting from widespread anthropogenic activity,

³ Further guidance on monitoring of WFD relevant substances in biota and sediment is under development within the Chemical Monitoring Activity of the European Commission

- monitor the progressive reduction in the concentrations of priority substances (PS) and the phasing out of priority hazardous substances (PHS).

Furthermore, the use of sediment and biota in monitoring hazardous substances is important in other issues of WFD implementations, viz.:

- identify fate and behaviour of pollutants,
- describe the general contaminant status and supply reference values for regional and local monitoring programmes,
- accumulating matrices give an integrated and less variable measure of the contaminant burden over a longer time period, and consequently, an improved statistical power for time series analysis

The selection of the monitoring matrix has implications on the monitoring frequencies on both scientific and cost grounds.

If sediment or biota are used for temporal trend monitoring it is recommended, if practicable, that the quantitative objectives of the monitoring are determined before any monitoring programme is started. For instance, the quantified objective could be to detect an annual change of 5 % within a time period of 10 years with a power of 90 % at a significance level of 5 % with a one-sided test.

Sediment samples should be collected at an appropriate frequency that will have to be defined on a local basis, where appropriate, taking into account the sedimentation rate of the studied water body and hydrological conditions (e.g., flood events). Typical sampling frequency will vary from once every 1 to 3 years for large rivers or estuaries that are characterised by high sedimentation rates, to once every 6 years for lakes or coastal areas with very low sedimentation rates.

The locations for sediment trend monitoring should be representative of a water body or a cluster of water bodies. Where possible, sampling should be performed in non-erosion areas, which are representative of sediment formation. For dynamic systems it might be useful to collect suspended matter for monitoring purposes.

In case of using biota in trend monitoring it is common practice to collect samples at least once per year during the non-spawning season.

Representativeness is a key point, i.e. how well a sample reflects a given area or how much area the sample represents given a certain level of statistical significance. For example, it is essential to collect specimens for analysis well away from the mixing zones when the sampling point is downstream of a significant discharge.

To improve the power of the monitoring programme samples should be collected from areas characterised by relatively low natural variability.

4.3. Use of Models as a Tool in WFD Monitoring

Numerical models are important tools for planning monitoring strategies and designing monitoring programmes. They can help to understand the spatial and temporal variations in pollutant concentrations. For instance, measurements in sediments and biota combined with

models can be used to estimate dissolved water concentrations for some contaminants, particularly hydrophobic organic compounds. Thus, appropriately validated and tested models can provide, within the impact and pressure assessments, additional evidence that EQS will not be violated in a specific water body under the most adverse conditions.

Given the current levels of uncertainty, concentrations of contaminants estimated by modelling cannot be used for the purpose of compliance checking for water bodies that are at risk of failing WFD provisions. The approach can, however, be used in surveillance monitoring for estimation of concentrations in water bodies that are shown to be not at risk when the uncertainty of the model is considered.

According to partitioning theory, relationship curves and/or mechanistic models can be used to estimate a corresponding, or equilibrium water concentration from measured levels of hydrophobic contaminants in biota/sediments. This way, areas can be cost-efficiently scanned using sediments and biota to compare contaminant levels in different areas and to identify possible sources of contaminants to the area.

Relationship curve models are based on correlations between chemical measurement data and some descriptor, whereas mechanistic models are based on processes giving rise to the observed data. Some examples are the relationship curve models such as OMEGA (EU Rebecca project) or BCFWIN (MEYLAN et al. 1999)⁴ and mechanistic models, such as Bioaccumulation Fish Model (MACKAY 2001)⁵ and SEDFLEX⁶. One example of relationship curve models is the use of bioaccumulation factors (BAF) in relation to the partitioning coefficient between octanol and water (K_{OW}). BAFs have been used for the past 25 years to describe the net increase of organic contaminant concentrations from water to biota, as $BAF = \text{CHEMICAL}_{\text{Animal}}/\text{CHEMICAL}_{\text{Water}}$. Because BAF is related linearly to K_{OW} ⁷, this relationship curve can be used to calculate the water concentration of a chemical when the level in biota and its partitioning coefficient are known. In the absence of environmental measurements of a chemical in biota and water to calculate BAFs, this relationship is also a useful tool for exposure and risk assessments of new chemicals. This issue is being explored by several programmes, such as: Registration, Evaluation and Authorisation of CHEMicals (REACH)⁸ in the EU (European Commission 2004), the Canadian Environmental Protection Act (CEPA)'s Domestic Substances List (DSL) (ENVIRONMENT CANADA 2003)⁹, and the US EPA high production chemicals assessments (WALKER et al. 2004)¹⁰.

⁴ Meylan, W. M.; Howard, P. H.; Boethling, R. S.; Aronson, D.; Printup, H.; Gouchie, S. (1999) Improved method for estimating bioconcentration/bioaccumulation factor from octanol/water partition coefficient. *Environ. Toxicol. Chem.* 18, 664-672.

⁵ Mackay, D. (2001) *Multimedia Environmental Models; The Fugacity Approach*. Lewis Publishers, CRC Press, Boca Raton, Florida.

⁶ Saloranta, T. M., Andersen, T., Næs, K. (2006) Flows of dioxins and furans in coastal food webs: inverse modeling, sensitivity analysis, and application of linear system theory. *Environmental Toxicology and Chemistry* 25, No. 1, pp. 253–264.

⁷ This only holds provided the contaminant is not metabolised by the animal quickly, and if the concentration in the animal is expressed on lipid weight basis

⁸ European Commission. Why do we need REACH? REACH in brief; European Commission, Environment Directorate General: Brussels, 2004; 18 pp.

⁹ Environment Canada. Existing Substances Evaluation Bulletin; Ottawa ON, 2003, 9 pp. http://www.ec.gc.ca/Substances/ese/eng/what_new.cfm.


¹⁰ Walker, J. D.; Knaebel, D.; Mayo, K.; Tunkel, J.; Gray, D. A. (2004) Use of QSARs to promote more cost-effective use of chemical monitoring resources. 1. Screening industrial chemicals and pesticides, direct food additives, indirect food additives and pharmaceuticals for biodegradation, bioconcentration and aquatic toxicity potential. *Water Qual. Res. J. Can.* 39, 35-39.

The mechanistic model SEDFLEX is composed of a dispersion part simulating the sources, transport and sinks of contaminants in a fjord, estuary or lake system, and a food web part that calculates uptake and accumulation in biota as well as quantification of different food sources, mainly from sediment or from water⁶. When emission data are added to the dispersion part, SEDFLEX can predict how changes in the environment would be reflected in water, biota or sediment concentrations, respectively, and what the response time would be.

The predictive power of models is only valid within the framework and limits defined by its assumptions. Models with a sufficient level of confidence can be helpful for designing the monitoring programmes. However, it is important to define the desired level of confidence and consider uncertainties associated with chemical measurements in biota/sediments as well as with other parameters used in the model. As a result, estimated water concentrations may vary considerably. By the use of model sensitivity analyses, combined with knowledge on uncertainty of measurement, the confidence of the modelled concentrations can be assessed. The level of confidence will be site and chemical specific. It is crucial that the model performance is carefully documented. Existing knowledge gaps must be quantified and taken into account as uncertainty factors when applying models.

In using sediments and biota as a first level screening for certain chemicals in the monitoring programme, water measurements may be downscaled. The initial screening will help to identify areas of concern and where to direct effort, such as a follow up with water samples and direct measurements. This process provides good grounds for using models, where appropriate.

4.4. Monitoring Frequency

	<p>Look in: Water Framework Directive 2000/60/EC Annex V 1.3.4</p> <p><i>For the surveillance monitoring period, the frequencies for monitoring parameters indicative of physico-chemical quality elements given below should be applied unless greater intervals would be justified on the basis of technical knowledge and expert judgement.</i></p> <p><i>For operational monitoring, the frequency of monitoring required for any parameter shall be determined by Member States so as to provide sufficient data for a reliable assessment of the status of the relevant quality element. As a guideline, monitoring should take place at intervals not exceeding those shown in the table below unless greater intervals would be justified on the basis of technical knowledge and expert judgement.</i></p> <p>Guidance document No. 7 - MONITORING UNDER THE WATER FRAMEWORK DIRECTIVE, 2.1</p>
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The monitoring frequencies given in WFD, Annex V 1.3.4 of once-a-month for priority substances and once-per-three-months for other pollutants will result in a certain confidence and precision. More frequent sampling may be necessary e.g., to detect long-term changes, to estimate pollution loads and to achieve acceptable levels of confidence and precision in

assessing the status of water bodies. In general, it is advisable to take samples in equidistant time intervals over a year, e.g., every four weeks resulting in 13 samples to compensate for missing data due to unusual weather conditions (drought, floods, etc.) or laboratory problems. In case of pesticides and other seasonally variable substances, which show peak concentrations within short time periods, enhanced sampling frequency compared to that specified in the WFD may be necessary in these periods. For example, the best sampling time for detecting concentration peaks of pesticides due to inappropriate application is after heavy rainfall within or just after the application period. Moreover, failure to comply with good agricultural practice, e.g., inappropriate cleaning of equipment during or at the end of the season before winter can also cause pesticide peak concentrations. Other reasons for enhanced sampling frequency include seasonal pressure from tourism, seasonal industrial activities, which are common practice for example in pesticide production etc. The results of those measurements should be compared with the MAC-EQS. For the calculation of the annual average concentrations results have to be weighted according to the associated time interval (time weighted average). For example, 12 equidistant values per year with two additional values in November could be accounted for with reduced weights for the three November values. In other words, the three November values would be averaged and a "November mean" be used in the calculation of the annual average value. Using this approach, any individual values should still trigger an immediate investigation if high levels are detected.

Collecting composite samples (24h to one week) might be another option to detect peak concentrations of seasonally variable compounds.

To estimate the pollutant load, which is transferred across Member State boundaries and into the marine environment, an enhanced sampling frequency may be advisable. In case of spot sampling for substances, which show a wide range of concentrations, biweekly sampling, i.e. 26 samples a year may be justified. Flow-proportional or time-proportional sampling may be beneficial in such cases.

Reduced monitoring frequencies, and under certain circumstances, even no monitoring may be justified when monitoring reveals/has revealed that concentrations of substances are far below the EQS, declining or stable and there is no obvious risk of increase.

The monitoring frequencies quoted in the Directive may not be practical for transitional and coastal waters, Nordic lakes, which can be iced for several months, and for Mediterranean rivers which may contain no water for several months each year.

4.5. Surveillance Monitoring

4.5.1. Objectives

According to WFD Annex V1.3.1 the objectives of surveillance monitoring of surface waters are to provide information for:

- supplementing and validating the impact assessment procedure detailed in Annex II;
- the efficient and effective design of future monitoring programmes;
- the assessment of long-term changes in natural conditions; and
- the assessment of long-term changes resulting from widespread anthropogenic activity.

It should be stressed that surveillance monitoring is not intended for:


- mapping and analysing water quality problems;
- testing the effectiveness of the programme of measures;
- obtaining a detailed or complete overview of the quality of all types of water.

Such information is to be gathered within operational monitoring, investigative monitoring, and existing non-WFD related monitoring activities.

It is recommended to use monitoring data, which have to be reported according to other European Directives and international river and sea conventions for the purpose of surveillance monitoring (e.g., 76/464/EEG, Nitrates Directive 91/676/EEC, OSPAR JAMP), where appropriate.

4.5.2. Selection of Monitoring Points

The criteria for selecting the surveillance monitoring points are given in WFD Annex V 1.3.1. Water bodies probably at risk, probably not at risk and not at risk of failing the environmental objectives should be covered adequately.

	<p>Look in: Water Framework Directive 2000/60/EC Annex V 1.3.1 Guidance document No. 7 - MONITORING UNDER THE WATER FRAMEWORK DIRECTIVE, 2.7.2</p>
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Sampling points should include major rivers as well as points at the downstream end of relevant sub-catchments.

Sampling points for general physico-chemical parameters supporting the biological quality elements need to be representative of the sampling site of the biological elements (although it is recognised that physical characteristics may necessitate some flexibility in this regard). For priority substances and other pollutants, other sampling points may be selected.

Where possible, it is recommended to establish surveillance monitoring sites with fixed monitoring stations and automatic samplers allowing the collection of mixed samples. If not available, spot samples should be collected. Where possible, water level and flow should be recorded as well as pH, conductivity, and temperature, e.g., by using suitable probes.

In case of transboundary waters, consultations about the proposed water body and surveillance monitoring sites should be held between the Member States involved.

Monitoring sites to be used for pollution load estimation (country boundaries and transition from inland waters to marine environment), should, where possible, include representative water quantity as well as quality monitoring.

Representative approaches related to diffuse and widespread sources are often relevant in surveillance monitoring. In such cases sufficient monitoring points must be sampled within a selection of water bodies in order to assess the magnitude and impact of the pressures. Results can be scaled up by using measurements of biota or sediment samples from a larger number of bodies.

4.5.3. Selection of Monitoring Parameters

Chemical monitoring comprises three categories of parameters:

- substances that have to be assessed in respect of compliance with European environmental quality standards (EQS), e.g., priority substances
- other polluting substances, e.g., river-basin-specific substances, for which no European EQS are available and which have, hence, to be assessed in respect of compliance with national or river-basin-specific EQS
- primary physico-chemical parameters, e.g., nutrients, oxygen, temperature, salinity, conductivity, pH, which support interpretation of biological data and those required for reliable interpretation of the results of chemical measurements (e.g., DOC, Ca, SPM content).

For the purpose of surveillance monitoring, priority substances discharged into river basins or sub-basins must be analysed. Other pollutants defined as any substance liable to cause pollution in particular those listed in Annex VIII also need to be monitored if they are discharged in significant quantities in the river basin or sub-basin. In addition, relevant physico-chemical parameters should be measured.

4.6. Operational Monitoring

4.6.1. Objectives

Operational monitoring shall be undertaken (Annex V.1.3.2) in order to:

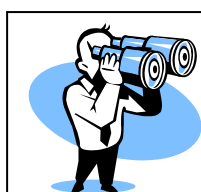
- establish the status of those bodies identified as being at risk of failing to meet their environmental objectives, and
- assess any changes in the status of such bodies resulting from the programmes of measures.

Contrary to surveillance monitoring, operational monitoring is characterised by spatial and temporal flexible monitoring networks, problem-oriented parameter selection and sampling.

The operational monitoring programme may be modified during the planning period (6 years) if the monitoring results indicate there is a reason to do so. The monitoring frequency can be reduced, for example, when an effect is no longer deemed to be significant or the pressure in question has been eliminated. This applies when good, or better, chemical and ecological status has been achieved. As soon as the good status has actually been achieved and there is no risk of failing the environmental objectives, the operational monitoring can be stopped and surveillance monitoring will suffice. If operational monitoring aims at the assessment of changes in the status of water bodies resulting from programme of measures, it might be justifiable to reduce monitoring frequencies or suspend monitoring for a certain time period as long as no change in the status can be expected.

4.6.2. Selection of Monitoring Points

The criteria for selecting operational monitoring sites are given in WFD Annex V 1.3.2.



Look in:

Water Framework Directive 2000/60/EC Annex V 1.3.2
Guidance document No. 7 - MONITORING UNDER THE WATER
FRAMEWORK DIRECTIVE, 2.8.2

If there are significant chemical pressures from point sources, sufficient locations must be selected to assess the magnitude and impact of these point sources according to Annex V of the WFD.

If there are significant chemical pressures from diffuse sources the water body selected for operational monitoring must be representative of the occurrence of the diffuse pressures, and of the relative risk of failure to achieve good surface water status. However, it should be taken into account that water bodies can only be grouped where the type and magnitude of pressure are similar.

Aggregation of water bodies is possible if the water bodies can be compared in respect of geography, hydrology, geomorphology, trophic level and extent of human pressures. In such cases, Member States shall provide evidence that the water body where monitoring is carried out is indeed representative of the group of water bodies.

Provided that there is a good documentation that local sources are absent, a few water samples from a number of representative bodies should be sufficient to identify non-problem areas affected only by diffuse input via long-range transport of pollutants.

4.6.3. Selection of Monitoring Parameters

In order to assess the magnitude of the chemical pressure to which bodies of surface water are subjected, Member States shall monitor for any priority substances and other pollutants discharged in significant amounts to the water body concerned. In addition, physico-chemical parameters relevant for reliable interpretation of the results of chemical measurements (e.g., DOC, Ca, SPM content) should be measured.

4.7. Investigative Monitoring

4.7.1. Objectives

Investigative monitoring may be required in specified cases (Annex V.1.3.3). These are given as:

- where the reason for any exceedance (of environmental objectives) is unknown,
- where surveillance monitoring indicates that the objectives set under Article 4 for a body of water are not likely to be achieved and operational monitoring has not already been established,
- in order to ascertain the causes of a water body or water bodies failing to achieve the environmental objectives,
- to ascertain the magnitude and impacts of accidental pollution.

Investigative monitoring may also include alarm or early warning monitoring, for example, for the protection of water bodies used for drinking water abstraction that may be subject to accidental pollution.

Investigative monitoring may also be triggered when a water body has been identified as being at risk of failing the objectives due to chemical pressures on the basis of the assessment of biological elements.

4.7.2. Selection of Monitoring Points/Matrix/Parameters

The starting point of investigative monitoring will often be that surveillance or operational monitoring have revealed that the EQS values are exceeded, but the causes of the failures are unknown or poorly understood. It is, however, very difficult to give general guidance on how to proceed in investigative monitoring since a case by case approach is the only way forward to take account of local conditions, the type of pressures, and the specific aim of the investigation. This will in general require expert knowledge and judgment. The necessary monitoring points, the matrix and parameters to be monitored as well as the frequency of sampling and the duration of the monitoring have to be adjusted to the specific case or problem under investigation. Investigative monitoring is characterised by spatial and temporal flexible sampling and can be stopped as soon as the cause of non-compliance has been identified. When a programme of measures is in operation and its effect can be expected to be measurable, a suitable operational monitoring has to be established. In the case of accidental pollution, investigative monitoring can be ceased as soon as the magnitude of the impact of the accidental pollution has been ascertained.

Before starting investigative monitoring, thorough pressure analysis may be required. In particular, it is important to clarify whether point or diffuse sources have to be taken into account as potential cause for non-compliance.

In order to identify the causes of exceedance of EQS in a water body or several water bodies, Member States shall monitor the priority substance(s) or other pollutant(s) of which the water concentration exceeds EQS.

5. TECHNIQUES FOR SAMPLING

5.1. General Remarks on Sampling

The quality of assessments based on the results from the chemical analyses is dependent on the quality of the sampling and on understanding the inherent variability in the media from which samples are taken. The variability of contaminant concentrations in aquatic systems is often difficult to quantify and can often be higher than uncertainties associated with the analyses themselves. Nevertheless, the overall uncertainty needs to be considered in the data evaluation and needs to be addressed in the design of a representative monitoring programme. The design of a monitoring programme includes the selection of sampling points and matrix as well as sampling frequencies as described in Chapter 4. For example in the case of water sampling, the exact position of sampling points including sampling depths depends on local conditions, e.g., parameters such as vertical and lateral mixing, water homogeneity and possibilities to use appropriate sampling equipment (see e.g., ISO 5667-6).


It is vital that all the personnel involved in sampling are sufficiently educated and trained in the procedures applied and fully aware of the risks and consequences of taking inappropriate samples. They should understand the objectives of the monitoring programme, the further treatment of the samples taken and have a certain understanding of the hydro-geochemical processes in the water body. The sampling should include a routine sampling report sufficiently detailed to document the sampling performed and include observations relevant for the assessment of the monitoring results.

QA/QC procedures are necessary to ensure the quality of the sampling activities of a monitoring programme, including care to preserve sample integrity (see ISO 5667-14 and other guidelines). Quality assurance of sampling including selection of sample, pre-treatment, sub-sampling, preservation, storage and transport is essential for the quality of final results of the chemical analyses. Quality control of the sampling should include measures that enable estimation of sampling precision. Other measures could be participation in sampling inter-comparison trials.

5.1.1. Existing Guidance Documents

Guidance on sampling techniques may be found in the ISO Standard on Water Quality – Sampling 5667 (www.iso.org), the guidelines of the OSPAR Convention (www.ospar.org) for the Joint Assessment and Monitoring Programme (JAMP) or the HELCOM COMBINE manual (http://www.helcom.fi/groups/monas/CombineManual/en_GB/main/).

5.2. Water Sampling

	<p>Look in: ISO Standard Series 5667, Part 1, 3, 4, 6 and 9</p> <p>OSPAR JAMP Guidelines: Chlorophyll a in Water, Nutrients and Oxygen</p> <p>Manual for Marine Monitoring in the COMBINE Programme of HELCOM</p>
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Water sampling procedures usually include in situ field measurements of physical and chemical parameters, e.g., water flow, temperature, conductivity (salinity), dissolved oxygen, pH, transparency, and fluorescence either in the surface water or in a vertical profile. When the results of these in situ measurements influence the sampling (e.g., the selection of sampling depths) precise guidelines on how to make decisions must be included in the sampling instructions. In stratified water bodies, the densities of phytoplankton and related chemical parameters can change dramatically across a vertical discontinuity. This must be reflected in the sampling strategy (see 4.2) and instructions.

The sampling equipment is selected according to the type of water body and to the sample requirements (e.g., size and integrity) for performing the analyses of the monitoring programme. It must be without risks of contaminating the sample, both from the construction materials of the sampler (adsorption and/or release of compounds) and from the previous use for sampling in other water bodies (memory effects).

Sample containers, transport and storage should not lead to any contamination or changes in the relevant chemical properties of the sample. Some precautions, depending on the nature of the contaminants to be analysed, must be taken to avoid contamination of the sample. Plastic materials except polytetrafluoroethylene (PTFE) must not be used for the samples to be analysed for hydrophobic organic contaminants (e.g., PCBs, PAHs). Samples taken for the analysis of organic contaminants must be stored in glass, PTFE or stainless steel containers. Samples collected for analysis of metals can be stored in closed plastic or glass containers. For mercury, samples must be stored in acid-washed borosilicate glass or quartz containers, as mercury can move through the walls of plastic containers. For organotins, samples are preferably stored in glass containers, but containers of other materials such as polycarbonate

or aluminium are also suitable. The type of containers should always be selected after consulting the laboratory performing the chemical analyses, or the containers should be supplied by the laboratory. Depending on the parameter to be determined, specific conditioning and/or cleaning of sample containers prior to use may be required.

Sample preservation is needed in many cases to avoid loss or transformation of substances due to redox processes, degradation of organic matter, and precipitation of metals as hydroxides or evaporation of gaseous or volatile constituents.


If samples are analysed within 24 h and stored in the dark at 1-5 °C, sample composition, and hence, results of chemical analyses will not change significantly. Examples of exceptions are nutrients in low concentrations. Storage of samples at temperatures below -20 °C may allow the sample to be stored for longer time periods. However, freezing is not appropriate for volatile components. It is also necessary to remove suspended matter, algae and other micro-organisms by filtering the sample before freezing to avoid changes in dissolved concentrations of substances caused by ,e.g., disruption of cells. Moreover, the risk of precipitation of, e.g., calcium carbonate at low temperatures and other processes such as co-precipitation and colloid coagulation during freezing should be considered.

The laboratory performing the chemical analyses should agree on the procedures for preservation and storage of samples.

The sampling report should include key parameters such as date, time, location and grid reference, depth, preservation method and a unique identifier, together with any field observation made for inclusion in the reporting of the monitoring results.

5.3. Sampling of Suspended Particulate Matter (SPM)

Analysis of strongly hydrophobic organic substances in SPM can be a suitable surrogate for whole water analysis. The separation of SPM from the water can be accomplished by appropriate filtration (limited to the collection of small amounts of SPM), centrifuging either in the field or in the laboratory or by sedimentation. Commonly, filtration through 0.45 µm glass-fibre depth filters is used. The qualities and quantities of SPM collected by centrifugation, filtration or by using sediment traps differ from each other. None of these techniques allows the collection of the total amount of suspended particles. Therefore, when using SPM for analysis the sampling technique has to be indicated.

	<p>Look in: ISO Standard Series 5667 Part 17</p> <p>OSPAR JAMP Guidelines for the Estimation of Riverine PAH Inputs into the North Sea and the North-East Atlantic</p>
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These guidance documents focus mainly on river sampling but the principles can be adapted for other categories of water body. The following factors are essential in deciding on the sampling regime:

- Horizontal and vertical variations in suspended solids.
- Variations in time and space in suspended solids considering especially seasonal variations, base-flow and storm flow conditions, tidal influence and influence from primary production on suspended solids.
- The volume of sample required to minimize the error producing effects caused by inhomogeneities in the water body and to meet analytical requirements.

The sampling report should also include a descriptive comments field to allow the sampler to record the procedure undertaken on site, the appearance of the water etc.

Regarding sampling containers and sample storage for SPM, see description in chapter 5.4.

5.4. Sediment Sampling³

	<p>Look in: ISO Standard Series 5667, Part 12, 15 and 19</p> <p>OSPAR JAMP Guidelines for Monitoring Contaminants in Sediments</p>
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As a general principle, the sampling procedure should not alter the properties of the sediment (e.g., by contamination or disturbing the sample). A wide range of sampling devices is available, especially for collecting marine sediments. The choice of equipment should be made depending on the local conditions at the site of sampling, e.g., water depth and type of sediment. Box or other corers, which are capable of sampling the surface sediment without disturbing the sediment structure, are recommended. In case grab samplers are used, all precautions should be taken to limit disturbing the sediment. Retrospective temporal trend studies necessarily involve the collection of samples using a box corer or large-diameter gravity corer, or an equivalent device. Alternatively, for shallow or tidal waters, hand coring may be appropriate.

As suggested above, it is good practice to complete a sampling report, which may include a general description of collected samples including colour, homogeneity (presence or absence of stratification), presence or absence of animals (indication of bioturbation), surface structures, odour and any visible contamination (e.g., oil sheen).

The sub-sampling of sediments should preferably be performed immediately after sampling. Some precautions, depending on the nature of analysed contaminants, must be taken to avoid contamination of the sample. Samples taken for the analysis of organic contaminants must be stored in glass, polytetrafluoroethylene (PTFE) or stainless steel containers. Sediments collected for analysis of metals can be stored in closed plastic or glass containers. For mercury, samples must be stored in acid-washed borosilicate glass or quartz containers, as mercury can move through the walls of plastic containers. For organotins, storage of samples is preferably done in amber glass bottles, but containers of other materials such as polycarbonate or aluminium are also suitable. If the monitoring programme requires analysis of the fine sediment fraction, the sample should be split using appropriate sieving techniques.

Samples which are analysed within 48 h after sampling should be stored at 1-5 °C in the dark (short-term storage). For long-term storage, samples should be stored frozen, at – 20 °C or below, or dried. Freeze-drying samples at low temperature (e.g., < 10 °C) is the preferred alternative to freezing, if it can be ensured that analytes do not evaporate to a substantial degree.

5.5. Biota Sampling³

	<p>Look in: OSPAR JAMP Guidelines for Monitoring Contaminants in Biota</p> <p>Manual for Marine Monitoring in the COMBINE Programme of HELCOM</p>
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Fish, mussels and seabird eggs are commonly used for monitoring of contaminants in the aquatic environment.

The natural variability within biota samples should be reduced by an appropriate sampling design, keeping in mind that age, size, sex and sexual maturity status are criteria to keep homogeneous in a given class of the sampled biota. Biota sampling should only take place when fish and bivalves are in a stable physiological state, and outside the normal period of spawning.

Fish should be collected from areas characterised by relatively low natural variability. Shellfish should preferably be collected from sub-tidal regions, or as near to the same depth and exposure (i.e. in terms of light and wave action) as possible in order to reduce variability in contaminant uptake.

Fish can be sampled from either research vessels or commercial vessels. In both cases, several precautions must be taken to reduce contamination. Clean containers should be available on deck to hold the samples temporarily before they are taken to the ship's laboratory. Personnel should wear clean gloves, free of the contaminants to be analysed, when collecting mussels by hand and when fish are taken from the net. Where appropriate, biota samples should be rinsed with water to remove any material adhering to the surface. When collecting mussels by ship, a commercial mussel dredge can be used.

Freezing of samples will degrade soft tissues. Therefore, sub-samples of particular tissue for analysis should be drawn immediately after catching the fish and immediately deep-frozen. Mussels should be depurated and cleaned prior to preservation and analysis. Dissection must be done under clean conditions on a clean bench by trained personnel, wearing clean gloves and using clean stainless steel knives. The use of blades made of ceramics or titanium is recommended to reduce the risk of Cr and Ni contamination. The soft tissue samples should be analysed immediately or stored at temperatures below – 20 °C.

Biological samples to be used for analysis of organic contaminants should be stored frozen e.g., wrapped in pre-cleaned alumina foil in suitable containers of glass, stainless steel or alumina. Plastic material, except PTFE, must not be used.

For metal analysis, biota samples should be wrapped separately in suitable material (e.g., polyethylene or PTFE) and frozen. Sub-samples (e.g., liver) should be stored in suitable acid-cleaned containers, preferably of glass, and frozen or freeze-dried immediately.

6. TECHNIQUES FOR ANALYSIS

Article 8, Paragraph 3 of the WFD requires that “technical specifications and standardised methods for analysis and monitoring of water status shall be laid down in accordance with the procedure laid down in Article 21”. Moreover, Annex V.1.3.6 of the WFD states that the standards for monitoring of quality elements for physico-chemical parameters shall be “*any relevant CEN/ISO standards or such other national or international standards which will ensure the provision of data of an equivalent scientific quality and comparability*”.

The strengths of such methods are that they are well established and have often been subjected to collaborative trials to give an illustration of their interlaboratory comparability and applicability. They may not represent the current state of the art in all cases, and usually, represent a compromise in performance that is tailored to a number of different users’ goals and operational needs.

In general, performance-based methods shall be used in surveillance and operational monitoring. They shall be described clearly, properly validated¹¹ and where possible leave laboratories the flexibility to select from several options. Irrespective of what method is applied in chemical monitoring certain minimum performance criteria have to be met, which are laid down in the Final Draft “Commission Directive laying down, pursuant to Directive 2000/60/EC of the European Parliament and of the Council, technical specifications for chemical analysis and monitoring of water status”, and discussed in the framework of the EAQC-WISE project¹².

According to this draft commission Directive the laboratories may select any analytical method of their choice for the purpose of monitoring under Article 8 and Annex V of the Directive 2000/60/EC provided they meet the minimum performance criteria set out in this document or by the national competent authorities.


Laboratories can consult chapter 6.5 and Annex II to identify suitable methods for monitoring of priority substances and other pollutants. Available certified reference materials relevant to WFD monitoring¹³ are listed in Annex III. The Annex III was elaborated within the EU-project EAQC-WISE¹².

¹¹ see e.g., the protocols for method validation developed within the NORMAN network, funded under the 6th RTD Framework Programme, European Commission, <http://www.norman-network.com>.

¹² EAQC-WISE project, funded under the 6th RTD Framework Programme, European Commission, <http://www.eaqc-wise.net/>

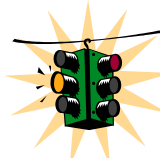
¹³ Bercaru, B. Gawlik, F. Ulberth, C. Vandecasteele (2003) Reference materials for the monitoring of the aquatic environment - a review with special emphasis on organic priority pollutants. Journal of Environmental Monitoring 5, 697-705.

6.1. Method Performance Criteria

	<p>Look in: Final Draft “Commission Directive laying down, pursuant to Directive 2000/60/EC of the European Parliament and of the Council, technical specifications for chemical analysis and monitoring of water status”</p>
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Minimum performance criteria have been defined for the limit of quantification (LOQ) and the measurement uncertainty U (expanded uncertainty of measurement). They are, where possible, linked to the EQS. In the following chapters 6.1.1/6.1.2 guidance will be given on how to determine/estimate these parameters in a pragmatic way.

If no suitable analytical method is available that meets these minimum performance criteria for a particular priority substance, e.g., tributyltin compounds or short-chain chloroalkanes, Member States shall ensure that monitoring is carried out using best available techniques not entailing excessive costs. The use of more resource intensive methodologies, if these can provide the needed performance, at reduced frequencies, is encouraged in these cases.

	<p>Look out! The mandate M/424 for standardisation addressed to CEN for the development or improvement of standards in support of the Water Framework Directive including methods for the analysis of tributyltin compounds, polybrominated diphenyl ethers, polynuclear aromatic compounds, C₁₀-C₁₃ chloroalkanes, and organochlorine pesticides in water has been adopted.</p>
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6.1.1. Uncertainty of Measurement^{14,15,16}

According to ISO guide 99¹⁷, measurement uncertainty has been defined as ‘*a non-negative parameter characterising the dispersion of the quantity values being attributed to a measurand, based on the information used*’.

Measurement uncertainty (U_m) is typically expressed as a laboratory result \pm the measurement uncertainty.

U_m should normally be expressed as the combined expanded uncertainty using a coverage factor $k = 2$ where k is a numerical factor used as a multiplier of the combined standard uncertainty in order to obtain an expanded uncertainty. This provides a confidence level of approximately 95 %.

¹⁴ Nordtest Report TR537. Handbook for calculation of measurement uncertainty in environmental laboratories, 2nd Edition, 2004.

¹⁵ EURACHEM/CITAC Guide: “Quantifying Uncertainty in Analytical Measurement”, 2nd Edition, 2000

¹⁶ ISO/IEC “GUM” (with BIPM, IFCC, IUPAC, IUPAP, OIML): “Guide to the expression of uncertainty in measurement”, 1993.

¹⁷ ISO guide 99 International vocabulary of metrology - Basic and general concepts and associated terms (VIM), ISO/IEC 2007

The ability to provide a measurement uncertainty is a requirement of ISO 17025, and hence, is necessary for laboratories providing analytical results for the WFD. The knowledge of the measurement uncertainty is also important to confirm that the limit of quantification is equal to or less than that required.

It should be noted that whichever method is used to obtain a value for the measurement uncertainty, the value obtained will always only represent an estimate of the true spread of possible results. The method selected for estimating the measurement uncertainty should be chosen so as to include as many principal sources of contributing errors as possible.

Detailed guidance on the statistical and practical approaches available for estimating the measurement uncertainty can be obtained from the references below.

In general, two possible approaches to estimating measurement uncertainty can be used, either separately or as complementary techniques.

Bottom-up Approach

Firstly, a detailed analysis of the contributing errors from each of the methodological elements can be undertaken. This requires a stepwise analysis of each of the principal causes of measurement uncertainty in the analytical process followed by an estimation of their individual contribution of possible error. Examples of the potential principal causes of error are measurements of mass and volume, instrumental variability and the imperfect correction of systematic errors. Potential sources of data to inform this estimation of measurement uncertainty are within laboratory calibration records for subsidiary equipment such as glassware and balances, instrument repeatability data, data on calibration standard purity etc. This general overall approach of summing individual errors can lead to an underestimation of the measurement uncertainty due to the risk of overlooking an important contributing element. However, knowledge of the magnitude of the contributing errors from each step or process in the analytical method can be helpful to identify the significant errors and target any improvement activities at the most significant sources of error contributing to the overall measurement uncertainty.

Top-down Approach

The second approach of estimating measurement uncertainty is to use data from the analysis of certified reference materials, routine control samples, or interlaboratory trials. Care should be taken to ensure that the control samples include all the analytical steps for the test method. As part of this consideration, any significant bias component to the overall error that is not included within the control samples should also be accommodated into the calculation. Any bias indicated from interlaboratory trials should also be included into the overall estimate of measurement uncertainty.

The measurement uncertainty will vary across the concentration range of the analytical method. Where the range of application of the analytical method is large and there are a number of key threshold values for the analytical results within that range, it may be necessary to estimate the measurement uncertainty at different concentration values. This can be undertaken by dividing the method analytical range into a series of representative sections and estimating the measurement uncertainty for each of them. Alternatively, the measurement uncertainty for any given concentration can be calculated by obtaining values for it at a number of different concentrations, and then, using this data to graphically plot change with

concentration and subsequently deriving an equation for change in uncertainty against concentration.

6.1.2. Limit of Detection/Limit of Quantification¹⁸

6.1.2.1 Limit of Detection

As the concentration of a substance being measured approaches the lower capabilities of the analytical system, it becomes increasingly difficult to distinguish the sample response from background noise. The analyst's confidence that the measurand is actually present diminishes and the consequent risk of reporting a false positive value or failing to detect the presence of a measurand increases.

Therefore, by convention analytical results below this lower confidence limit are referred to as less than the limit of detection. There has historically been a range of definitions for limit of detection. However, the limit of detection is now commonly defined as the concentration of a substance for which there is an adequately high probability of detection when making a single analytical measurement.

It is important to recognise that the value obtained by either calculation will only ever be an estimate of the 'true' limit of detection. If only a few replicates are used in the following calculations, the uncertainty in the value obtained for the limit of detection can be very high. Undertaking more measurements increases the confidence in the limit of detection value obtained, but typically 10 or 11 degrees of freedom are taken as satisfactory. For example, if a limit of detection is calculated with 11 degrees of freedom, an observed limit of detection of 1 could correspond to a 'true' value of any value between 0.7 and 2.0.

Therefore, caution should be used when comparing values for limit of detection from different laboratories or methodologies as an apparently 'better' limit of detection may not be significantly different from an alternative.

Calculation of the Limit of Detection

The limit of detection may be calculated as follows:

$$\text{LOD} = 3 * \text{sbl}$$

where sbl is the standard deviation of the blank in the signal domain.

A number of separate analyses are undertaken of a real sample containing concentrations of the measurand at or near the blank level and the total standard deviation of the blank corrected results calculated. In order to obtain a reasonable estimate of the LOD, it is preferable to base the calculation on 10 or more measurements of the signal response for the blanks.

¹⁸ WRC report NS30 (1989) A Manual on Analytical Quality Control for the Water Industry. ISBN 0902156853

Chromatographic Analyses

Measurement of blank concentrations in some analytical techniques can be difficult as the instrumental software or hardware may impose peak detection threshold values or peak smoothing algorithms etc., which suppress small signals. This occurs most often for chromatographic methods. When this situation is encountered, it is normal to artificially increase the signal using one of the following methods:

- Use a real sample containing a very low, but measurable concentration of the analyte.
- Fortify a sample that contains no analyte to a very low, but measurable concentration.
- Dilute a sample extract containing a higher concentration of the analyte to achieve the required very low but measurable concentration.

It should be noted that when uncorrected blank signals are used to calculate the limit of detection, increasing the absolute concentration of the blank as above will inevitably produce a higher value for the estimate of the limit of detection.

6.1.2.2 Limit of Quantification

Within the normal range of application of an analytical method, as the concentration of a substance undergoing measurement decreases, there is a tendency for the uncertainty in the results obtained to increase. In principle, it is possible to quote any analytical result and an associated uncertainty of measurement. However, at the lower reaches of an analytical system's capability the uncertainty of measurement increases to a degree such as to make interpretation of the subsequent data difficult. Therefore, a limit of quantification is used to express the concentration at which the accuracy is satisfactory for quantitative measurement.

Definition of Limit of Quantification The Limit of Quantification means a stated multiple of the limit of detection at a concentration of the determinand that can reasonably be determined with an acceptable level of accuracy and precision. The limit of quantification can be calculated using an appropriate standard or sample, and may be obtained from the lowest calibration point on the calibration curve, excluding the blank;

LOQ should be determined experimentally following the procedure given in 6.1.2.1.

6.2. Water Analysis

According to the European Parliament legislative resolution of 17 June 2008 on the Council common position with a view to the adoption of a directive of the European Parliament and of the Council on environmental quality standards in the field of water policy and amending Directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/491/EEC, 86/280/EEC and 2000/60/EC (11486/3/2007 – C6-0055/2008 – [2006/0129\(COD\)](#)), EQS are expressed as total concentrations in the whole water sample except for cadmium, lead, mercury and nickel. The EQS for metals refers to the dissolved concentration measured in the liquid (dissolved) fraction of a water sample obtained by filtration through a 0.45 µm filter.

This implies reporting monitoring results except for metals as whole water concentrations. Whole water data may be generated by analysis of the whole water sample, or by separate analyses of the liquid and SPM fractions.

Unfortunately, most available analytical methods have not been validated for water samples containing substantial amounts of SPM. This can result in incomplete extraction of hydrophobic organic contaminants adsorbed to SPM, and thus, to an underestimation of the whole water concentration. Specific information whether methods can be applied to the

analysis of SPM containing samples can be found in the substance guidance sheets (Annex II).

The SPM content of the water sample is not critical for the analyses of polar and highly water soluble compounds such as some pesticides (e.g., alachlor, atrazine, simazine, diuron, isoproturon) and volatile compounds (benzene, dichloromethane, 1,2-dichloromethane, trichloroethane, tetrachloroethene, trichloroethene, tetrachloromethane, trichlorobenzene, naphthalene). Those compounds can be analysed in the whole water or in the filtered sample.

In case of hydrophobic compounds, which strongly adsorb to particles, including e.g., pentabromodiphenylether or 5 and 6 ring polycyclic aromatic hydrocarbons special care is required to ensure complete extraction of the particle bound fraction. Separate analysis of SPM and of the liquid could be a good option. If it can be justified, for example by considerations of expected contaminant partitioning, analysis of the SPM fraction as surrogate for whole water may be appropriate. Nevertheless, in water bodies with extremely low SPM content (e.g., < 3 mg/L) the dissolved fraction of those contaminants has to be determined.

Dependent on the SPM content of the sample and its organic carbon content, medium polar compounds can adsorb in varying amounts to SPM. In such cases, both fractions (dissolved and adsorbed concentrations) have to be considered.


For the determination of dissolved metal concentrations water samples have to be passed through a membrane filter of 0.45 µm pore size. In principle and if possible, this filtration should be done in the field to prevent changes during transportation and subsequent storage due to adsorption processes etc. It is essential to ensure that filters are clean and to pre-clean them, if necessary. In addition, filters should be pre-washed with small sample volumes before collecting the filtrate for metal analysis. If possible (in the light of health and safety instructions), the filtrate shall be acidified with nitric acid to ensure that the pH is less than 2. For more information consult the respective substance guidance sheets and the methods referred to therein.

Bioavailable metal concentrations depend on various parameters including pH, Ca and Mg concentrations, as well as dissolved organic carbon concentration. Hence, measuring these parameters in parallel with the metals can assist in the interpretation of results, where appropriate. In case of cadmium, the measurement of hardness is mandatory because EQS values have been derived for five classes of hardness.

6.3. Sediment/SPM Analysis³

With the exception of PBDE, there are no standardised methods specifically developed for the analysis of sediments/SPM available for priority substances likely to be found in sediment. However, existing standard methods for soil analysis summarized in Annex I may probably be applied to sediments with or without slight modification.

Comprehensive guidance on the analysis of marine sediments including sample pre-treatment, storage, and normalisation is given in OSPAR JAMP Guidelines for Monitoring Contaminants in Sediments.

	<p>Look in: OSPAR JAMP Guidelines for Monitoring Contaminants in Sediments</p>
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In general, < 2 mm fraction of the sediment should be analysed for organic contaminants while the less than 63 µm fraction should be analysed for metals. If the specific purpose of the monitoring requires analysis of the fine sediment fraction, the sample should be split using appropriate sieving techniques¹⁹.


The degree of accumulation of a contaminant depends on the sediment and SPM characteristics (grain size, composition and surface properties). It is essential to compare analytical results from sediments and SPM with similar properties or to compare normalised results to assess the degree of contamination. Therefore, particle size analyses, measurements of organic carbon content or measurement of other common normalisation parameters, such as Li and Al are advised. Detailed guidance for sediments on the use of normalizing parameters is given in Annex 5 of the JAMP Guideline for Monitoring Contaminants in Sediments.

For sediments, measurements of the two operationally defined parameters Acid Volatile Sulfides (AVS) and Simultaneously Extractable Metals (SEM) can provide information on the bioavailability of metals, although guidance on the interpretation of AVS is still in preparation in the EU EQS Technical Guidance – Metals section.

6.4. Biota Analysis³

At present, formally approved standard methods for the analysis of priority pollutants and other contaminants in biota are scarce and only available for metals, PAH, PCB and some other organic contaminants.

Comprehensive guidance on the analysis of marine biota (seabird eggs, fish, shellfish) including selection of species and suitable tissue, sampling, sample pre-treatment and storage is given in OSPAR JAMP Guidelines for Monitoring Contaminants in Biota.

	<p>Look in: OSPAR JAMP Guidelines for Monitoring Contaminants in Biota Manual for Marine Monitoring in the COMBINE Programme of HELCOM</p>
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Most organic contaminants accumulate in the lipid tissue of the species studied. Therefore, concentrations should be provided on lipid weight basis as well as weight basis or the lipid

¹⁹ Smedes, F., Davies, I.M., Wells, D., Allan, A., Besada, V.: Quality assurance of sampling and sample handling (QUASH). Interlaboratory study on sieving and normalisation of geographically different sediments; QUASH Round 5 – August 2000. QUASH report, QUASH Project Office, FRS Marine Laboratory, PO Box 101, Victoria Road, Aberdeen, AB11 9DB, GB

content of the sample should be provided together with the analytical results. It is important to state whether total lipids or extractable lipids have been determined and the method for lipid determination should be specified. Whether or not a normalisation should be performed has to be adjusted to the objective of the monitoring.

6.5. Substance Guidance Sheets

According to the Final Draft “Commission Directive laying down, pursuant to Directive 2000/60/EC of the European Parliament and of the Council, technical specifications for chemical analysis and monitoring of water status”, laboratories may select any analytical method of its choice for the purpose of monitoring under Article 8 and Annex V of the Directive 2000/60/EC, except for operationally defined parameters, provided they meet the minimum method performance criteria.

To assist Member States in selecting appropriate methods, substance guidance sheets are provided as an Annex II to this guidance document, summarising basic information on physico-chemical properties of each substance and preliminary environmental quality standards expressed as annual average, AA-EQS, or expressed as maximum allowable concentration, MAC-EQS, respectively, for inland and other surface waters. Available EN or ISO standard methods for the analysis in water, and where appropriate, in sediment or biota, are specified including information on sampling, storage and pre-treatment, performance characteristics and a short description of the principle. Where required other analytical methods are mentioned and respective references given. For laboratories wishing to undertake their own method surveys important links to websites providing information on standardised analytical methods are given in Table 1.

Table 1: List of html- links regarding Standard Methods

http://www.cenorm.be/catweb/cwen.htm	On-line Catalogue of European Standards
http://www.iso.org/iso/en/CatalogueListPage.CatalogueList	ISO standards
http://standards.mackido.com/	This is a comprehensive catalogue of international standards, their nomenclature, and their reference details. ISO Standards EN Standards British Standards IEC Standards
http://standardmethods.org/	Since 1905, Standard Methods for the Examination of Water and Wastewater has represented "the best current practice of American water analysts." This comprehensive reference covers all aspects of water and wastewater analysis techniques. Standard Methods is a joint publication of the American Public Health Association (APHA), the American Water Works Association (AWWA), and the Water Environment Federation (WEF).
http://www.nemi.gov	List of all methods in the National Environmental Methods Index (NEMI)
http://www.epa.gov/epahome/standards.html	EPA methods and guidelines

6.6. Group Parameters and Definition of Indicator Substances

Some substances of interest are described in generic terms only. These generic substances may be composed of a finite number of isomeric forms where the potential number of different individual isomers can range from 2 (e.g., Endosulfan) to more than 200 (e.g., polybrominated diphenylethers) of which only a few are of environmental relevance. Moreover, it is often difficult or impossible to analyse all those isomers. Hence, analysis of indicator substances representative for the entire group is common practice. Indicator substances, which have to be analysed have been specified in the Position of the European Parliament adopted on 17 June 2008 on the Council common position with a view to the adoption of a directive of the European Parliament and of the Council on environmental quality standards in the field of water policy and amending Directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/491/EEC, 86/280/EEC and 2000/60/EC (11486/3/2007 – C6-0055/2008 (Table 2).

Table 2: Components of Group Parameters and Indicator Substances

Priority Substance	Recommended Components	Comments
Chlorpyrifos	Chlorpyrifos-ethyl	
Endosulfan	α -Endosulfan and β -Endosulfan	Total concentration to be reported.
Pentabromodiphenyl Ether	BDE congener numbers 28, 47, 99, 100, 153, 154	These congeners constitute approximately 85 % of technical Penta – BDE formulations; Total concentration to be reported.
Hexachlorocyclohexane	α , β , γ , and δ -isomer*	Total concentration to be reported.
C10-13 Chloroalkanes	All C ₁₀ to C ₁₃ chlorinated paraffins (49 % to 70 % Chlorine)	Total of all isomers to be reported. Measurement will usually be done against a technical mixture.
Nonylphenol	All 4-nonylphenol isomers present**	Total concentration of all para isomers to be reported.
Octylphenol	para-tert-Octylphenol***	
PAH	Benzo[b]fluoranthene/ Benzo[k]fluoranthene	Total concentration to be reported. Benzo[j]fluoranthene interferes with the determination of either Benzo [b]fluoranthene or Benzo[k]fluoranthene
Trichlorobenzenes (all isomers)	1,2,3-, 1,2,4- and 1,3,5-trichlorobenzene	Total concentration to be reported.
DDT total	<i>p,p'</i> -DDT, <i>o,p'</i> -DDT, <i>p,p'</i> -DDE, <i>p,p'</i> -DDD	Total concentration and concentration of <i>p,p'</i> -DDT to be reported.

* The CAS number 608-73-1 refers to technical HCH, hence, all relevant isomers have to be analysed for

** Technical nonylphenol consists mainly (~ 90 %) of para-substituted nonylphenols and comprises theoretically 211 isomers; only 4-nonylphenols are of toxicological relevance


*** Octylphenol (CAS No 140-66-9) is a single isomeric compound: 4-(1,1',3,3'-tetramethylbutyl)-phenol (4-tert-octylphenol)

Although it is possible to calculate the value of a group parameter from its individual components, the interpretation of this value as regards EQS compliance may pose several practical difficulties with respect to the generation and interpretation of data. Principal amongst these difficulties is the uncertainty associated with a group parameter. If the group parameter comprises two substances that are present at equal concentrations, and the standard uncertainty of each substance is 10 %, the standard uncertainty of the sum of their concentrations will be 14 %. If, on the other hand, one concentration greatly predominates over the other, the standard uncertainty of the sum remains near to 10 %. If, for a similar example, there are 6 components of the group, the standard uncertainty could vary between 25 % and 10 % depending on whether the concentrations are similar, or if one is much larger than all the others. This dependency of the uncertainty on the number of components comprising a group and on their concentrations requires consideration when deriving requirements on measurement uncertainty for group parameters and their components.

6.7. Results below the Limit of Quantification

For the calculation of annual average concentrations, values below the limit of quantification shall be set to half of the value of the limit of quantification concerned. If the resulting annual average concentration is below the limits of quantification, the value shall be referred to as 'less than limit of quantification'.

This rule does not apply to total sums of a given group of substances. In those cases, results below the limit of quantification of the individual substances/isomers shall be set to zero.

	<p>Look in: Final Draft “Commission Directive laying down, pursuant to Directive 2000/60/EC of the European Parliament and of the Council, technical specifications for chemical analysis and monitoring of water status”</p>
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7. COMPLEMENTARY METHODS^{20,21}

7.1. Introduction

While checking compliance with the WFD provisions is currently based on chemical analysis of spot samples taken in a defined frequency, it is desirable to introduce other techniques for improving the quality of the assessment and to benefit from resource saving developments, as they become available. Currently advanced methods for environmental assessment (referred to as 'complementary methods in this chapter') are under development and evaluation.

²⁰ This chapter was elaborated in close cooperation with the EU-project SWIFT (www.swift-wfd.com).

²¹ Allan, I. J., Vrana, B., Greenwood, R., Mills, G. A., Roig, B., Gonzalez, C. (2006) A “toolbox” for biological and chemical monitoring requirements for the European Union’s Water Framework Directive. *Talanta* 69, 302-322.

Examples of techniques are:

- In-situ probes for measuring physico-chemical characteristics (e.g., Dissolved Organic Carbon (DOC), pH, temperature, dissolved oxygen)
- Biological assessment techniques (e.g., biomarker analyses, bioassays/biosensors and biological early warning systems, immunosensors, etc.)
- Sampling and chemical analytical methods (e.g., sensors, passive sampling devices, test kits (see e.g., ISO 17381:2003 Water quality - Selection and application of ready-to-use test kit methods in water analysis), GC-MS or LC-MS screening methodologies)

Two types of complementary methods – (1) equipment for measuring physico-chemical characteristics and (2) chemical analytical methods – usually yield direct measures of the quality elements as defined in the WFD.

The third type – biological assessment techniques – are designed to respond to a wide range of (chemical) stressors, and are therefore, not exclusively linked to individual quality elements such as the different priority substances. Although very useful for many monitoring purposes, they cannot be used to check compliance of individual quality elements against an EQS.

These analytical and biological methods, as well as in-situ sampling techniques, are summarised in the table below. This table aims to provide simple guidance in the use of these tools, with a particular focus on typical indicators monitored, the type and relevance of the information obtained and a selection of performance criteria for these tools. Performance criteria tend to depend on the technique or method selected, and more importantly, on the type of information required. For example, performance criteria for the laboratory-based analysis of extracts from passive sampling devices are mostly similar to those for more conventional spot sampling²². Additional performance criteria for passive sampling are the result of (i) the requirement for accurate uptake rates to be used in the calculation of time-weighted average contaminant concentrations in water, and (ii) the in-situ field deployment that needs to follow relatively strict protocols²³ to ensure that data obtained are fit-for-purpose. A few examples of these techniques, some of them either well-known (e.g., the measurement of metallothionein in aquatic organisms upon exposure to trace metals) or tested during the SWIFT-WFD project²⁴ (e.g., the Multi-species Freshwater Biomonitor that allow real-time monitoring of changes in water quality based on physiological and behavioural monitoring of aquatic organisms) are given. These methods may be able to provide additional weight-of-evidence, mostly in cases where additional information on chemical quality or links between chemical and biological data is required. This is particularly important for situations that do not involve only comparisons with EQS (e.g., investigative monitoring). Scenarios for the efficient use of these tools and techniques are also given and support the possible uses described in section 7.2.

²² STAMPS project, funded under the 5th RTD Framework Programme, European Commission, www.port.ac.uk/research/stamps/

²³ BSI PAS 61:2006 Publicly available specification – Determination of priority pollutants in surface water using passive sampling

²⁴ SWIFT-WFD project, funded under the 6th RTD Framework Programme, European Commission, www.swift-wfd.com

7.2. Applications of Complementary Methods in WFD Monitoring

Use of Complementary Methods in the Design of Monitoring Programmes

Complementary methods can be used in the design of monitoring programmes for:

- Identification of problem as well as non-problem areas, e.g., by using screening methods (test kits) or passive sampling devices
- Selection of monitoring points, e.g., in the grouping of water bodies for operational monitoring complementary methods may be used to demonstrate the representativeness of sampling points.
- Selection of quality elements, e.g., the selection of other pollutants that are part of the ecological status. Information derived from bioassays and toxic identification and evaluation (TIE) may be used to select compounds based on ecological relevance.
- Justification of a reduction in sampling frequency, e.g., the use of sensors as screening tools. Sampling for chemical analysis with a validated method is triggered by a response of a sensor above a certain threshold. In that case, validation of the sensor can be limited to a performance criterion for false negative responses.

Use of Complementary Methods in Surveillance and Operational Monitoring

Complementary methods can be used in surveillance and operational monitoring provided that they meet the requirements laid down in the Final Draft “Commission Directive laying down, pursuant to Directive 2000/60/EC of the European Parliament and of the Council, technical specifications for chemical analysis and monitoring of water status”.

Complementary methods may be used in surveillance monitoring to detect long-term changes. Biological assessment techniques can be used as a sum parameter to screen for the presence of substances in ecologically relevant concentrations. Passive samplers could be used alongside spot sampling in order to corroborate or contradict spot sampling data. This would be important weight-of-evidence for water bodies where contaminant concentrations are expected to show large temporal variation or when the contaminant source fluctuates.

Passive samplers (e.g., Semi-Permeable Membrane Devices (SPMD), Polar Organic Chemical Integrative Samplers (POCIS), Diffusion Gradient Thin Films (DGTs), Chemcatcher) are exposed in the aquatic environment for several days or up to weeks to yield time-integrated average concentration of organic contaminants or heavy metals. Passive sampling is less influenced by short-term fluctuations in concentrations than spot sampling. Since one of the primary objectives of the WFD is the assessment of the average concentrations of pollutants in water bodies, the determination of time-integrated concentrations using passive samplers seems to be a promising approach. Some of the passive samplers have been validated and provide high sampling rates (litre/day) for various contaminants (e.g., organic compounds of medium hydrophobicity, heavy metals), and thus, allow quantification of extremely low pollution levels in water²³. This is a first step towards an internationally recognized standard.

Passive sampling can also be combined with ecotoxicology, where the extracts from the passive monitors are passed through multiple toxicological tests in a laboratory. This will enable assessment of the effects of a mixture of contaminants from an environmental monitoring point over a period of time. This integration of exposure and effects monitoring will facilitate more cost effective monitoring programmes as well as forming the basis of a risk based pollution control strategy.

Difficulties encountered include bio-fouling, back-calculating to water concentration and calibration. Thus, further research and validation is required before using this technology for compliance checking.

Passive samplers sample the freely-dissolved bioavailable water concentrations. Results may, therefore, deviate from the total water concentrations measured in spot samples. It may be possible, if average values for the levels of DOC, SPM and TOC content of the SPM are known, to use partitioning theory and $\text{Log}K_{oc}$ - $\text{log}K_{ow}$ relationships to estimate the total concentrations with uncertainties for all assumptions made accounted for.

Use of Complementary Methods in Investigative Monitoring

The main goals of investigative monitoring are to identify the reason for any failure to achieve environmental objectives, in circumstances where the reason is unknown and to ascertain the magnitude and impact of accidental pollution.

For both purposes, test kits including, e.g., immunoassays specific to certain priority substances or other pollutants allow fast screening of large number of samples and can be cost-effective tools to identify pollution sources as well as to characterise the extent of accidental pollution.

Passive sampling devices might be of use in identifying sources of pollution, in particular, if extremely low levels have to be detected or when the source of pollution is not constant.

In case of MAC-EQS exceedance, investigative monitoring should be used to ascertain this non-compliance in more detail. Both, spot sampling and time-integrated measurements may not detect acutely toxic spikes of seasonally-variable compounds like pesticides; the use of *in situ* bioassays may be beneficial. These biological early warning systems also have the potential to help identify compounds that may need to be included in future risk assessments.

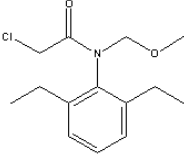
Table 3: A list of complementary methods relevant to WFD chemical monitoring including method performance criteria

<i>Technique</i>	Analytical Methods			<i>In-situ</i> Sampling Techniques		Biological Methods		
	Lab	On-site	<i>In-situ</i>	Biomonitoring	Passive sampling	Direct toxicity assessment	Biological Early warning system	Biomarkers
<i>Examples</i>	Immunoassay (e.g., atrazine), test kits, hand-held sensors (e.g., Palmsens)			MusselWatch programmes	Semi-permeable membrane device (SPMD), Chemcatcher	Daphtokit®	Mossmelmonitor®, multi-species freshwater biomonitor	Measurement of metallothionein synthesis
<i>Measurement</i>	Analyte (operationally-defined) concentration or ranges of concentrations, general physico-chemical characteristics			Indicator of exposure to bioavailable analytes	Time-weighted average & operationally-defined analyte concentrations (truly dissolved and labile fractions for organic and metal contaminants, respectively)	(Non)-specific (e.g., genotoxicity) acute/chronic toxicity in water/sediment	Real-time monitoring of acute toxicity in an organism	Chemical and biological indicators of non-specific or specific exposure or effects of contaminants in water and sediments
<i>Type of information obtained</i>	Qualitative, semi-quantitative, quantitative			Semi-quantitative, qualitative	Qualitative, semi-quantitative or quantitative	Qualitative	Qualitative	Qualitative
<i>Performance criteria</i>	- LOD - LOQ - Calibration, quantification range				- LOD, LOQ (field) - Bias - Sensitivity		- Levels of false positives and negatives	
<i>Implementation</i>	- Rapid and/or on-site determination of concentrations, or screening of levels - Mapping of an area - Selection of samples for more accurate laboratory-based analysis			- Linking ecological and chemical information - Linking concentration with exposure and effects	- Assess long-term changes and trends in pollutant concentrations - Extrapolate total and total filtered concentrations - Screening for contaminant presence/absence - Metal speciation	- Detect adverse biological effects to indicate where operational or investigative monitoring required	- Early warning of changes in water quality at crucial sites - Detect and assess significant pollutant for updating risk assessments	- Early detection of biological imbalance - Linking ecological and chemical information - Linking concentration with exposure and effects
<i>Applicable to:</i>	Operational & investigative monitoring			Operational & investigative monitoring	Surveillance, operational & investigative monitoring	Operational & investigative monitoring	Operational & investigative monitoring	Operational & investigative monitoring

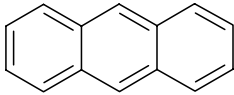
ANNEX I: List of ISO Standards for soil analysis

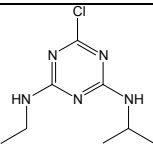
ISO 11465:1993	Soil quality - Determination of dry matter and water content on a mass basis - Gravimetric method
ISO 11466:1995	Soil quality - Extraction of trace elements soluble in aqua regia
ISO 11277:1998	Soil quality - Determination of particle size distribution in mineral soil material - Method by sieving and sedimentation
ISO 10694:1995	Soil quality - Determination of organic and total carbon after dry combustion (elementary analysis)
ISO 14869-1:2001	Soil quality - Dissolution for the determination of total element content - Part 1: Dissolution with hydrofluoric and perchloric acids
ISO 11047:1998	Soil quality - Determination of cadmium, chromium, cobalt, copper, lead, manganese, nickel and zinc - Flame and electrothermal atomic absorption spectrometric methods
ISO 14507:2003	Soil quality - Pretreatment of samples for determination of organic contaminants
ISO 14154:2005	Soil quality - Determination of some selected chlorophenols - Gas-chromatographic method with electron-capture detection
ISO 15009:2002	Soil quality - Gas chromatographic determination of the content of volatile aromatic hydrocarbons, naphthalene and volatile halogenated hydrocarbons - Purge-and-trap method with thermal desorption
ISO 16772:2004	Soil quality - Determination of mercury in aqua regia soil extracts with cold-vapour atomic spectrometry or cold-vapour atomic fluorescence spectrometry
ISO 22155:2005	Soil quality - Gas chromatographic quantitative determination of volatile aromatic and halogenated hydrocarbons and selected ethers - Static headspace method
ISO 11264:2005	Soil quality - Determination of herbicides - Method using HPLC with UV-detection
ISO 10382:2002	Soil quality - Determination of organochlorine pesticides and polychlorinated biphenyls - Gas-chromatographic method with electron capture detection
ISO 13877:1998	Soil quality - Determination of polynuclear aromatic hydrocarbons - Method using high-performance liquid chromatography
ISO 18287:2006	Soil quality - Determination of polycyclic aromatic hydrocarbons (PAH) - Gas chromatographic method with mass spectrometric detection (GC-MS)
ISO/DIS 22036	Soil quality - Determination of trace elements in extracts of soil by inductively coupled plasma atomic emission spectrometry (ICP/AES)
ISO 22892:2006	Soil quality - Guidelines for the identification of target compounds by gas chromatography and mass spectrometry
ISO/DIS 23161	Soil quality - Determination of selected organotin compounds - Gas-chromatographic method

ANNEX II: Substance Guidance Sheets

Compound <i>Alachlor</i>			
CAS Number 15972-60-8	Log K_{ow} ~ 2.97	Water Solubility [mg/L] ~ 240	
AA-EQS [µg/L]		MAC-EQS [µg/L]	
Inland Surface Waters 0.3	Other Surface Waters 0.3	Inland Surface Waters 0.7	Other Surface Waters 0.7
Available Standard Method <i>EN ISO 10695:2000</i> Determination of selected organic nitrogen and phosphorus compounds - Gas chromatography methods [Note: <i>Alachlor is not explicitly mentioned in this standard but the method may also be applied to the analysis of alachlor provided the method has been properly validated for this compound</i>].		Method Description Liquid/liquid extraction with dichloromethane or liquid/solid extraction (SPE) on reversed-phase (RP)-C18 material or other adsorbent. Elution of the cartridges with e.g. methanol or acetone. After concentration, the sample extracts are analysed by gas chromatography, using a nitrogen-phosphorus or mass spectrometric detector.	
Matrix Drinking waters, ground waters, surface waters and waste waters containing up to 50 mg/L of suspended solids		Limit of Quantification (LOQ): 0.04 µg/L	
Sampling <i>ISO 5667-2:1991</i>			
Pretreatment			
Storage			
Method Validation: no data available			
Other Analytical Methods			
SPE-GC-MS Separation by gas chromatography, identification and quantification of the analyte by gas chromatography coupled to mass spectrometric detection (GC-MS) using electron impact (EI) mode. GC-MS fragment ions: m/z 160, 188, 161 and 146 [1-3] SPE extraction of 500 mL water; LOQ ~ 12 ng/L [1] SPE extraction of 1 L water; LOQ ~ 3 ng/L [2] SPE extraction of 200 mL water; LOQ ~ 30 ng/L [3]			
GC-NPD EPA method 507 [4]			
LC-ESI-MS/MS C18 SPE of 50 mL water; MRM 270 > 161.5; LOQ ~ 0.1 µg/L [5]			
On-line SPE-LC-MS-MS On-line SPE of 10 mL samples; MRM 270 > 238; LOQ ~ 47 ng/L [6]			
References			
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
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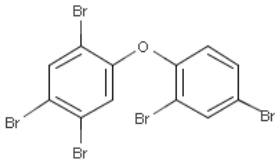
Compound <i>Anthracene</i>					
CAS Number 120-12-7		Log K_{ow} 4.55		Water Solubility [mg/L] 0.0434	
AA-EQS [µg/L]			MAC-EQS [µg/L]		
Inland Surface Waters 0.1		Other Surface Waters 0.1		Inland Surface Waters 0.4	
				Other Surface Waters 0.4	
Available Standard Method <i>EN ISO 17993:2003</i> Determination of 15 polycyclic aromatic hydrocarbons (PAH) in water by HPLC with fluorescence detection after liquid-liquid extraction Matrix Drinking, ground, waste and surface water Sampling Pretreatment Storage			Method Description <i>EN ISO 17993:2003</i> specifies a method using high performance liquid chromatography (HPLC) with fluorescence detection for the determination of 15 selected polycyclic aromatic hydrocarbons (PAH). Limit of Quantification (LOQ): 0.01 µg/L		
Method Validation					
l Number of laboratories n_{AP} percental rate of outliers \bar{x} Total mean after elimination of outliers s_R standard deviation between the laboratories CV_R reproducibility variation coefficient <i>Interlaboratory study 1996 in Germany</i>					
Matrix	l	n_{AP} in %	\bar{x} in µg/L	s_R in µg/L	CV_R in %
Drinking water	33	0	26.84	4.474	16.7
Other Analytical Methods					
USA EPA 8270c, 1996 [1] Semivolatile organic compounds by GC/MS This method claims detection limits of 10 µg/L which is obviously too high. Other analytical methods based on this standard using modern GC/MS equipment however may attain the required low LOQs.					
Comments					
References					
[1] http://www.accustandard.com/asi/pdfs/epa_methods/8270c.pdf					

Compound <i>Atrazine</i>					
CAS Number 1912-24-9		Log K_{ow} ~ 2.5		Water Solubility [mg/L] ~ 33	
AA-EQS [µg/L]			MAC-EQS [µg/L]		
Inland Surface Waters 0.6		Other Surface Waters 0.6		Inland Surface Waters 2.0	
				Other Surface Waters 2.0	
Available Standard Method <i>EN ISO 10695:2000</i> Determination of selected organic nitrogen and phosphorus compounds - Gas chromatography methods			Method Description Liquid/liquid extraction with dichloromethane or liquid/solid extraction (SPE) on reversed-phase (RP)-C18 material or other adsorbent. Elution of the cartridges with e.g. methanol or acetone. After concentration, the sample extracts are analysed by gas chromatography, using a nitrogen-phosphorus or mass spectrometric detector.		
Matrix Drinking waters, ground waters, surface waters and waste waters containing up to 50 mg/L of suspended solids			Limit of Quantification (LOQ): Liquid/liquid extraction method: 0.5 µg/L Liquid/solid extraction method: 0.015 µg/L		
Sampling <i>ISO 5667-1 and 5667-2</i>					
Pretreatment					
Storage					
Method Validation					
<p style="text-align: right;"><i>l</i> Number of laboratories n_{AP} percental rate of outliers \bar{x} Total mean after elimination of outliers s_R standard deviation between the laboratories CV_R reproducibility variation coefficient</p>					
<i>Interlaboratory study 1993 for liquid/solid extraction</i>					
Matrix	<i>l</i>	<i>n_{AP} in %</i>	\bar{x} in µg/L	<i>s_R</i> in µg/L	<i>CV_R</i> in %
Drinking water	13	0	0.133	0.0104	35.6
Other Analytical Methods					
Gas Chromatography - Mass Spectrometry GC-MS determination of the ions 200 and 215; LOQ ~ 1 ng/L (after SPE) [1-3] (EPA method 525)					
GC-NPD EPA method 507 [4]					
GC-ECD EPA method 505; microextraction with hexane and GC-ECD analysis [4]]					
Liquid Chromatography - Mass Spectrometry Identification and quantification of atrazine (and other pesticides) by liquid chromatography coupled to (tandem) mass spectrometric detection (LC-MS-MS) using positive electrospray ionization (ESI) LC-MS fragment ions: m/z 216 and 174 [5] LC-MS-MS transitions: 216 > 174 and 132 [6] LOQ ~ 1 ng/L (depending on the SPE enrichment factor)					
Comments					

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Compound <i>Benzene</i>					
CAS Number 71-43-2		Log K_{ow} 2.13		Water Solubility [mg/L] 1750	
AA-EQS [µg/L]			MAC-EQS [µg/L]		
Inland Surface Waters 10		Other Surface Waters 8		Inland Surface Waters 50	
				Other Surface Waters 50	
Available Standard Method <i>ISO 11423-1:1997</i> Determination of benzene and some derivatives – Head-space gas chromatographic method			Method Description A defined volume of unfiltered water sample is heated in a gas-tight septum-covered vial. After establishment of equilibrium between the gaseous and the liquid phases, an aliquot of the gaseous phase is transferred to a gas chromatograph.		
Matrix Water			Limit of Quantification (LOQ): ~ 2 µg/L		
Sampling					
Pretreatment					
Storage					
Method Validation					
<i>l</i> Number of laboratories n_{AP} percental rate of outliers \bar{x} Total mean after elimination of outliers s_R standard deviation between the laboratories CV_R reproducibility variation coefficient					
Interlaboratory study 1991 (Head Space GC – ISO 11423-1)					
Matrix	<i>l</i>	<i>n_{AP} in %</i>	\bar{x} in µg/L	<i>s_R in µg/L</i>	<i>CV_R in %</i>
Surface water	8	14.3	5.6	0.88	15.7
Interlaboratory study 1991 (GC-FID – ISO 11423-2)					
Surface water	9	6.5	4.55	1.34	29.4
Other Analytical Methods					
<u>Determination of benzene and some derivatives - Method using extraction and gas chromatography (ISO 11423-2)</u> The unfiltered water sample is extracted with a non-polar solvent (e.g. pentane) and the extract is analysed by GC-MS. LOQ ~ 5 µg/L <u>ISO 15680:2003</u> Gas-chromatographic determination of a number of monocyclic aromatic hydrocarbons, naphthalene and several chlorinated compounds using purge-and-trap and thermal desorption. (Selected ion: 78) LOQ ~ 2 ng/L for benzene					
Comments					
References					

Compound <i>Pentabromodiphenylether</i>						
CAS Number 32534-81-9		Log K_{ow} 6.57		Water Solubility [µg/L] 13.3		
AA-EQS [µg/L]			MAC-EQS [µg/L]			
Inland Surface Waters 0.0005		Other Surface Waters 0.0002		Inland Surface Waters <i>not applicable</i>		Other Surface Waters <i>not applicable</i>
Available Standard Method <i>No standardised method for the determination of PBDE in water available</i> <i>ISO 22032:2006</i> Determination of selected polybrominated diphenylethers (PBDE) in sediment and sewage sludge - Method using extraction and gas chromatography/mass spectrometry Matrix Sediment Sampling <i>ISO 5667-13</i> Pretreatment homogenizing, freezing and freeze-drying, grind and sieve it Storage at 4 °C in the darkness in wide necked bottles			Method Description <i>ISO 22032:2006</i> specifies a method for the determination of selected PBDEs representative for penta-, octa-, and decaBDE technical formulations in sediment using gas chromatography/mass spectrometry in the electron impact or electron capture ionisation mode. Extraction of PBDEs from the dried sample by an organic solvent is followed by clean-up of the extract by e.g. multi-layer silica gel column chromatography. For quantification an internal standard calibration is applied. Limit of Quantification (LOQ): When applying GC-EI-MS, the method is applicable to samples containing 0.05 µg/kg to 25 µg/kg of tetra- to decabromo congeners. Approximately ten times lower concentrations can be quantified when using GC-ENCI-MS.			
Method Validation <p style="text-align: right;"><i>l</i> Number of laboratories = <i>n_{AP}</i> percental rate of outliers = \bar{x} Total mean after elimination of outliers <i>s_R</i> standard deviation between the laboratories <i>CV_R</i> reproducibility variation coefficient</p> <i>Interlaboratory Study 2004/2005</i>						
Matrix	Substance	<i>l</i>	<i>n_{AP}</i> in %	\bar{x} in µg/kg	<i>s_R</i> in µg/kg	<i>CV_R</i> in %
Sediment	BDE 47	16	0	362	50.5	14.0
	BDE 100	16	0	93.3	28.96	31.0
	BDE 99	16	0	518	99.6	19.2
	BDE 154	16	0	39.2	9.11	23.2
	BDE 153	16	0	47.7	9.28	19.5
Other Analytical Methods Numerous studies of PBDEs in environmental samples are based on the determination by gas chromatography/mass spectrometry in the electron impact or negative ion chemical ionisation mode [1]. U.S. EPA Method 527 employs solid-phase extraction with analysis by gas chromatography/mass spectrometry as described in PEPICH et al. 2005 [2], but MDL is fairly high (0.39 µg/l). EPA Method 1614, 2007 [3] applies HRGC/HRMS for the analysis of PBDE in water, soil, sediment and tissue. MDL for BDE 99 is 0.00004 µg/l.						

Comments

There are a few reports on extremely low levels of PBDEs in surface water samples [4,5]. The authors enriched 100 and 2500 L of water, respectively, on XAD resin. SPME has been proposed to extract selected BDE congeners from water samples by POLO et al. 2004 [6].

Environmental studies conducted primarily in Europe, Japan and North America indicate that these chemicals are ubiquitous in sediment and biota [7].

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Compound <i>Cadmium and its compounds</i>					
CAS Number 7440-43-9	Log K_D [L/kg] <i>suspended matter/water: 4.7 (Cd) [1]</i> <i>sediment/water: 3.6 (Cd) [1]</i>		Water Solubility [mg/L] depending on compound		
Water hardness [mg CaCO₃/L]	AA-EQS [µg/L] <i>(depending on water hardness classes)</i>		MAC-EQS [µg/L] <i>(depending on water hardness classes)</i>		
	Inland Surface Waters	Other Surface Waters	Inland Surface Waters	Other Surface Waters	
Class 1: < 40	≤ 0.08	0.2	≤ 0.45	≤ 0.45	
Class 2: 40 to < 50	0.08		0.45	0.45	
Class 3: 50 to < 100	0.09		0.6	0.6	
Class 4: 100 to < 200	0.15		0.9	0.9	
Class 5: ≥ 200	0.25		1.5	1.5	
Available Standard Method <i>EN ISO 17294-2:2004</i> Application of inductively coupled plasma mass spectrometry (ICP-MS) - Part 2: Determination of 62 elements Matrix Drinking waters, ground waters, surface waters and waste waters Sampling <i>ISO 5667-1, 5667-2 and 5667-3</i> Pretreatment For dissolved elements, filter aqueous sample through a 0.45-µm pore membrane filter. Adjust the pH of the filtrate to < 2 with HNO ₃ . Storage		Method Description <i>EN ISO 17294-2:2004</i> specifies a method for the determination of the cadmium in water (for example drinking water, surface water, groundwater, wastewater and eluates). Taking into account the specific and additionally occurring interferences, these elements can also be determined in digests of water, sludges and sediments. The detection limits of most elements are affected by blank contamination and depend predominantly on the laboratory air-handling facilities available. The lower limit of application is higher in cases where the determination is likely to suffer from interferences or in case of memory effects.			
		Limit of Quantification (LOQ): Drinking water and relatively unpolluted water: 0.1 µg/L - 1.0 µg/L			
Method Validation					
<p style="text-align: right;"><i>l</i> Number of laboratories <i>n_{AP}</i> percental rate of outliers = <i>x</i> Total mean after elimination of outliers <i>s_R</i> standard deviation between the laboratories <i>CV_R</i> reproducibility variation coefficient</p>					
Interlaboratory study 1997 in Germany					
Matrix	<i>l</i>	<i>n_{AP} in %</i>	\bar{x} <i>in µg/L</i>	<i>s_R in µg/L</i>	<i>CV_R in %</i>
Surface water	37	5.2	5.75	0.491	8.5

Other Analytical Methods

EN ISO 5961:1995 specifies two methods for the determination of cadmium using atomic absorption spectrometry (AAS) in an air-acetylene flame (aspiration of the acidified sample into the flame and measurement of the cadmium concentration at a wavelength of 228.8 nm) and by electrothermal atomization AAS (injection of the acidified sample into an electrically heated graphite tube of an electrothermal atomization atomic absorption spectrometer and measurement of the absorbance at a wavelength of 228.8 nm).

EN ISO 15586:2003 determination using atomic absorption spectrometry with electrothermal atomization in a graphite furnace. The detection limit of the method for each element depends on the sample matrix as well as of the instrument, the type of atomizer and the use of chemical modifiers. For water samples with a simple matrix (i.e. low concentration of dissolved solids and particles), the method detection limits will be close to instrument detection limits. The minimum acceptable LOQ for a 20 µL sample volume are specified.

EN ISO 11885:1997 specifies a method by inductively coupled plasma atomic emission spectroscopy.

EPA 200.8 (1994): Determination of trace elements in waters by inductively coupled plasma - mass spectrometry (LOQ: 0.5 µg/L); http://www.accustandard.com/asi/pdfs/epa_methods/200_8.pdf

Standard Methods Online (<http://standardmethods.org/>) 3125: Metals in Water by ICP/MS (LOQ: 0.003 µg/L)

Comments

References

Compound <i>C₁₀₋₁₃-Chloroalkanes</i>		$C_xH_{(2x-y+2)}Cl_y$ where x = 10-13 AND y = 1-13	
CAS Number 85535-84-8	Log K_{ow} 4.39-8.69 (depending on chlorine content)	Water Solubility [mg/L] 0.15-0.47 (59% chlorine content)	
AA-EQS [µg/L]		MAC-EQS [µg/L]	
Inland Surface Waters 0.4	Other Surface Waters 0.4	Inland Surface Waters 1.4	Other Surface Waters 1.4
Available Standard Method ISO CD 12010 Error! Reference source not found. Matrix Sampling Pretreatment Storage		Method Description Determination of the sum of SCCP in technical mixtures with chlorine contents 49 % to 67 % independent of the chlorine content and independent of the C-number distribution pattern of the congeners. No recognition of the chlorine content is necessary. Extraction of the whole water sample by liquid-liquid-extraction by an organic solvent, alternatively by solid phase extraction. After concentration and clean up, capillary gas chromatography of the approximately 6300 congeners at a relatively short column within a short retention range. Detection of selected mass fragments by mass spectrometry in the selected ion monitoring mode using negative ion chemical ionisation (NCI). The selection of the mass fragments is specific for the variety of technical mixtures as well as for the chlorine content and C-number distribution patterns in environmental samples. Alternative selections of mass fragment combinations for quantification are given in this standard too. The chromatogram is to be integrated over the full retention range of the SCCP. The quantification of the sum of SCCP is performed after calibrating by a multiple linear regression model with solutions of different technical mixtures and internal standardisation. The method works with at minimum three different defined standard mixtures, which resemble the C-number distribution and the chlorine content of different technical mixtures. This reflects the fact that the variety in respect of chlorine content and C-number distribution of technical SCCP-mixtures as well as of SCCP in environmental samples cannot be described by a single defined standard. The selection of the mass fragments for quantification and the special calibration allow a quantification of the sum of SCCP independently of chlorine content and C-number distribution within an expanded measurement uncertainty of 35% to 45%.	
Method Validation no data available			
Other Analytical Methods GC-ECNI-HRMS in the SIM mode at an ion source temperature of 120°C [1]. The molecular compositions of commercial SCCPs and of SCCP-containing extracts were determined by monitoring the two most intensive ions in the [M-Cl]- cluster, one for quantification and the other for confirmation for the following formula groups:			

C10 (C15 to Cl10), C11 (C15 to Cl10), C12 (Cl6 to Cl10), and C13 (Cl7 to Cl9), and assuming that integrated signals are proportional to molar concentrations weighted by the number of chlorine atoms in the formula group. Quantification was achieved by selecting the biggest peak corresponding to [M-Cl]⁻ ion in the most abundant formula group present in the sample and correcting for variations in the formula group abundances between standard and sample. The analytical detection limit was 60 pg of injected SCCP at a signal-to-noise ratio of 4:1, while LOQ was 23 ng/g.

Short-column (62 cm) GC-ECNI- LRMS at an ion source temperature of 100°C using methane as reagent gas [2]. Detection limits in the full- scan mode ranged from 10 to 100 pg depending on carbon chain length of the n-alkane and on the degree of chlorination. The method was applied to the analysis of SCCP in fish samples.

Metastable atom bombardment ionisation (MAB) and high resolution mass spectrometry [3]. The detection limits were estimated to be between 10 and 100 pg/L. The MAB method has been applied to the analysis of high-volume water samples.

GC-MS/MS electron ionisation (EI) for fast determination of the sum of short medium chain chlorinated paraffins [4]. Collision-induced reactions of m/z 91 → 53 (LOQ = 0.15 ng/μL), 102 → 65 (LOQ = 0.2 ng/μL), and 102 → 67 (LOQ = 0.1 ng/μL) were used to quantify the total short- and medium-chain PCA content of pooled fish liver samples.

Quantification procedure using GC-ECNI-MS, which is independent of the chlorine content of the reference standard used for calibration [5]. The authors calculated the total response factors for seven standard CP mixtures of various chlorine contents (51-70%) from the relative total CP areas and found a linear correlation between the total response factors of CP mixtures and their chlorine contents (R² = 0.9494). Using this correlation, total response factors according to the chlorine content of the SCCPs present in the sample can be calculated and used for quantification.

SPE and carbon skeleton analysis after simultaneous catalytic dechlorination and hydrogenation by gas chromatography with mass spectrometric detection seems to be promising option for routine analysis of SCCPs in water even though the method has not yet been fully validated [6,7]

Comments

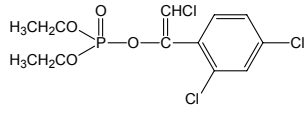
Although some work has been conducted on development of selective and sensitive methods for SCCP analysis in recent years, for the time being, no fully validated procedure is available that could be recommended for routine monitoring of SCCPs in environmental samples.

SCCP concentrations in environmental samples analysed by GC-ECNI-MS can vary widely (by a factor of ten) depending on chlorine content of the standard used for quantification [8].

References

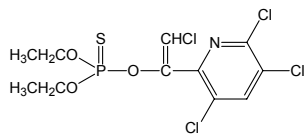
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Compound <i>Chlorfenvinphos</i>			
CAS Number 470-90-6	Log K_{OW} ~ 3.81	Water Solubility [mg/L] ~ 145 [1]	
AA-EQS [µg/L]		MAC-EQS [µg/L]	
Inland Surface Waters 0.1	Other Surface Waters 0.1	Inland Surface Waters 0.3	Other Surface Waters 0.3
Available Standard Method <i>EN ISO 10695:2000</i> Determination of selected organic nitrogen and phosphorus compounds - Gas chromatography methods <i>Note: Chlorfenvinphos is not explicitly mentioned in this standard but the method may also be applied to the analysis of chlorfenvinphos provided the method has been properly validated for this compound.</i>		Method Description Liquid/liquid extraction with dichloromethane or liquid/solid extraction (SPE) on reversed-phase (RP)-C18 material or other adsorbent. Elution of the cartridges with e.g. methanol or acetone. After concentration, the sample extracts are analysed by gas chromatography, using a nitrogen-phosphorus or mass spectrometric detector.	
Matrix Drinking waters, ground waters, surface waters and waste waters containing up to 50 mg/L of suspended solids		Limit of Quantification (LOQ): 0.01 µg/L	
Sampling			
Pretreatment			
Storage			
Method Validation no data available			
Other Analytical Methods			
Solid-phase microextraction (SPME) SPME in 4 mL glass vials with a 60 µm PDMS-DVB coated fibre at 60°C [2].			
Gas Chromatography - Mass Spectrometry GC-MS determination of the ions 267, 323, 295 [2, 4] LOQ ~ 25 ng/L [2] LOQ ~ 1 ng/L (after SPE of 500 mL water) [4]			
GC tandem MS-MS Parent ion m/z 267; product ions m/z 159 and 203 [2] LOQ ~ 25 ng/L [2]			
Solid-phase extraction (SPE) – HPLC/UV LOQ ~ 25 ng/L [5]			
GC - Flame Photometric Detection (FPD) EPA method 1657; LOQ ~ 2 ng/L (solvent extraction) [1, 6]			
Comments Existence of E and Z double bond isomers; the Z-isomer has a water solubility of 121 mg/L and the E-isomer of 7.3 mg/L (at 20°C); the mixture 145 mg/L at 23°C; log K _{OW} ~ 3.85 (Z-isomer) and 4.22 (E-isomer).			

References

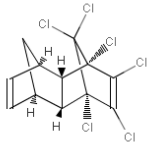
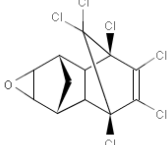
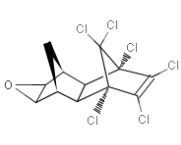
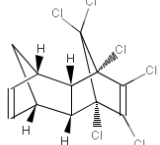
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Compound <i>Chlorpyrifos</i>			
CAS Number 2921-88-2	Log Kow ~ 4.96	Water Solubility [mg/L] ~ 0.762	
AA-EQS [µg/L]		MAC-EQS [µg/L]	
Inland Surface Waters 0.03	Other Surface Waters 0.03	Inland Surface Waters 0.1	Other Surface Waters 0.1
Available Standard Method <i>EN ISO 10695:2000</i> Determination of selected organic nitrogen and phosphorus compounds - Gas chromatography methods <i>Note: Chlorpyrifos is not explicitly mentioned in this standard but the method may also be applied to the analysis of chlorpyrifos provided the method has been properly validated for this compound.</i>		Method Description Liquid/liquid extraction with dichloromethane or liquid/solid extraction (SPE) on reversed-phase (RP)-C18 material or other adsorbent. Elution of the cartridges with e.g. methanol or acetone. After concentration, the sample extracts are analysed by gas chromatography, using a nitrogen-phosphorus or mass spectrometric detector.	
Matrix Drinking waters, ground waters, surface waters and waste waters containing up to 50 mg/L of suspended solids		Limit of Quantification (LOQ): 0.01 µg/L	
Sampling			
Pretreatment			
Storage			
Method Validation no data available			
Other Analytical Methods <u>Solid-phase microextraction (SPME)</u> SPME in 4 mL glass vials with a 60 µm PDMS-DVB coated fibre at 60°C [2] <u>Solid-phase extraction (SPE)</u> SPE with C18 cartridges; elution with ethylacetate [3] <u>Gas Chromatography - Mass Spectrometry</u> GC-MS determination of the ions 199, 197, 314, 316 [1-5] LOQ ~ 1-2 ng/L [2, 5] <u>GC tandem MS-MS</u> Parent ion m/z 314; product ions m/z 286 and 258 [2] LOQ ~ 1 ng/L [2] <u>GC-NPD:</u> LOQ ~ 20 ng/L [3] <u>GC - Flame Photometric Detection (FPD)</u> [7]			
Comments Chlorpyrifos is a non-polar insecticide. If released to water, chlorpyrifos partitions significantly from the water			

column to sediments.

References

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- [4] K. Kawata, T. Asada, K. Oikawa, Determination of pesticides in compost by pressurized liquid extraction and gas chromatography–mass spectrometry. *Journal of Chromatography A* 1090, 2005, 10-15.
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- [6] US Department of Health and Human Services, Agency for Toxic Substances and Disease Registry (ATSDR), Toxicological Profile Information Sheet, URL: <http://www.atsdr.cdc.gov/toxprofiles/tp84.html>
- [7] F. J. Lopez, J. Beltran, M. Forcada, F. Hernandez, Comparison of simplified methods for pesticide residue analysis; Use of large-volume injection in capillary gas chromatography. *Journal of Chromatography. A* 823, 1998, 25-33.

Compound					
 <p><i>Aldrin</i></p>		 <p><i>Dieldrin</i></p>		 <p><i>Endrin</i></p>	
 <p><i>Isodrin</i></p>					
		CAS Number		Log Kow	
				Water Solubility [mg/L]	
Aldrin		309-00-2		~ 6.50	
Dieldrin		60-57-1		~ 6.2	
Endrin		72-20-8		~ 5.6	
Isodrin		465-73-6		~ 6.75	
AA-EQS [µg/L]			MAC-EQS [µg/L]		
Inland Surface Waters Σ = 0.01		Other Surface Waters Σ = 0.005		Inland Surface Waters <i>not applicable</i>	
				Other Surface Waters <i>not applicable</i>	
Available Standard Method <i>EN ISO 6468:1996</i> Determination of certain organochlorine insecticides, polychlorinated biphenyls and chlorobenzenes – Gas chromatographic method after liquid-liquid extraction			Method Description Liquid-liquid extraction of organochlorine insecticides, chlorobenzenes and PCBs by an extraction solvent. After concentration and clean-up the sample extracts are analysed by gas chromatography, using an electron-capture detector (GC-ECD).		
Matrix Drinking, ground, surface and waste waters			The method is applicable to samples containing up to 50 mg/L of suspended solids.		
Sampling			Limit of Quantification (LOQ): ~ 0.001 – 0.01 µg/L		
Pretreatment					
Storage					
Method Validation					
l Number of laboratories n_{AP} percental rate of outliers \bar{x} Total mean after elimination of outliers s_R standard deviation between the laboratories CV_R reproducibility variation coefficient					
Interlaboratory study (Extraction of surface water with Hexane)					
Substance	<i>l</i>	<i>n_{AP} in %</i>	\bar{x} in ng/L	<i>s_R in µg/L</i>	<i>CV_R in %</i>
Dieldrin	14	0	33.3	17.2	51.7
Endrin	14	9.8	50.0	11.1	22.3

Other Analytical Methods

Solid-phase extraction gas chromatography - mass spectrometry

SPE with Oasis HLB cartridges; elution with dichloromethane.

GC-MS determination of the ions 66 for aldrin, 79 for dieldrin, 281 for endrin, and 193 for isodrine [1,2].

LOQ ~ 20 ng/L for aldrin,
10 ng/L for dieldrin,
15 ng/L for endrin, and
12 ng/L for isodrin

(SPE extraction of 200 mL water) [1]

SPME GC-MS

SPME in 4 mL glass vials with a 60 µm PDMS-DVB coated fibre at 60°C;

LOQ ~ 12 ng/L for aldrin, 9 ng/L for dieldrin, 60 ng/L for endrin, and 10 ng/L for isodrin [2]

SPE-GC- triple quadrupole-MS-MS

C18-SPE, 100 mL, SRM 263 > 193 (dieldrin), 261 > 191 (aldrin), 193 > 157 (isodrin); LOQ ~ 25 ng/L [3]

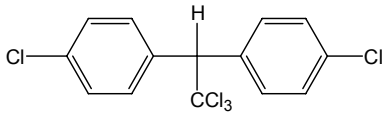
SPE-GC-NCI-MS

C18-SPE, 100 mL, LOQ ~ 25 ng/L [3]

Comments

References

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- [2] C. Gonçalves, M.F. Alpendurada, Solid-phase micro-extraction–gas chromatography–(tandem) mass spectrometry as a tool for pesticide residue analysis in water samples at high sensitivity and selectivity with confirmation capabilities. *Journal of Chromatography A* 1026, 2004, 239-250.
- [3] E. Pitarch, C. Medina, T. Portolés, F.J. López, F. Hernández, Determination of priority organic micro-pollutants in water by gas chromatography coupled to triple quadrupole mass spectrometry. *Analytica Chimica Acta* 583, 2007, 246–258.

Compound <i>DDT total para-para-DDT</i>					
CAS Number DDT total <i>not applicable</i> para-para-DDT 50-29-3		Log K_{ow} <i>p,p'</i> -DDT ~ 6.91 <i>o,p'</i> -DDT ~ 6.79 <i>p,p'</i> -DDE ~ 6.51 <i>p,p'</i> -DDD ~ 6.02		Water Solubility [mg/L] <i>p,p'</i> -DDT ~ 0.025 <i>o,p'</i> -DDT ~ 0.085 <i>p,p'</i> -DDE ~ 0.12 <i>p,p'</i> -DDD ~ 0.090	
AA-EQS [µg/L]			MAC-EQS [µg/L]		
Inland Surface Waters		Other Surface Waters		Inland Surface Waters	
DDT total 0.025 para-para-DDT 0.01		DDT total 0.025 para-para-DDT 0.01		<i>not applicable</i>	
Available Standard Method <i>EN ISO 6468:1996</i> Determination of certain organochlorine insecticides, polychlorinated biphenyls and chlorobenzenes – Gas chromatographic method after liquid-liquid extraction			Method Description Liquid-liquid extraction of organochlorine insecticides, chlorobenzenes and PCBs by an extraction solvent. After concentration and clean-up the sample extracts are analysed by gas chromatography, using an electron-capture detector (GC-ECD).		
Matrix Drinking, ground, surface and waste waters			The method is applicable to samples containing up to 50 mg/L of suspended solids.		
Sampling			Limit of Quantification (LOQ): ~ 0.001 – 0.01 µg/L		
Pretreatment					
Storage					
Method Validation					
l Number of laboratories n_{AP} percental rate of outliers \bar{x} Total mean after elimination of outliers s_R standard deviation between the laboratories CV_R reproducibility variation coefficient					
Interlaboratory study (Extraction of <i>p,p'</i>-DDT with Hexane)					
Matrix	l	n_{AP} in %	\bar{x} in ng/L	s_R in µg/L	CV_R in %
Drinking water	11	10.3	35.7	22.9	64.1
Other Analytical Methods					
Solid-phase extraction - gas chromatography - mass spectrometry SPE with Oasis HLB cartridges; elution with dichloromethane. GC-MS determination of the ions 235 for DDT and DDD, and 246 for DDE. The second qualitative ions are 165 for DDT and DDD, and 176 for DDE.					
LOQ ~ 4 ng/L for <i>p,p'</i> -DDT, 11 ng/L for <i>o,p'</i> -DDT, 4 ng/L for <i>p,p'</i> -DDE, and 12 ng/L for <i>p,p'</i> -DDD (SPE extraction of 200 mL water) [1,2]					
SPME - GC-MS SPME in 4 mL glass vials with a 60 µm PDMS-DVB coated fibre at 60°C; LOQ ~ 12 ng/L for DDT, 2 ng/L for					

DDD and 1 ng/L for DDE [3]

GC-ECD

Bettinetti et al. detected 0.05 and 0.16 ng/L of dissolved pp'DDT and pp'DDE in the liquid water fraction of Lake Maggiore, Italy [4].

EPA methods 508 (GC-ECD) and 625 (GC-MS): Liquid-liquid extraction of 1 L water with dichloromethane.

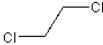
Comments


Technical grade DDT consists of 65-80 % of *p,p'*-DDT, 15-21 % of *o,p'*-DDT, up to 4 % of *p,p'*-DDD. *p,p'*-DDE is a metabolite of DDT.

DDT is very persistent in the environment with a reported half-life between 2-25 years; it has a low solubility in water.

References

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- [2] D. de Almeida Azevedo, S. Lacorte, T. Vinhas, P. Viana, D. Barceló, Monitoring of Priority Pesticides and Other Organic Pollutants in River Water From Portugal by Gas Chromatography Mass Spectrometry and Liquid Chromatography–Atmospheric Pressure Chemical Ionization Mass Spectrometry. *Journal of Chromatography A* 879, 2000, 13-26.
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- [4] R. Bettinetti, V. Croce, S. Galassi, P. Volta, Pp'DDT and pp'DDE accumulation in a food chain of Lake Maggiore (Northern Italy): testing steady-state condition, *Environmental Science and Pollution Research International* 13, 2006, 59-66.

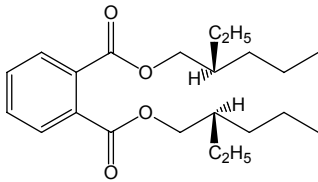
Compound <i>1,2-Dichloroethane</i>			
CAS Number 107-06-2	Log K_{ow} 1.45	Water Solubility [g/L] 8.5-9.0	
AA-EQS [µg/L]		MAC-EQS [µg/L]	
Inland Surface Waters 10	Other Surface Waters 10	Inland Surface Waters <i>not applicable</i>	Other Surface Waters <i>not applicable</i>
Available Standard Method <i>EN ISO 15680: 2003</i> Gas-chromatographic determination of a number of monocyclic aromatic hydrocarbons, naphthalene and several chlorinated compounds using purge-and-trap and thermal desorption		Method Description <i>EN ISO 15680:2003</i> specifies a general method for the determination of volatile organic compounds (VOCs) in water by purge-and-trap isolation and gas chromatography (GC).	
Matrix drinking water, ground water, surface water, seawater and (diluted) waste water		Detection is preferably carried out by mass spectrometry in the electron impact mode (EI), but other detectors may be applied as well.	
Sampling <i>ISO 5667-1, 5667-2 and ISO 5667-3</i>		Limit of Quantification (LOQ): 0.01 µg/L	
Pretreatment			
Storage hermetically sealed at 4 °C, avoid direct sunlight, analysis within 5 days			
Method Validation no data available			
Other Analytical Methods EN ISO 10301:1997 specifies two methods for the determination of highly volatile halogenated hydrocarbons in water using gas chromatography with e.g. electron capture detector after: a) the extraction by an organic solvent or using, b) a head-space method (LOQ: 100 µg/L). The EPA Method 1624 is designed to determine the volatile organic pollutants in water amenable to purge and trap gaschromatography-mass spectrometry. Huybrechts et al. 2003 give a review of gas chromatography-based methods for analysis of volatile organic compounds in estuarine waters with special emphasis on monitoring [1]. Purge and trap GC-MS SIM-GC-MS detection of the ions 62, 98, 64; LOQ ~ 2 ng/L [2] (Modification of EPA method 524.2:VOCs in Water Using GC-MS, http://www.accustandard.com/asi/pdfs/epa_methods/524_2.pdf .)			
Comments			
References [1] T. Huybrechts, J. Dewulf, H. Van Langenhove, State-of-the-art of gas chromatography-based methods or analysis of anthropogenic volatile organic compounds in estuarine waters, illustrated with the river Scheldt as an example. <i>Journal of Chromatography A</i> 1000, 2003, 283-297. [2] E. Martínez, S. Lacorte, I. Llobet, P. Viana, D. Barceló, Multicomponent analysis of volatile organic compounds in water by automated purge and trap coupled to gas chromatography–mass spectrometry. <i>Journal of Chromatography A</i> 959, 2002, 181-190.			

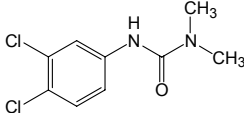
Compound <i>Dichloromethane</i>					
CAS Number 75-09-2		Log K_{ow} ~ 1.3		Water Solubility [g/L] ~ 20	
AA-EQS [µg/L]			MAC-EQS [µg/L]		
Inland Surface Waters 20		Other Surface Waters 20		Inland Surface Waters <i>not applicable</i>	
				Other Surface Waters <i>not applicable</i>	
Available Standard Method <i>EN ISO 15680:2003</i> Gas-chromatographic determination of a number of monocyclic aromatic hydrocarbons, naphthalene and several chlorinated compounds using purge-and-trap and thermal desorption			Method Description <i>EN ISO 15680:2003</i> specifies a general method for the determination of volatile organic compounds (VOCs) in water by purge-and-trap isolation and gas chromatography (GC).		
Matrix drinking water, ground water, surface water, seawater and (diluted) waste water			Detection is preferably carried out by mass spectrometry in the electron impact mode (EI), but other detectors may be applied as well.		
Sampling <i>ISO 5667-1, 5667-2 and ISO 5667-3</i>			Limit of Quantification (LOQ): 0.01 µg/L		
Pretreatment					
Storage at 4 °C air tight and no direct sunlight, analysis within 5 days					
Method Validation					
l Number of laboratories n_{AP} percental rate of outliers \bar{x} Total mean after elimination of outliers s_R standard deviation between the laboratories CV_R reproducibility variation coefficient n.a. = not available					
Interlaboratory study					
Matrix	l	n_{AP} in %	\bar{x} in µg/L	s_R in µg/L	CV_R in %
Drinking water (0.2 µg/L)	11	n.a.	n.a.	n.a.	55
Surface water (0.2 µg/L)	10	n.a.	n.a.	n.a.	68
Other Analytical Methods					
EN ISO 10301:1997 specifies two methods for the determination of highly volatile halogenated hydrocarbons in water using gas chromatography with e.g. electron capture detector after: a) the extraction by an organic solvent or using, b) a head-space method (LOQ: 100 µg/L).					
The EPA Method 1624 is designed to determine the volatile organic pollutants in water amenable to purge and trap gaschromatography-mass spectrometry.					
Huybrechts et al. 2003 give a review of gas chromatography-based methods for analysis of volatile organic compounds in estuarine waters with special emphasis on monitoring [1].					
Purge and trap GC-MS SIM-GC-MS detection of the ions 84, 86, 49; LOQ ~ 62 ng/L [2] (Modification of EPA method 524.2 "VOCs in Water Using GCMS")					

Comments

References

- [1] T. Huybrechts, J. Dewulf, H. Van Langenhove, State-of-the-art of gas chromatography-based methods or analysis of anthropogenic volatile organic compounds in estuarine waters, illustrated with the river Scheldt as an example. *Journal of Chromatography A* 1000, 2003, 283-297.
- [2] E. Martínez, S. Lacorte, I. Llobet, P. Viana, D. Barceló, Multicomponent analysis of volatile organic compounds in water by automated purge and trap coupled to gas chromatography–mass spectrometry. *Journal Chromatography A* 959, 2002, 181-190.

Compound <i>Di(2-ethylhexyl)phthalate (DEHP)</i>					
CAS Number 117-81-7		Log K_{ow} 7.5		Water Solubility [µg/L] 3	
AA-EQS [µg/L]			MAC-EQS [µg/L]		
Inland Surface Waters 1.3		Other Surface Waters 1.3	Inland Surface Waters <i>not applicable</i>		Other Surface Waters <i>not applicable</i>
Available Standard Method <i>EN ISO 18856: 2005</i> Determination of selected phthalates using gas chromatography/mass spectrometry Matrix ground water, surface water, wastewater and drinking water Sampling <i>ISO 5667-1, 5667-2 and 5667-3</i> Pretreatment Storage at 4 °C in the darkness, analysis within 4 days			Method Description <i>EN ISO 18856:2005</i> specifies a method for the determination of phthalates in water after solid phase extraction and gas chromatography/mass spectrometry. Limit of Quantification (LOQ): 0.02 µg/L - 0.150 µg/L depending on the blank		
Method Validation					
l n_{AP} \bar{x} s_R CV_R <i>l</i> Number of laboratories <i>n_{AP}</i> percental rate of outliers \bar{x} Total mean after elimination of outliers <i>s_R</i> standard deviation between the laboratories <i>CV_R</i> reproducibility variation coefficient					
Interlaboratory study 2003					
Matrix	<i>l</i>	<i>n_{AP} in %</i>	\bar{x} in ng/L	<i>s_R in ng/L</i>	<i>CV_R in %</i>
Surface water	7	0	373	257	69
Other Analytical Methods					
SPME-GC-MS GC-MS determination of the ion 149; LOQ ~ 15 to 30 ng/L [1,2]					
Comments The analysis is difficult due to the omnipresence of phthalates. Specific care shall be taken to minimise blanks. The use of plastic material shall be avoided unconditionally.					
References					
[1] A. Peñalver, E. Pocurull, F. Borrull, R.M. Marcé, Comparison of different fibers for the solid-phase microextraction of phthalate esters from water. <i>Journal of Chromatography A</i> 922, 2001, 377-384.					
[2] J. B. Baugros, B. Giroud, G. Dessalces, M. F. Grenier-Loustalot, C. Cren-Olivé. Multiresidue analytical methods for the ultra-trace quantification of 33 priority substances present in the list of REACH in real water samples. <i>Analytica Chimica Acta</i> 607, 2008, 191-203					

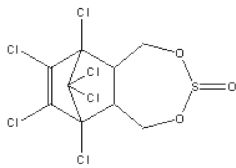
Compound <i>Diuron</i>					
CAS Number 330-54-1		Log K_{ow} ~ 2.7		Water Solubility [mg/L] ~ 42	
AA-EQS [µg/L]			MAC-EQS [µg/L]		
Inland Surface Waters 0.2		Other Surface Waters 0.2		Inland Surface Waters 1.8	
				Other Surface Waters 1.8	
Available Standard Method <i>EN ISO 11369:1997</i> Determination of selected plant treatment agents in water by high performance liquid chromatography with UV detection after solid-liquid extraction.			Method Description The plant treatment substances in the water sample are extracted by solid-liquid extraction (SPE) on reversed-phase (RP)-C18 material, eluted with a solvent, and then separated, identified and quantified by high performance liquid chromatography (HPLC) using UV detection.		
Matrix Drinking and ground water					
Sampling					
Pretreatment					
Storage			Limit of Quantification (LOQ): 0.1 µg/L		
Method Validation					
l Number of laboratories n_{AP} percental rate of outliers \bar{x} Total mean after elimination of outliers s_R standard deviation between the laboratories CV_R reproducibility variation coefficient					
Interlaboratory trial					
Matrix	l	n_{AP} in %	\bar{x} in µg/L	s_R in µg/L	CV_R in %
Drinking water	33	0	0.1026	0.0299	29.1
Ground water	32	5.1	0.2815	0.0570	20.2
Other Analytical Methods					
Liquid Chromatography - Mass Spectrometry Identification and quantification of diuron (and other pesticides) by liquid chromatography coupled to (tandem) mass spectrometric detection (LC-MS-MS) using positive electrospray ionization (ESI) LC-MS fragment ions: m/z 233 [1,2] LC-MS-MS transitions: 233 > 72 and 46 [3,4,5] LOQ ~ 1 ng/L (depending on the SPE enrichment factor)					
Liquid Chromatography – Diode Array Detector Sea water analysis: Off-line SPE – LC-DAD; LOQ ~ 0.01 µg/L [6]					
Gas Chromatography - Mass Spectrometry (after derivatisation) Phenylurea herbicides require a derivatisation step to prevent the degradation of these thermolabile compounds in the GC injector; LOQ ~ 1 ng/L [7] SPE-derivatisation-GC-MS; LOQ ~ 50 ng/L [8]					

Comments

The EN ISO 11369 HPLC-UV method is only applicable for drinking and ground water, not to the analysis of contaminated surface water. GC-MS determination of phenylurea herbicides is difficult due to the necessary derivatisation step. LC-MS-MS seems to be the method of choice.

References

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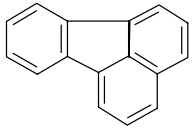
Compound <i>Endosulfan</i> <i>(alfa and beta isomer)</i>					
CAS Number 115-29-7		Log K_{ow} 3.83		Water Solubility [mg/L] 0.325	
AA-EQS [µg/L]			MAC-EQS [µg/L]		
Inland Surface Waters 0.005		Other Surface Waters 0.0005		Inland Surface Waters 0.01	
				Other Surface Waters 0.004	
Available Standard Method <i>EN ISO 6468:1996</i> Determination of certain organochlorine insecticides, polychlorinated biphenyls and chlorobenzenes - Gas chromatographic method after liquid-liquid extraction			Method Description <i>EN ISO 6468:1996</i> describes a method for determination of certain organochlorine insecticides, polychlorinated biphenyls (PCBs) and chlorobenzenes (except the mono- and dichlorobenzenes) in drinking water, ground water, surface waters and waste waters. The method is applicable to samples containing up to 50 mg/L of suspended solids.		
Matrix Drinking, ground, waste and surface water					
Sampling					
Pretreatment					
Storage			Limit of Quantification (LOQ): 0.001 up to 0.01 µg/L		
Method Validation					
l Number of laboratories n_{AP} percental rate of outliers \bar{x} Total mean after elimination of outliers s_R standard deviation between the laboratories CV_R reproducibility variation coefficient					
Interlaboratory study (Extraction of β-Endosulfan with Hexane)					
Matrix	l	n_{AP} in %	\bar{x} in ng/L	s_R in µg/L	CV_R in %
Surface water	14	6.6	21.2	14.4	67.9
Other Analytical Methods					
SPE extraction of 500 ml water with 200 mg SDB, elution with ethyl acetate; GC-MS determination <u>LOQ for α-endosulfan ~ 11 ng/L [1]</u>					
SPE-GC-NCI-MS C18-SPE, 100 mL, LOQ for α- or β-endosulfan ~ 25 ng/L [2]					
The LOQ of these alternative SPE-GC-MS methods may be low enough if good equipment and well trained personnel are available. The uncertainty however is rather high (depends on required U whether this method will be feasible).					
Comments					
Technical endosulfan is a mixture of two stereoisomers, α- and β-endosulfan (in a ratio of 7:3). In the environment in particular in soil the metabolite endosulfan-sulfate is also present.					
By the SPE extraction of higher water volumes lower LOQs could be achieved. New research results show that sufficient LOQs in the low ng/L or even pg/L range can be achieved with negative chemical ionization (NCI) GC-MS, using SPE of 1 or 10 L water [3].					

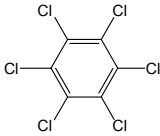
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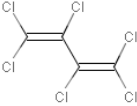
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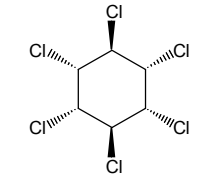
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Compound <i>Fluoranthene</i>					
CAS Number 206-44-0		Log K_{ow} 5.16		Water Solubility [mg/L] 0.265	
AA-EQS [µg/L]			MAC-EQS [µg/L]		
Inland Surface Waters 0.1		Other Surface Waters 0.1		Inland Surface Waters 1	
				Other Surface Waters 1	
Available Standard Method <i>EN ISO 17993:2003</i> Determination of 15 polycyclic aromatic hydrocarbons (PAH) in water by HPLC with fluorescence detection after liquid-liquid extraction			Method Description <i>EN ISO 17993:2003</i> specifies a method using high performance liquid chromatography (HPLC) with fluorescence detection for the determination of 15 selected polycyclic aromatic hydrocarbons (PAH).		
Matrix Drinking, ground, waste and surface water					
Sampling					
Pretreatment			Limit of Quantification (LOQ): Drinking and ground water: > 0.005 µg/L Surface water: > 0.01 µg/L		
Storage					
Method Validation					
l Number of laboratories n_{AP} percental rate of outliers \bar{x} Total mean after elimination of outliers s_R standard deviation between the laboratories CV_R reproducibility variation coefficient					
<i>Interlaboratory study 1996 in Germany</i>					
Matrix	l	n_{AP} in %	\bar{x} in µg/L	s_R in µg/L	CV_R in %
Spiked drinking water	30	10	46.48	4.225	9.1
Other Analytical Methods					
<u>USA EPA 8270c, 1996 [1]</u> : Semivolatile organic compounds by GC/MS. This method claims detection limits of 10 µg/L which is obviously too high. Other analytical methods based on this standard using modern GC/MS equipment however may attain the required low LOQs.					
Comments					
References					
[1] http://www.accustandard.com/asi/pdfs/epa_methods/8270c.pdf					

Compound <i>Hexachlorobenzene</i>					
CAS Number 118-74-1		Log K_{ow} 5.73		Water Solubility [mg/L] 0.006	
AA-EQS [µg/L]			MAC-EQS [µg/L]		
Inland Surface Waters 0.01		Other Surface Waters 0.01	Inland Surface Waters 0.05		Other Surface Waters 0.05
Available Standard Method <i>EN ISO 6468:1996</i> Determination of certain organochlorine insecticides, polychlorinated biphenyls and chlorobenzenes – Gas chromatographic method after liquid-liquid extraction Matrix Drinking, ground, surface and waste waters Sampling Pretreatment Storage			Method Description Liquid-liquid extraction of organochlorine insecticides, chlorobenzenes and PCBs by an extraction solvent. After concentration and clean-up the sample extracts are analysed by gas chromatography, using an electron-capture detector (GC-ECD). The method is applicable to samples containing up to 50 mg/L of suspended solids. Limit of Quantification (LOQ): ~ 0.001 – 0.01 µg/L		
Method Validation					
l = Number of laboratories n_{AP} = percental rate of outliers \bar{x} = Total mean after elimination of outliers s_R = standard deviation between the laboratories CV_R = reproducibility variation coefficient					
<i>Interlaboratory study (Extraction with Hexane)</i>					
Matrix	l	n_{AP} in %	\bar{x} in ng/L	s_R in µg/L	CV_R in %
Surface water	15	0	48.8	16.6	34.1
Other Analytical Methods					
<u>Gas chromatography - mass spectrometry</u> GC-MS determination of the ion 284.					
<u>GC-ECD</u> EPA methods 505 (GC-ECD) and 625 (GC-MS): Liquid-liquid extraction of 1 L water with dichloromethane. LOQ ~ 3 ng/L					
Comments An overview of HCB levels in the aquatic environment is given by Barber et al. (2005) [1]					
References					
[1] J. L. Barber, A. J. Sweetman, D. van Wijk, K. C. Jones, Hexachlorobenzene in the global environment: Emissions, levels, distribution, trends and processes. <i>Science of The Total Environment</i> 349, 2005, 1-44.					

Compound <i>Hexachlorobutadiene</i>			
CAS Number 87-68-3	Log K_{ow} 4.9	Water Solubility [mg/L] 2.55 at 20 °C	
AA-EQS [µg/L]		MAC-EQS [µg/L]	
Inland Surface Waters 0.1	Other Surface Waters 0.1	Inland Surface Waters 0.6	Other Surface Waters 0.6
Available Standard Method <i>EN ISO 10301:1997</i> Determination of highly volatile halogenated hydrocarbons - Gas-chromatographic methods		Method Description <i>EN ISO 10301:1997</i> specifies two methods for the determination of highly volatile halogenated hydrocarbons in water using gas chromatography with e.g. electron capture detector after: a) the extraction by an organic solvent or using, b) a head-space method. The static headspace method may not offer sufficient sensitivity dependent on the instrumentation available.	
Matrix Sampling <i>ISO 5667-1, 5667-2 and ISO 5667-3</i>		Limit of Quantification (LOQ): 100 µg/L	
Pretreatment			
Storage			
Method Validation no data available			
Other Analytical Methods EPA method 8260B [1]. Volatile Organic Compounds by GC/MS. This method is suitable for a variety of matrices.			
Comments			
References [1] http://www.accustandard.com/asi/pdfs/epa_methods/8260b.pdf			

Compound <i>Hexachlorocyclohexane (HCH)</i> α -, β -, γ - and δ - isomers		 (γ -HCH; lindane)			
CAS Number 608-73-1		Log K_{ow} α -HCH ~ 3.8 β -HCH ~ 3.78 γ -HCH ~ 3.72 δ -HCH ~ 4.14		Water Solubility [mg/L] α -HCH ~ 10 β -HCH ~ 5 γ -HCH ~ 7.3 δ -HCH ~ 10	
AA-EQS [μg/L]			MAC-EQS [μg/L]		
Inland Surface Waters 0.02		Other Surface Waters 0.002	Inland Surface Waters 0.04		Other Surface Waters 0.02
Available Standard Method <i>EN ISO 6468:1996</i> Determination of certain organochlorine insecticides, polychlorinated biphenyls and chlorobenzenes – Gas chromatographic method after liquid-liquid extraction			Method Description Liquid-liquid extraction of organochlorine insecticides, chlorobenzenes and PCBs by an extraction solvent. After concentration and clean-up the sample extracts are analysed by gas chromatography, using an electron-capture detector (GC-ECD).		
Matrix Drinking, ground, surface and waste waters			The method is applicable to samples containing up to 50 mg/L of suspended solids.		
Sampling			Limit of Quantification (LOQ): ~ 0.001 – 0.01 μ g/L		
Pretreatment					
Storage					
Method Validation					
<p style="text-align: right;"><i>l</i> Number of laboratories <i>n_{AP}</i> percental rate of outliers \bar{x} Total mean <i>s_R</i> standard deviation between the laboratories <i>CV_R</i> reproducibility variation coefficient</p>					
Interlaboratory study (Extraction of γ-HCH with Hexane)					
Matrix	<i>l</i>	<i>n_{AP}</i> in %	\bar{x} in ng/L	<i>s_R</i> in μg/L	<i>CV_R</i> in %
Surface water	15	14.3	38.6	14.3	38.4
Other Analytical Methods					
Solid-phase extraction gas chromatography - mass spectrometry GC-MS determination of the ions 181, 217, and 219 for the HCHs [1-4]					
LOQ ~ 10 ng/L for α -HCH, 5 ng/L for β -HCH, 5 ng/L for γ -HCH and 10 ng/L for δ - HCH (SPE extraction of 200 mL water) [1,2]					
LOQ for γ -HCH (lindane) ~ 9 ng/L (SPE extraction of 500 mL water) [3]. LOQ for γ -HCH (lindane) ~ 2 ng/L (SPE extraction of 500 mL water) [4].					
SPE-GC- triple quadrupole-MS-MS C18-SPE, 100 mL, SRM 219 > 183; LOQ ~ 25 ng/L (for lindane) [5]					

SPE-GC-NCI-MS

C18-SPE, 100 mL, LOQ ~ 25 ng/L (for lindane) [5]

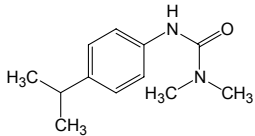
EPA methods 508, 608 (GC-ECD). EPA 625 (GC-MS) may also be used but losses of HCH can occur due to the alkaline extraction procedure.

Comments

HCH exists in eight isomer forms. Technical-grade HCH was used as an insecticide and typically contained 10-15% γ -HCH (lindane) as well as the alpha (α), beta (β), and delta (δ) forms of HCH.

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Compound <i>Isoproturon</i>					
CAS Number 34123-59-6		Log K_{ow} ~ 2.5		Water Solubility [mg/L] ~ 70	
AA-EQS [µg/L]			MAC-EQS [µg/L]		
Inland Surface Waters 0.3		Other Surface Waters 0.3		Inland Surface Waters 1.0	
				Other Surface Waters 1.0	
Available Standard Method <i>EN ISO 11369:1997</i> Water quality - Determination of selected plant treatment agents in water by high performance liquid chromatography with UV detection after solid-liquid extraction. Matrix Drinking and ground water Sampling Pretreatment Storage			Method Description The herbicides in the water sample are extracted by solid-liquid extraction (SPE) on reversed-phase (RP)-C18 material, eluted with a solvent, and then separated, identified and quantified by high performance liquid chromatography (HPLC) using UV detection. Limit of Quantification (LOQ): 0.1 µg/L		
Method Validation					
l Number of laboratories n_{AP} percental rate of outliers \bar{x} Total mean after elimination of outliers s_R standard deviation between the laboratories CV_R reproducibility variation coefficient					
Interlaboratory study					
Matrix	l	n_{AP} in %	\bar{x} in µg/L	s_R in µg/L	CV_R in %
Drinking water	32	0	0.1727	0.0394	22.8
Ground water	32	6	0.1110	0.0249	22.5
Other Analytical Methods					
Liquid Chromatography - Mass Spectrometry Identification and quantification of isoproturon (and other pesticides) by liquid chromatography coupled to (tandem) mass spectrometric detection (LC-MS-MS) using positive electrospray ionization (ESI). LC-MS fragment ions: m/z 207 [1,2] LC-MS-MS transitions: 207 > 72 [3,4] LOQ ~ 1 ng/L (depending on the SPE enrichment factor)					
Gas Chromatography - Mass Spectrometry (after derivatisation) Phenylurea herbicides require a derivatisation step to prevent the degradation of these thermolabile compounds in the GC injector; LOQ ~ 1 ng/L [5]. SPE-derivatisation-GC-MS: LOQ ~ 40 ng/L [6]					

Comments

The EN ISO 11369 HPLC-UV method is only applicable for drinking and ground water, not to the analysis of contaminated surface water. GC-MS determination of phenylurea herbicides is difficult due to the necessary derivatisation step. LC-MS-MS seems to be the method of choice.

References

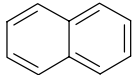
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- [6] P. Frank, M. Karg, Determination of phenylurea pesticides in water by derivatisation with heptafluorobutyric anhydride and gas chromatography – mass spectrometry. *Journal of Chromatography A* 634, 1993, 87-100.

Compound <i>Lead and its compounds</i>					
CAS Number 7439-92-1		Log K_D [L/kg] <i>suspended matter/water: 5.6 (Pb) [1]</i> <i>sediment/water: 5.1 (Pb) [1]</i>		Water Solubility [mg/L] depending on compound	
AA-EQS [µg/L]			MAC-EQS [µg/L]		
Inland Surface Waters 7.2	Other Surface Waters 7.2	Inland Surface Waters <i>not applicable</i>		Other Surface Waters <i>not applicable</i>	
Available Standard Method <i>EN ISO 17294-2:2004</i> Application of inductively coupled plasma mass spectrometry (ICP-MS) - Part 2: Determination of 62 elements Matrix Drinking waters, ground waters, surface waters and waste waters Sampling <i>ISO 5667-1, 5667-2 and 5667-3</i> Pretreatment For dissolved elements, filter aqueous sample through a 0.45-µm pore membrane filter. Adjust the pH of the filtrate to < 2 with HNO ₃ . Storage			Method Description <i>EN ISO 17294-2:2004</i> specifies a method for the determination of the lead in water (for example drinking water, surface water, groundwater, wastewater and eluates). Taking into account the specific and additionally occurring interferences, these elements can also be determined in digests of water, sludges and sediments. The working range depends on the matrix and the interferences encountered.		
			Limit of Quantification (LOQ): Drinking water and relatively unpolluted water: 0.1 up to 1 µg/L		
Method Validation					
l Number of laboratories n_{AP} percental rate of outliers $=$ \bar{x} Total mean after elimination of outliers s_R standard deviation between the laboratories CV_R reproducibility variation coefficient					
<i>Interlaboratory study 1997 in Germany</i>					
Matrix	<i>l</i>	<i>n_{AP} in %</i>	\bar{x} in µg/L	<i>s_R in µg/L</i>	<i>CV_R in %</i>
Surface water	39	2.5	13.6	1.13	8.3
Other Analytical Methods					
<p>EN ISO 15586:2003 determination using atomic absorption spectrometry with electrothermal atomization in a graphite furnace. The detection limit of the method for each element depends on the sample matrix as well as of the instrument, the type of atomizer and the use of chemical modifiers. For water samples with a simple matrix (i.e. low concentration of dissolved solids and particles), the method detection limits will be close to instrument detection limits. The minimum acceptable detection limit values for a 20 µL sample volume are specified.</p> <p>EN ISO 11885:1997 specifies a method by inductively coupled plasma atomic emission spectroscopy.</p> <p>DIN 38406-6:1998-07 determination using atomic absorption spectrometry</p> <p>DIN 38406-16 (1990-03) specifies a voltammetric determination.</p> <p>EPA 200.8 (1994) determination of trace elements in waters by inductively coupled plasma - mass spectrometry (LOQ: 0.6 µg/L)</p> <p>Standard Methods Online (http://standardmethods.org/) 3125: Metals in Water by ICP/MS (LOQ: 0.005 µg/L)</p>					

Comments

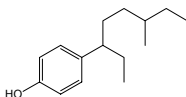
References

Compound <i>Mercury and its compounds</i>					
CAS Number 7439-97-6	Log K_D [L/kg] <i>suspended matter/water: 5.3 (Hg) [1]</i> <i>sediment/water: 4.9 (Hg) [1]</i>		Water Solubility [mg/L] Depending on compound		
AA-EQS [µg/L]		MAC-EQS [µg/L]			
Inland Surface Waters 0.05	Other Surface Waters 0.05	Inland Surface Waters 0.07	Other Surface Waters 0.07		
Available Standard Method EN ISO 17852:2008 Determination of mercury by atomic fluorescence spectrometry Matrix Drinking waters, ground waters and surface waters Sampling ISO 5667-1, 5667-2 and 5667-3 Pretreatment stabilise with Potassium dichromate and acidification to pH < 2 with high purity Nitric Acid Storage		Method Description EN ISO 17852:2008 specifies a method for the determination of mercury in water using atomic fluorescence spectrometry. Limit of Quantification (LOQ): appr. 0.001 µg/L (largely depends on the operational parameters)			
Method Validation					
l / Number of laboratories n_{AP} percental rate of outliers \bar{x} Total mean after elimination of outliers s_R standard deviation between the laboratories CV_R reproducibility variation coefficient					
Interlaboratory study 1999 in Great Britain					
Matrix	l	n_{AP} in %	\bar{x} in µg/L	s_R in µg/L	CV_R in %
Surface water	18	9.4	44.2	11.57	25.8
Other Analytical Methods					
EN 12338:1998 specifies the determination after enrichment by amalgamation					
ISO 16590:2000 specifies methods involving enrichment by amalgamation					
Comments					
References					

Compound <i>Naphthalene</i>					
CAS Number 91-20-3		Log K_{ow} 3.3		Water Solubility [mg/L] 31	
AA-EQS [µg/L]			MAC-EQS [µg/L]		
Inland Surface Waters 2.4		Other Surface Waters 1.2		Inland Surface Waters <i>not applicable</i>	
				Other Surface Waters <i>not applicable</i>	
Available Standard Method <i>EN ISO 17993:2003</i> Determination of 15 polycyclic aromatic hydrocarbons (PAH) in water by HPLC with fluorescence detection after liquid-liquid extraction <i>EN ISO 15680: 2003</i> Gas-chromatographic determination of a number of monocyclic aromatic hydrocarbons, naphthalene and several chlorinated compounds using purge-and-trap and thermal desorption Matrix Drinking, ground, waste and surface water Sampling Pretreatment Storage			Method Description <i>EN ISO 17993:2003</i> specifies a method using high performance liquid chromatography (HPLC) with fluorescence detection for the determination of 15 selected polycyclic aromatic hydrocarbons (PAH). <i>EN ISO 15680:2003</i> specifies a general method for the determination of volatile organic compounds (VOCs) in water by purge-and-trap isolation and gas chromatography (GC). Annexes A, B and C provide examples of analytes that can be determined. Detection is carried out by mass spectrometry in the electron impact mode (EI). Limit of Quantification (LOQ): HPLC - Drinking and ground water: > 0.005 µg/L HPLC - Surface water: > 0.01 µg/L Purge-and-Trap/Thermal Desorption GC-MS: > 0.01 µg/L		
Method Validation					
l Number of laboratories n_{AP} percental rate of outliers = \bar{x} Total mean after elimination of outliers s_R standard deviation between the laboratories CV_R reproducibility variation coefficient n.a. = not available					
Interlaboratory study (ISO 17993)					
Matrix	l	n_{AP} in %	\bar{x} in µg/L	s_R in µg/L	CV_R in %
Spiked drinking water	33	3	52.85	15.5	29.3
Interlaboratory study (ISO 15680)					
Matrix	l	n_{AP} in %	\bar{x} in µg/L	s_R in µg/L	CV_R in %
Surface water (0.2 µg/L)	17	n.a.	n.a.	n.a.	32
Other Analytical Methods					
USA EPA 8270c.1996. [1] claims detection limit of 10 µg/L, which is obviously too high. Other analytical methods based on this standard using modern GC/MS equipment however may attain the required low LOQs.					
Comments					
References					
[1] http://www.accustandard.com/asi/pdfs/epa_methods/8270c.pdf					

Compound <i>Nickel and its compounds</i>					
CAS Number 7440-02-0		Log K_D [L/kg] <i>suspended matter/water: 4.6 (Ni) [1]</i> <i>sediment/water: 4.0 (Ni) [1]</i>		Water Solubility [mg/L] depending on compound	
AA-EQS [µg/L]			MAC-EQS [µg/L]		
Inland Surface Waters 20		Other Surface Waters 20		Inland Surface Waters <i>not applicable</i>	
				Other Surface Waters <i>not applicable</i>	
Available Standard Method <i>EN ISO 17294-2:2004</i> Application of inductively coupled plasma mass spectrometry (ICP-MS) - Part 2: Determination of 62 elements Matrix Drinking waters, ground waters, surface waters and waste waters Sampling <i>ISO 5667-1, 5667-2 and 5667-3</i> For dissolved elements, filter aqueous sample through a 0.45 µm pore membrane filter. Adjust the pH of the filtrate to < 2 with HNO ₃ . Storage			Method Description <i>EN ISO 17294-2:2004</i> specifies a method for the determination of the nickel in water (for example drinking water, surface water, groundwater, wastewater and eluates). Taking into account the specific and additionally occurring interferences, these elements can also be determined in digests of water, sludges and sediments. The working range depends on the matrix and the interferences encountered. Limit of Quantification (LOQ): Drinking water and relatively unpolluted water: 0.1 - 1.0 µg/l		
Method Validation					
l Number of laboratories n_{AP} percental rate of outliers $=$ \bar{x} Total mean after elimination of outliers s_R standard deviation between the laboratories CV_R reproducibility variation coefficient					
<i>Interlaboratory study 1997 in Germany</i>					
Matrix	<i>l</i>	<i>n_{AP} in %</i>	\bar{x} in µg/L	<i>s_R in µg/L</i>	<i>CV_R in %</i>
Surface water	35	11	5.44	0.786	14.5
Other Analytical Methods					
EN ISO 15586:2003 determination using atomic absorption spectrometry with electrothermal atomization in a graphite furnace. The detection limit of the method for each element depends on the sample matrix as well as of the instrument, the type of atomizer and the use of chemical modifiers. For water samples with a simple matrix (i.e. low concentration of dissolved solids and particles), the method detection limits will be close to instrument detection limits. The minimum acceptable detection limit values for a 20 µL sample volume are specified. EN ISO 11885:1997 specifies a method by inductively coupled plasma atomic emission spectroscopy. EPA 200.8 1994 [1]: Determination of trace elements in waters by inductively coupled plasma - mass spectrometry (LOQ: 0.5 µg/L) Standard Methods Online (http://standardmethods.org/) 3125: Metals in Water by ICP/MS (LOQ: 0.02 µg/L)					
Comments					
References					

[1] http://www.accustandard.com/asi/pdfs/epa_methods/200_8.pdf

Compound <i>Nonylphenol</i> (4-nonylphenol)		(selected isomer) 			
CAS Number 84852-15-3		Log K_{ow} ~ 4.48		Water Solubility [mg/L] ~ 6	
AA-EQS [µg/L]			MAC-EQS [µg/L]		
Inland Surface Waters 0.3		Other Surface Waters 0.3		Inland Surface Waters 2.0	
				Other Surface Waters 2.0	
Available Standard Method <i>EN ISO 18857-1:2006</i> Determination of selected alkylphenols - Part 1: Method for non-filtered samples using liquid extraction and gas chromatography with mass selective detection			Method Description Method for the determination of 4-nonylphenols (mixture of isomers) in non-filtered samples of drinking water, ground water and surface water. Extraction of nonylphenol from the acidified water sample with toluene. Cleaning of the extract, if necessary with silica. Gas chromatographic separation and identification of the alkylphenol by mass spectrometry without derivatisation (mass fragments m/z 135 and 107). Quantification with an internal standard (¹³ C p-n-NP; m/z 113).		
Matrix Drinking, ground and surface water					
Sampling					
Pretreatment					
Storage			Limit of Quantification (LOQ): 0.02 to 0.2 µg/L		
Method Validation					
l Number of laboratories n_{AP} percental rate of outliers \bar{x} Total mean after elimination of outliers s_R standard deviation between the laboratories CV_R reproducibility variation coefficient					
<i>Interlaboratory study 2002</i>					
Matrix	l	n_{AP} in %	\bar{x} in µg/L	s_R in µg/L	CV_R in %
Surface water	11	26.7	0.0828	0.016	18.8
Other Analytical Methods					
Solid-phase extraction Extraction of alkylphenols from water with solid-phase extraction (SPE) using C18 or polymeric adsorbents. Elution with methanol, acetone, ethylacetate, or dichloromethane [2-6].					
Liquid Chromatography - Mass Spectrometry Identification and quantification of the analytes by liquid chromatography coupled to (tandem) mass spectrometric detection (LC-MS-MS) using negative electrospray ionization (ESI). LC-MS fragment ion: m/z 219 [2] LC-MS-MS transitions: 219 > 133 and 219 > 147 [3,4]; LOQ ~ 5 ng/L Internal standard: 4n-NP; transition 219 > 106					
GC-MS after derivatisation Several derivatisation techniques for alkylphenols prior to GC-MS determination have been reported. E.g., the phenol group can be converted to a pentafluorobenzoylate ester (LOQ ~ 0.05 ng/L) [5], or silylated using bis(trimethylsilyl)trifluoroacetamide (BSTFA) (LOQ ~ 1 ng/L) [6], or methyl-N-(trimethylsilyl)trifluoroacetamide (MSTFA) [7].					

Comments

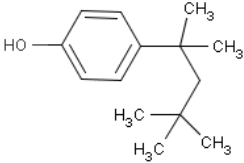
Technical nonylphenol consists of 211 differently branched nonyl chains isomers; it consists mainly (~ 90 %) of 4-nonylphenol. Only recently, it was recognized that for a correct risk assessment, isomer-specific toxicological studies and analysis are important because the estrogenic effect of the individual nonylphenol isomers is heavily dependent on the structure of the alkyl side chain. It is estimated that in biological and environmental relevant matrices approximately 50 – 80 isomers are present [8,9]. Chromatographic separation of all isomers is not possible (at the time being); it might become feasible in the future with two-dimensional GC [8]. Therefore (for now), the sum of the different nonylphenol isomers should be analysed.

When using liquid chromatography (LC), the nonylphenols have to get chromatographically separated from the ethoxy carboxylate metabolites (NPECs) because they produce the same MS ions.

Nonylphenols are relatively polar compounds, and therefore GC-MS without derivatisation can give rise to poor chromatographic peaks. Thus, nonylphenols are often derivatized prior to GC-MS.

References

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- [9] K. Guenther, V. Heinke, B. Thiele, E. Kleist, H. Prast, T. Raecker, Response to Comments on "Endocrine Disrupting Nonylphenols Are Ubiquitous in Food". *Environmental Science & Technology*. 37, 2003, 2624.

Compound <i>Octylphenol</i> (4- <i>tert</i> -octylphenol)					
CAS Number 140-66-9	Log K_{ow} 5.28	Water Solubility [mg/L] 5			
AA-EQS [µg/L]			MAC-EQS [µg/L]		
Inland Surface Waters 0.1	Other Surface Waters 0.01	Inland Surface Waters <i>not applicable</i>	Other Surface Waters <i>not applicable</i>		
Available Standard Method <i>EN ISO 18857-1:2006</i> Determination of selected alkylphenols - Part 1: Method for non-filtered samples using liquid extraction and gas chromatography with mass selective detection		Method Description Method for the determination of octylphenol in non-filtered samples of drinking water, ground water and surface water. Extraction of octylphenol from the acidified water sample with toluene. Cleaning of the extract, if necessary with silica. Gas chromatographic separation and identification of the alkylphenol by mass spectrometry without derivatisation (mass fragments m/z 135 and 107). Quantification with an internal standard (¹³ C p-n-NP; m/z 113).			
Matrix Drinking, ground and surface water		Limit of Quantification (LOQ): 0.005 – 0.2 µg/L			
Sampling					
Pretreatment					
Storage					
Method Validation					
$\frac{l}{n_{AP}}$ = $\frac{\bar{x}}{s_R}$ <i>l</i> Number of laboratories <i>n_{AP}</i> percental rate of outliers \bar{x} Total mean after elimination of outliers <i>s_R</i> standard deviation between the laboratories <i>CV_R</i> reproducibility variation coefficient					
Interlaboratory study 2002					
Matrix	<i>l</i>	<i>n_{AP}</i> in %	\bar{x} in µg/L	<i>s_R</i> in µg/L	<i>CV_R</i> in %
Surface water	13	13.3	0.0668	0.01789	26.8
Other Analytical Methods					
Solid-phase extraction Extraction of alkylphenols from water with solid-phase extraction (SPE) using C18 or polymeric adsorbents. Elution with methanol, acetone, ethylacetate, or dichloromethane [2-6].					
Liquid Chromatography - Mass Spectrometry Identification and quantification of the analytes by liquid chromatography coupled to (tandem) mass spectrometric detection (LC-MS-MS) using negative electrospray ionization (ESI). LC-MS fragment ion: m/z 205 [2] LC-MS-MS transitions: 205 > 133 [3-4] Internal standard: 4n-NP; transition 219 > 106					
GC-MS after derivatisation Several derivatisation techniques for alkylphenols prior to GC-MS determination have been reported. E.g., the phenol group can be converted to a pentafluorobenzoylate ester (LOQ ~ 0.05 ng/L) [5], or silylated (LOQ ~ 2.6 ng/L) [6].					

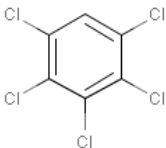
Comments

The term *octylphenol* represents a large number of isomeric compounds of the general formula $C_8H_{17}C_6H_4(OH)$. The octyl group may be branched in a variety of ways or be a straight chain. Of these potential isomers, 4-*tert*-octylphenol (CAS No. 140-66-9) is the most commercially (and toxicologically) important [7]. It has the MS-MS transition 205 > 133.

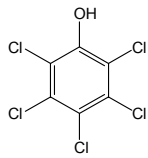
Another analytical standard is available: 4-octylphenol (CAS No. 1806-26-4). This standard contains linear octylphenol; it shows the characteristic MS-MS transition 205 > 106.

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- [5] H. M. Kuch, K. Ballschmiter, Determination of Endocrine-Disrupting Phenolic Compounds and Estrogens in Surface and Drinking Water by HRGC-(NCI)-MS in the Picogram per Liter Range. *Environmental Science & Technology* 35, 2001, 3201-3206.
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Compound <i>Pentachlorobenzene</i>			
CAS Number 60-93-5	Log Kow 5.17	Water Solubility [mg/L] 0.831	
AA-EQS [µg/L]		MAC-EQS [µg/L]	
Inland Surface Waters 0.007	Other Surface Waters 0.0007	Inland Surface Waters <i>not applicable</i>	Other Surface Waters <i>not applicable</i>
Available Standard Method <i>EN ISO 6468:1996</i> Determination of certain organochlorine insecticides, polychlorinated biphenyls and chlorobenzenes – Gas chromatographic method after liquid-liquid extraction		Method Description Liquid-liquid extraction of organochlorine insecticides, chlorobenzenes and PCBs by an extraction solvent. After concentration and clean-up the sample extracts are analysed by gas chromatography, using an electron-capture detector (GC-ECD). The method is applicable to samples containing up to 50 mg/L of suspended solids.	
Matrix Drinking, ground, surface and waste waters		Limit of Quantification (LOQ): ~ 0.001 – 0.01 µg/L	
Sampling			
Pretreatment			
Storage			
Method Validation no data available			
Other Analytical Methods <u>Gas chromatography - mass spectrometry</u> GC-MS determination of the ions 250, 215, 180 <u>GC-ECD</u> EPA methods 505 (GC-ECD) [1] and 625 (GC-MS) [2]: Liquid-liquid extraction of 1 L water with dichloromethane. LOQ ~ 3 ng/L <u>GC- triple-quad MS-MS</u> [3] SPE extraction of 100 mL water (elution with ethyl acetate / DCM) followed by GC- triple-quad MS-MS. Precursor ions 248 and 250, product 142; LOQ = 25 ng/L. With NCI and the extraction of bigger water volumes, a lower LOQ might be achieved.			
Comments If released to water, pentachlorobenzene will adsorb strongly to sediments and will bioconcentrate in fish. It will be subject to evaporation with a half-life of 6.5 hours estimated for evaporation from a river 1 m deep, flowing at 1 m/sec and a wind velocity of 3 m/sec. The volatilization half-life from a model pond, which considers the effects of adsorption, can be estimated to be about 60 days. It will not be expected to significantly biodegrade or hydrolyze.			
References [1] http://www.accustandard.com/asi/pdfs/epa_methods/505.pdf [2] http://www.accustandard.com/asi/pdfs/epa_methods/625.pdf			

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Compound <i>Pentachlorophenol</i>					
CAS Number 87-86-5		Log K_{ow} ~ 5.0		Water Solubility [mg/L] ~ 14	
AA-EQS [µg/L]			MAC-EQS [µg/L]		
Inland Surface Waters 0.4		Other Surface Waters 0.4	Inland Surface Waters 1		Other Surface Waters 1
Available Standard Method <i>EN 12673:1998</i> Gas chromatographic determination of some selected chlorophenols in water			Method Description This European Standard describes the gas chromatographic determination of 19 chlorophenols in water. The methods consists of acetylation of the chlorophenols with acetic anhydride followed by liquid/liquid extraction with hexane and determination by gas chromatography (GC) and electrone capture detection (ECD) or mass selective detection (MSD).		
Matrix Drinking, ground, rain, waste, sea and surface water			Limit of Quantification (LOQ): 0.1 µg/L (Extraction volume:50 mL)		
Sampling					
Pretreatment					
Storage					
Method Validation					
l Number of laboratories n_{AP} percental rate of outliers \bar{x} Total mean after elimination of outliers s_R standard deviation between the laboratories CV_R reproducibility variation coefficient					
Interlaboratory study November 1996					
Matrix	<i>l</i>	<i>n_{AP} in %</i>	\bar{x} in µg/L	<i>s_R</i> in µg/L	<i>CV_R</i> in %
Drinking water	12	22.2	0.11	0.028	24
Surface water	13	7.1	0.20	0.042	21
Other Analytical Methods					
Gas Chromatography - Mass Spectrometry Characteristic ions for MS detection (of acetate): 266, 264, 268, 270 (DIN EN 12673).					
Silyl derivatisation GC-MS Derivatisation with Bis(trimethylsilyl)trifluoroacetamide (BSTFA); MS quantification ions 323, 321, 93. Dynamic concentration range: 1-1500 µg/L (without enrichment)					
Solid-phase extraction SPE with styrene-divinylbenzene (SDB) cartridges at pH 2.6; elution with 4 mL methanol; recovery ~ 90 % [2].					
SPME-GC-MS SPME from 2 mL sample volume; scan MS acquisition; claiming a LOQ of ~ 5 ng/L [3]					
Derivatisation SPME-GC-MS Derivatisation with acetic anhydride in 22 mL headspace vials followed by SPME and GC-MS determination (scan mode); LOQ ~ 3 ng/L [4].					

SPE-LC-MS

LC-MS of Pentachlorophenol is difficult due to bad ionisation of the hydroxy group. However, off- and on-line SPE-LC-MS methods have been reported.

On-line SPE extraction of 100 mL river water (pH 3) using LiChrolut EN precolumns; elution with the water-acetonitrile-methanol gradient; LC-APCI-MS analysis; LOQ in SIM mode ~ 0.1 ng/L [5]

On-line SPE extraction of 10 mL river (pH 2.5) water using polymeric adsorbents; LC-APCI-MS analysis; LOQ in SIM mode ~ 5 ng/L [6]

Off-line SPE with PS-DVB membrane extraction disk of 500 mL tap water, elution with acetonitrile; LC-APCI-MS with post-column addition of diethylamine; SIM ions 263, 265, 267; LOQ ~ 20 ng/L [7].

Comments

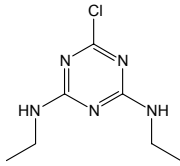
The SPME-GC-MS and SPE-on-line-LC-MS methods have lower LOQ but are not standardized. Other derivatisation reagents such as pentafluorobenzoyl chloride can be used prior to GC analysis.

References

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Compound					
<i>Benzo[a]pyrene</i> <i>Benzo[b]fluoroanthene</i> <i>Benzo[g,h,i]perylene</i> <i>Benzo[k]fluoroanthene</i> <i>Indeno[1,2,3-cd]pyrene</i>		$C_{20}H_{12}$ $C_{20}H_{12}$ $C_{22}H_{12}$ $C_{20}H_{12}$ $C_{22}H_{12}$			
	CAS Number	Log K_{ow}	Water Solubility [mg/L]		
<i>Benzo[a]pyrene</i> <i>Benzo[b]fluoroanthene</i> <i>Benzo[k]fluoroanthene</i> <i>Benzo[g,h,i]perylene</i> <i>Indeno[1,2,3-cd]pyrene</i>	50-32-8 205-99-2 207-08-9 191-24-2 193-39-5	6.13 5.78 6.11 6.63 6.70	0.00162 0.0015 0.0008 0.00026 0.00019		
	AA-EQS [$\mu\text{g/L}$]		MAC-EQS [$\mu\text{g/L}$]		
	Inland Surface Waters	Other Surface Waters	Inland Surface Waters	Other Surface Waters	
<i>Benzo[a]pyrene</i>	0.05	0.05	0.1	0.1	
<i>Benzo[b]fluoroanthene</i>	$\Sigma = 0.03$	$\Sigma = 0.03$	not applicable	not applicable	
<i>Benzo[k]fluoroanthene</i>					
<i>Benzo[g,h,i]perylene</i>	$\Sigma = 0.002$	$\Sigma = 0.002$	not applicable	not applicable	
<i>Indeno[1,2,3-cd]pyrene</i>					
Available Standard Method		Method Description			
<i>EN ISO 17993: 2003</i> Determination of 15 polycyclic aromatic hydrocarbons (PAH) in water by HPLC with fluorescence detection after liquid-liquid extraction		<i>EN ISO 17993:2003</i> specifies a method using high performance liquid chromatography (HPLC) with fluorescence detection for the determination of 15 selected polycyclic aromatic.			
Matrix Drinking, ground, waste and surface water					
Sampling		Limit of Quantification (LOQ):			
Pretreatment		Drinking and ground water: > 0.005 $\mu\text{g/L}$ Surface water: > 0.01 $\mu\text{g/L}$			
Storage					
Method Validation					
l Number of laboratories n_{AP} percental rate of outliers \bar{x} Total mean after elimination of outliers s_R standard deviation between the laboratories CV_R reproducibility variation coefficient					
<i>National interlaboratory study for spiked drinking water 1996 (German)</i>					
Substance	l	n_{AP} in %	\bar{x} in $\mu\text{g/L}$	s_R in $\mu\text{g/L}$	CV_R in %
<i>Benzo[a]pyrene</i>	33	3.1	20.43	4.17	20.4
<i>Benzo[b]fluoroanthene</i>	33	3.1	27.41	4.719	17.2
<i>Benzo[k]fluoroanthene</i>	32	3.2	10.87	2.382	21.9

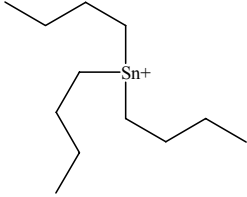
<i>Benzo[g,h,i]perylene</i>	32	6.2	25.21	5.941	23.6
<i>Indeno[1,2,3-cd]pyrene</i>	29	12	26.31	4.417	17.9
<u>Other Analytical Methods</u>					
EPA 8270c [1] claims detection limit of 10 µg/L which is obviously too high. Other analytical methods based on this standard using modern GC/MS equipment however may attain the required low LOQs.					
<u>Comments</u>					
The methods do not attain low enough LOQs and uncertainties for compliance checking with the AA-EQS for the sum of <i>Benzo[b]fluoranthene</i> and <i>Benzo[k]fluoranthene</i> as well as the sum of <i>Benzo[g,h,i]perylene</i> and <i>Indeno[1,2,3-cd]pyrene</i> . In addition, not enough validation data are available regarding the analysis of surface water samples in particular samples containing substantial amounts of SPM.					
A new ISO standard for the determination of PAH in water using gas chromatography with mass spectrometry detection is under development (ISO/CD 28540)					
<u>References</u>					
[1] http://www.accustandard.com/asi/pdfs/epa_methods/8270c.pdf					

Compound <i>Simazine</i>					
CAS Number 1912-24-9		Log K_{ow} ~ 2.2		Water Solubility [mg/L] ~ 6.2	
AA-EQS [µg/L]			MAC-EQS [µg/L]		
Inland Surface Waters 1		Other Surface Waters 1	Inland Surface Waters 4		Other Surface Waters 4
Available Standard Method <i>EN ISO 10695:2000</i> Determination of selected organic nitrogen and phosphorus compounds - Gas chromatography methods			Method Description Liquid/liquid extraction with dichloromethane or liquid/solid extraction (SPE) on reversed-phase (RP)-C18 material or other adsorbent. Elution of the cartridges with e.g. methanol or acetone. After concentration, the sample extracts are analysed by gas chromatography, using a nitrogen-phosphorus or mass spectrometric detector.		
Matrix Drinking waters, ground waters, surface waters and waste waters containing up to 50 mg/L of suspended solids			Limit of Quantification (LOQ): Liquid/liquid extraction method: 0.5 µg/L Liquid/solid extraction method: 0.012 µg/L		
Sampling					
Pretreatment					
Storage					
Method Validation					
l Number of laboratories n_{AP} percental rate of outliers \bar{x} Total mean after elimination of outliers s_R standard deviation between the laboratories CV_R reproducibility variation coefficient					
Interlaboratory study 1993 for liquid/solid extraction					
Matrix	l	n_{AP} in %	\bar{x} in µg/L	s_R in µg/L	CV_R in %
Drinking water	12	16.4	0.058	0.0044	27.3
Other Analytical Methods					
Gas Chromatography - Mass Spectrometry GC-MS determination of the ions 201 and 186; LOQ ~ 1 ng/L (after SPE) [1, 2] (EPA method 525)					
GC-NPD EPA method 507 [3]					
GC-ECD EPA method 505; microextraction with hexane and GC-ECD analysis [32]					
Liquid Chromatography - Mass Spectrometry Identification and quantification of simazine (and other pesticides) by liquid chromatography coupled to (tandem) mass spectrometric detection (LC-MS-MS) using positive electrospray ionization (ESI). LC-MS fragment ions: m/z 202 and 124 [4] LC-MS-MS transition: 202 > 132 [5, 6] LOQ ~ 1 ng/L (depending on the SPE enrichment factor)					

Comments

References

- [1] T. D. Bucheli, F. C. Grüebler, S. R. Müller, R. P. Schwarzenbach, Simultaneous Determination of Neutral and Acidic Pesticides in Natural Waters at the Low Nanogram per Liter Level. *Analytical Chemistry* 69, 1997, 1569-1576.
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Compound <i>Tributyltin compounds</i>					
CAS Number 688-73-3		Log K_{ow} 3.1 - 4.1		Water Solubility [mg/L] ~ 2 mg/L	
AA-EQS [µg/L]			MAC-EQS [µg/L]		
Inland Surface Waters 0.0002		Other Surface Waters 0.0002		Inland Surface Waters 0.0015	
				Other Surface Waters 0.0015	
Available Standard Method <i>EN ISO 17353:2005</i> Determination of selected organotin compounds - Gas chromatographic method			Method Description		
Matrix Drinking, surface and waste waters containing not more than 2g/L of suspended material.			Method for the identification and quantification of organotin compounds and/or cations in water. Compounds: Monobutyltin cation (MBT) BuSn ³⁺ Dibutyltin cation (DBT) Bu ₂ Sn ²⁺ Tributyltin cation (TBT) Bu ₃ Sn ⁺ Tetrabutyltin (TTBT) Bu ₄ Sn		
Sampling			Organotin compounds in water are ethylated with sodium tetraethyl-borate (NaBEt ₄) and extracted with hexane. The extract can be cleaned with silica. After concentration, the tetra-substituted OTC are separated by capillary gas chromatography and detected with a suitable system (MS, FPD, AED). The concentration is determined by calibration over the total procedure using an internal standard mixture.		
Pretreatment					
Storage					
			Limit of Quantification (LOQ): 0.010 – 1 µg/L		
Method Validation					
<i>l</i> Number of laboratories <i>n_{AP}</i> percental rate of outliers \bar{x} Total mean <i>s_R</i> standard deviation between the laboratories <i>CV_R</i> reproducibility variation coefficient					
<i>Interlaboratory study 1998 in Germany</i>					
Matrix	<i>l</i>	<i>n_{AP} in %</i>	\bar{x} in ng/L	<i>s_R in µg/L</i>	<i>CV_R in %</i>
Spiked surface water	11	8.3	388.2	92.16	23.7
Other Analytical Methods					
LLE-EI-GC-MS 100 mL seawater, pH 5.4, derivatisation with NaBEt ₄ , hexane extraction; LOQ ~ 0.8 ng/L [1].					
GC-NCI-MS LOQ 0.1 ng/L [2].					
Liquid phase microextraction (LPME) – GC-MS-MS 4mL water sample; 4-fluorophenyl derivatisation; LOQ 0.36 ng/L [3].					

LLE-GC-FDP

1 L sea water, pH 5.5, ethylation in aqueous phase with NaBEt₄, iso-octane/n-pentane extraction; LOQ 0.01 ng/L [4].

LLE-LC-MS

At pH 4 using hexane-ethylacetate (70:30); ion-trap LC–APCI-MS; m/z 323 and 307; LOD 35 µg/L for TBT [5].

GC-ICP-MS

Extraction of 1 L sample at clean room conditions. Derivatisation followed by GC-ICP/MS, LOQ ~0.01 ng/L [6,7]

Comments

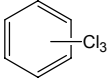
Only tributyltin cation is required for WFD monitoring. In the environment different anions (OH⁻, Cl⁻, Br⁻, acetate) are associated with TBT. Analytical methods are assumed to derivatise all forms.

EQS values for TBT refer to the tributyl-cation, hence result shall be expressed in the same way.

Care has to be taken when comparing result with data from scientific literature because some authors express results as µg Sn /L.

References

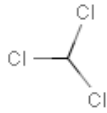
- [1] G. Centineo, P. Rodríguez-González, E. Blanco González, J. I. García Alonso, A. Sanz-Medel, N. Font Cardona, J. Luis Aranda Mares, S. Ballester Nebot. Isotope dilution GC-MS routine method for the determination of butyltin compounds in water. *Anal. Bioanal. Chem.* 384, 2006, 908-914.
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- [3] H. Shioji, S. Tsunoi, H. Harino, M. Tanaka. Liquid-phase microextraction of tributyltin and triphenyltin coupled with gas chromatography–tandem mass spectrometry. *Journal of Chromatography A*, 1048, 2004, 81-88.
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- [6] M. Monperrus, E. Tessier, D. Amouroux, O.F.X. Donard. Simultaneous speciation of mercury and butyltin compounds in natural waters and snows by propylation and species specific isotope dilution mass spectrometry analysis. *Anal Bioanal Chem*, 381, 2005, 854-862.
- [7] M. Monperrus, O. Zuloaga, E. Krupp, D. Amouroux, R. Wahlen, B. Fairman, O.F.X. Donard. Rapid, accurate and precise determination of tributyltin in sediments and biological samples by species specific isotope dilution-microwave extraction-gas chromatography-ICP mass spectrometry. *J. Anal. Atomic Spectrosc.* 18(3), 2003, 247-253.

Compound <i>Trichlorobenzenes</i> <i>(all isomers)</i>					
CAS Number 12002-48-1		Log K_{OW} 4.02 – 4.49		Water Solubility [mg/L] 6-19	
AA-EQS [µg/L]			MAC-EQS [µg/L]		
Inland Surface Waters 0.4		Other Surface Waters 0.4	Inland Surface Waters <i>not applicable</i>		Other Surface Waters <i>not applicable</i>
Available Standard Method <i>EN ISO 15680</i> Water quality - Gas-chromatographic determination of a number of monocyclic aromatic hydrocarbons, naphthalene and several chlorinated compounds using purge-and-trap and thermal desorption Matrix drinking water, ground water, surface water, seawater and (diluted) waste water Sampling <i>ISO 5667-1, 5667-2 and ISO 5667-3</i> Pretreatment Storage at 4 °C air tight and no direct sunlight, analysis within 5 days			Method Description EN ISO 15680:2003 specifies a general method for the determination of volatile organic compounds (VOCs) in water by purge-and-trap isolation and gas chromatography (GC). Detection is preferably carried out by mass spectrometry in the electron impact mode (EI), but other detectors may be applied as well Selected ions: 180, 182, 145 Limit of Quantification (LOQ): 0.01 µg/L		
Method Validation					
<i>l</i> Number of laboratories <i>n_{AP}</i> percental rate of outliers = Total mean after elimination of outliers <i>s_R</i> standard deviation between the laboratories <i>CV_R</i> reproducibility variation coefficient n.a. = not available					
Interlaboratory study					
Matrix	<i>l</i>	<i>n_{AP} in %</i>	\bar{x} in ng/L	<i>s_R in ng/L</i>	<i>CV_R in %</i>
Drinking water (0.2 µg/L)	5	n.a.	n.a.	n.a.	27
Surface water (0.2 µg/L)	4	n.a.	n.a.	n.a.	35
Other Analytical Methods ISO 6468:1996: Water quality - Determination of certain organochlorine insecticides, polychlorinated biphenyls and chlorobenzenes - Gas chromatographic method after liquid-liquid extraction. LOQ ~ 0.01µg/l.					

Comments

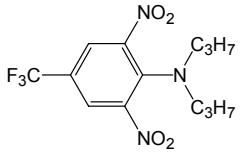
In water, trichlorobenzenes are likely to be adsorbed onto sediments and to bioconcentrate in aquatic organisms. Evaporation from water may be a significant removal process.

References

Compound <i>Trichloromethane</i>					
CAS Number 67-66-3		Log K_{ow} 1.97		Water Solubility [mg/L] 8.7	
AA-EQS [µg/L]			MAC-EQS [µg/L]		
Inland Surface Waters 2.5		Other Surface Waters 2.5		Inland Surface Waters <i>not applicable</i>	
				Other Surface Waters <i>not applicable</i>	
Available Standard Method <i>EN ISO 15680: 2003</i> Gas-chromatographic determination of a number of monocyclic aromatic hydrocarbons, naphthalene and several chlorinated compounds using purge-and-trap and thermal desorption			Method Description <i>EN ISO 15680:2003</i> specifies a general method for the determination of volatile organic compounds (VOCs) in water by purge-and-trap isolation and gas chromatography (GC).		
Matrix drinking water, ground water, surface water, seawater and (diluted) waste water			Detection is preferably carried out by mass spectrometry in the electron impact mode (EI), but other detectors may be applied as well.		
Sampling <i>ISO 5667-1, 5667-2 and ISO 5667-3</i>					
Pretreatment					
Storage at 4 °C air tight and no direct sunlight, analysis within 5 days			Limit of Quantification (LOQ): 0.01 µg/L		
Method Validation					
l Number of laboratories n_{AP} percental rate of outliers = \bar{x} Total mean after elimination of outliers s_R standard deviation between the laboratories CV_R reproducibility variation coefficient n.a. = not available					
Interlaboratory study					
Matrix	<i>l</i>	<i>n_{AP} in %</i>	\bar{x} in ng/L	<i>s_R in ng/L</i>	<i>CV_R in %</i>
Drinking water (0.2 µg/L)	15	n.a.	n.a.	n.a.	29
Surface water (0.2 µg/L)	13	n.a.	n.a.	n.a.	30
Other Analytical Methods					
EN ISO 10301:1997 specifies two methods for the determination of highly volatile halogenated hydrocarbons in water using gas chromatography with e.g. electron capture detector after: a) the extraction by an organic solvent or using, b) a head-space method (LOQ: 100 µg/L).					
The EPA Method 1624 is designed to determine the volatile organic pollutants in water amenable to purge and trap gas chromatography-mass spectrometry.					
Huybrechts et al. 2003 give a review of gas chromatography-based methods for analysis of volatile organic compounds in estuarine waters with special emphasis on monitoring. [1]					
Comments					

References


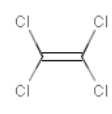
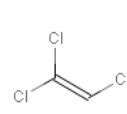
- [1] T. Huybrechts, J. Dewulf, H. Van Langenhove, State-of-the-art of gas chromatography-based methods for analysis of anthropogenic volatile organic compounds in estuarine waters, illustrated with the river Scheldt as an example. *Journal of Chromatography A* 1000, 2003, 283-297.

Compound <i>Trifluralin</i>					
CAS Number 1582-09-8		Log K_{ow} ~ 5.3		Water Solubility [mg/L] ~ 0.3	
AA-EQS [µg/L]			MAC-EQS [µg/L]		
Inland Surface Waters 0.03		Other Surface Waters 0.03		Inland Surface Waters <i>not applicable</i>	
				Other Surface Waters <i>not applicable</i>	
Available Standard Method <i>EN ISO 10695:2000</i> Determination of selected organic nitrogen and phosphorus compounds - Gas chromatography methods Matrix Drinking waters, ground waters, surface waters and waste waters containing up to 50 mg/L of suspended solids Sampling Pretreatment Storage			Method Description Liquid/liquid extraction with dichloromethane or liquid/solid extraction (SPE) on reversed-phase (RP)-C18 material or other adsorbent. Elution of the cartridges with e.g. methanol or acetone. After concentration, the sample extracts are analysed by gas chromatography, using a nitrogen-phosphorus or mass spectrometric detector. Limit of Quantification (LOQ): ~ 0.05 µg/L		
Method Validation					
l n_{AP} \bar{x} s_R CV_R <p style="text-align: right;"> <i>l</i> Number of laboratories <i>n_{AP}</i> percental rate of outliers \bar{x} Total mean after elimination of outliers <i>s_R</i> standard deviation between the laboratories <i>CV_R</i> reproducibility variation coefficient </p>					
<i>Interlaboratory study 1993 for liquid/solid extraction</i>					
Matrix	<i>l</i>	<i>n_{AP} in %</i>	\bar{x} <i>in µg/L</i>	<i>s_R in µg/L</i>	<i>CV_R in %</i>
Raw water	14	8.6	0.296	0.0264	46.3
Other Analytical Methods					
Gas Chromatography - Mass Spectrometry GC-MS determination of the ions 306, 264, 336 [1-5] LOQ ~ 13 ng/L (SPE extraction of 500 mL water) [1] LOQ ~ 5 ng/L (SPE extraction of 200 mL water) [4] LOQ ~ 1 ng/L (SPE extraction of 500 mL water) [5] EPA method 508.1 (GC-ECD) [6] SPE-GC- triple quadrupole-MS-MS C18-SPE, 100 mL, 306 > 264; LOQ ~ 25 ng/L [7] SPE-GC-NCI-MS C18-SPE, 100 mL, LOQ ~ 25 ng/L [7]					
Comments					
If released to water, trifluralin is expected to biodegrade under both aerobic and anaerobic conditions and to undergo direct photolytic degradation. It is expected to bioconcentrate in fish and aquatic organisms and adsorb					

strongly to sediment and suspended organic matter. It may also volatilize from water to the atmosphere. If released to the atmosphere, trifluralin is expected to undergo a rapid gas-phase photolysis.

References

- [1] J. Quintana, I. Martí, F. Ventura, Monitoring of Pesticides in Drinking and Related Waters in NE Spain with a Multiresidue SPE-GC-MS Method Including an Estimation of the Uncertainty of the Analytical Results. *Journal of Chromatography A* 938, 2001, 3-13.
- [2] M. Kochman, A. Gordin, P. Goldshlag, S. J. Lehotay, A. Amirav, Fast, High-Sensitivity, Multipesticide Analysis of Complex Mixtures With Supersonic Gas Chromatography-Mass Spectrometry. *Journal of Chromatography A* 974, 2002, 185-212.
- [3] S. Lacorte, I. Guiffard, D. Fraisse, D. Barceló, Broad Spectrum Analysis of 109 Priority Compounds Listed in the 76/464/CEE Council Directive Using Solid-Phase Extraction and GC/EI/MS. *Analytical Chemistry* 72, 2000, 1430-1440.
- [4] D. de Almeida Azevedo, S. Lacorte, T. Vinhas, P. Viana, D. Barceló, Monitoring of Priority Pesticides and Other Organic Pollutants in River Water From Portugal by Gas Chromatography-Mass Spectrometry and Liquid Chromatography-Atmospheric Pressure Chemical Ionization Mass Spectrometry. *Journal of Chromatography A* 879, 2000, 13-26.
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- [6] http://www.accustandard.com/asi/pdfs/epa_methods/508_1.pdf
- [7] E. Pitarch, C. Medina, T. Portolés, F.J. López, F. Hernández, Determination of priority organic micro-pollutants in water by gas chromatography coupled to triple quadrupole mass spectrometry. *Analytica Chimica Acta* 583, 2007, 246-258.

Compound					
<p><i>Carbontetrachloride</i></p> 		<p><i>Tetrachloroethylene</i></p> 		<p><i>Trichloroethylene</i></p> 	
CAS Number		Log K_{ow}		Water Solubility [mg/L]	
<i>Carbontetrachloride</i> 56-23-5		2.83		1160	
<i>Tetrachloroethylene</i> 127-18-4		3.4		100	
<i>Trichloroethylene</i> 79-01-6		2.42		1100	
AA-EQS [µg/L]			MAC-EQS [µg/L]		
	Inland Surface Waters	Other Surface Waters	Inland Surface Waters	Other Surface Waters	
<i>Carbontetrachloride</i>	12	12	<i>not applicable</i>	<i>not applicable</i>	
<i>Tetrachloroethylene</i>	10	10			
<i>Trichloroethylene</i>	10	10			
Available Standard Method <i>EN ISO 10301:1997</i> Determination of highly volatile halogenated hydrocarbons - Gas-chromatographic methods			Method Description <i>EN ISO 10301:1997</i> specifies two methods for the determination of highly volatile halogenated hydrocarbons in water using gas chromatography with e.g. electron capture detector after: a) the extraction by an organic solvent or using, b) a head-space method.		
Matrix Drinking, ground, surface and waste waters			Limit of Quantification (LOQ [µg/L]):		
Sampling				Solvent	Headspace
Pretreatment			Carbon tetrachloride	0.01-0.1	0.1
Storage			Tetrachloroethylene	0.1	0.2
			Trichloroethylene	0.05-0.1	0.2
Method Validation					
<p><i>l</i> Number of laboratories <i>n_{AP}</i> percental rate of outliers \bar{x} Total mean after elimination of outliers <i>s_R</i> standard deviation between the laboratories <i>CV_R</i> reproducibility variation coefficient</p>					
Interlaboratory study					
Wastewater	<i>l</i>	<i>n_{AP} in %</i>	\bar{x} in ng/L	<i>s_R in µg/L</i>	<i>CV_R in %</i>
Solvent Extraction:					
Carbon Tetrachloride	18	0	76.2	7.2	9.4
Tetrachloroethylene	18	0	81.3	6.4	7.8
Trichloroethylene	18	6	74.7	7.3	9.7
Headspace:					
Carbon Tetrachloride	10	0	0.29	0.05	17.6
Tetrachloroethylene	17	0	27.63	0.62	2.3
Trichloroethylene	23	5	41.07	1.226	3.0
Other Analytical Methods					
EPA method 502.2 - Purge and Trap concentration with photoionisation and electrolytical conductivity detection [1]. GC/MS confirmation can also be used.					
EPA method 524.2 – Purge and Trap concentration with GC/MS analysis [2].					

Comments

Modern GC/MS instrumentation may allow the use of full scan mass spectra for identification and quantification of these substances at levels below EQS.

References

[1] http://www.accustandard.com/asi/pdfs/epa_methods/502_2.pdf

[1] http://www.accustandard.com/asi/pdfs/epa_methods/524_2.pdf

ANNEX III: Existing certified reference materials²⁵

Table 1: Reference materials producers

BAM, Germany	http://www.bam.de/
CMI, Czech Republic	http://www.cmi.cz/
EUROFINS, Denmark	http://www.eurofins.dk/
GUM, Poland	http://www.gum.gov.pl/pl/site/
IAEA, Austria	http://www.iaea.org/programmes/aqcs/
IPO, Poland	http://www.ipo.waw.pl/
IRMM, European Commission	http://www.irmm.jrc.be
LGC, GB	http://www.lgcstandards.com/home/home_de.aspx
NIST, USA	http://www.nist.gov/
NRC-CNRC, Canada	http://inms-ienm.nrc-cnrc.gc.ca/
National Institute of Metrology, China	http://www.en.nim.ac.cn/
National Measurement Institute, Australia	http://www.measurement.gov.au/
SMU, Slovakia	http://www.smu.gov.sk/

²⁵ EAQC-WISE project, funded under the 6th RDT Framework Programme, European Commission

Table 2: Certified reference materials related to the WFD priority substances
P – Pure compounds or solutions

Priority substance	Matrix	CRM-Identifier	Producer	Certified value	Reference
Alachlor	P	SRM-3070	NIST	24.0 mg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
Anthracene	P	DPAC-1	NRC-CNRC, Canada	13 µg/g	http://inms-ienm.nrc-cnrc.gc.ca/calserv/crm_e.html
	P	SIRM 10-2-30s	Q-chem Ltd., Slovakia	48.7 µg/g	http://www.comar.bam.de/
	P	SRM-1647d	NIST	20.77 µg/mL	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	P	SRM-2260a	NIST	3.231 µg/mL	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
Atrazine	P	SRM-3070	NIST	39.2 mg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
Benzene	P	7141-95M/1	GUP TSIKV	0.99 g/L	http://www.comar.bam.de/
	P	7141-95M/2	GUP TSIKV	0.495 g/L	http://www.comar.bam.de/
	P	7141-95M/3	GUP TSIKV	0.097 g/L	http://www.comar.bam.de/
	P	7141-95M	GUP TSIKV	99.87 %	http://www.comar.bam.de/
	P	C03	SMU	99.9 %	http://www.comar.bam.de/
	P	GBW 06104	Tian Jin Institute of Metrological Technology	99.95 %	http://www.comar.bam.de/
Cadmium and its compounds	P	6690-93/1	GUP TSIKV	1 g/L	http://www.comar.bam.de/
	P	7325-96	GUP TSIKV	0.0101 %	http://www.comar.bam.de/
	P	DMR-85c	CENAM, Mexico	1001.0 mg/L	http://www.comar.bam.de/
	P	DMR-8i	CENAM, Mexico	1 mg/L	http://www.comar.bam.de/
	P	GBW-08602	National Institute of Metrology, China	0.100 µg/kg	http://www.comar.bam.de/
	P	GBW-08607	National Institute of Metrology, China	0.100 µg/g	http://www.comar.bam.de/
	P	GBW-08608	National Institute of Metrology, China	10.0 µg/kg	http://www.comar.bam.de/
1,2-Dichloroethane	P	7332-96	GUP TSIKV, Russia	99.76 %	http://www.comar.bam.de/
	P	SRM-3012	NIST	0.010039 g/g	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
Endosulfan	P	SRM-3069	NIST	4.66 mg/kg (I) 5.29 mg/kg (II)	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	P	SRM-2275	NIST	2.880 mg/kg (I) 2.943 mg/kg (II)	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
Hexachlorobenzene	P	SRM-1492	NIST	308 µg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	P	SRM-2261	NIST	1.968 µg/mL	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	P	SRM-3069	NIST	4.39 mg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
Hexachlorocyclohexane gamma-isomer	P	SLRM-10-2-08	Slovak Institute of Metrology, Slovakia	0.1 %	http://www.comar.bam.de/
	P	SRM-1492	NIST	310 µg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	P	SRM-2261	NIST	1.972 µg/mL	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	P	SRM-3069	NIST	4.22 mg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	P	SRM-8466	NIST	99.9 weight %	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
Lead and its compounds	P	7012-93/1	GUP TSIKV	1.01 g/L	http://www.comar.bam.de/
	P	DMR-63c	CENAM, Mexico	1002.1 mg/L	http://www.comar.bam.de/
	P	DMR-8i	CENAM, Mexico	10 mg/L	http://www.comar.bam.de/
Naphthalene	P	DPAC-1	NRC-CNRC, Canada	116 µg/g	http://inms-ienm.nrc-cnrc.gc.ca/calserv/crm_e.html
	P	SIRM 10-2-30s	Q-chem Ltd., Slovakia	49.8 µg/g	http://www.comar.bam.de/
	P	SRM-1586-1	NIST	126.5 µg /g	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	P	SRM-1586-2	NIST	126.6 µg /g	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	P	SRM-1647d	NIST	20.13 µg /mL	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	P	SRM-2270	NIST	77.0 mg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
Nickel and its compounds	P	DMR-8i	CENAM, Mexico	1 mg/L	http://www.comar.bam.de/
Pentachlorophenol	P	SRM-1584	NIST	15.4 µg/mL	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	P	SRM-3066	NIST	100.7 mg/L	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
PAHs benzo[a]pyrene	P	DPAC-1	NRC-CNRC, Canada	35 µg/g	http://inms-ienm.nrc-cnrc.gc.ca/calserv/crm_e.html
	P	GBW-08701	Beijing Municipal Environmental Monitoring Centre, China	5.75 µg/g	http://www.comar.bam.de/
	P	GBW-08702	Beijing Municipal Environmental Monitoring Centre, China	10.0 µg/g	http://www.comar.bam.de/
	P	SIRM 10-2-30s	Q-chem Ltd., Slovakia	49.4 µg/g	http://www.comar.bam.de/
	P	SRM-1586-1	NIST	49.2 µg /g	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	P	SRM-1586-2	NIST	44.1 µg /g	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	P	SRM-1647d	NIST	4.91 µg /mL	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	P	SRM-2260a	NIST	4.07 µg/mL	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
P	SRM-2270	NIST	37.3 mg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm	
fluoranthene	P	DPAC-1	NRC-CNRC, Canada	116 µg/g	http://inms-ienm.nrc-cnrc.gc.ca/calserv/crm_e.html
	P	DPAC-2	NRC-CNRC, Canada	117 µg/g	http://inms-ienm.nrc-cnrc.gc.ca/calserv/crm_e.html
	P	SRM-1647d	NIST	7.64 µg /mL	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	P	SRM-2260a	NIST	7.200 µg/mL	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	P	SRM-2269	NIST	62.6 mg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm

Priority substance	Matrix	CRM-Identifier	Producer	Certified value	Reference
benzo[b]fluoranthene	P	BCR-048R	EC-JRC-IRMM	0.995 g/g	http://http://www.irmm.jrc.be/html/reference_materials_catalogue/index.htm/html/reference_materials_catalogue/index.htm
	P	DPAC-1	NRC-CNRC, Canada	35 µg/g	http://inms-ienm.nrc-cnrc.gc.ca/calserv/crm_e.html
	P	SRM-1647d	NIST	4.17 µg /mL	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	P	SRM-2260a	NIST	6.80 µg/mL	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	P	SIRM 10-2-30s	Q-chem Ltd., Slovakia	49.9 µg/g	http://www.comar.bam.de/
benzo[k]fluoranthene	P	BCR-048R	EC-JRC-IRMM	0.995 g/g	http://http://www.irmm.jrc.be/html/reference_materials_catalogue/index.htm/html/reference_materials_catalogue/index.htm
	P	SRM-1647d	NIST	4.72 µg /mL	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	P	SRM-2260a	NIST	2.979 µg/mL	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	P	SIRM 10-2-30s	Q-chem Ltd., Slovakia	49.9 µg/g	http://www.comar.bam.de/
indeno[1,2,3-cd]pyrene	P	SIRM 10-2-30s	Q-chem Ltd., Slovakia	49.5 µg/g	http://www.comar.bam.de/
	P	SRM-1647d	NIST	4.28 µg /mL	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
benzo[g,h,i]perylene	P	BCR-052	EC-JRC-IRMM	0.990 g/g	http://http://www.irmm.jrc.be/html/reference_materials_catalogue/index.htm/html/reference_materials_catalogue/index.htm
	P	DPAC-1	NRC-CNRC, Canada	23 µg/g	http://inms-ienm.nrc-cnrc.gc.ca/calserv/crm_e.html
	P	SIRM 10-2-30s	Q-chem Ltd., Slovakia	48.8 µg/g	http://www.comar.bam.de/
	P	SRM-1647d	NIST	3.68 µg /mL	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	P	SRM-2260a	NIST	4.904 µg/mL	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	P	SRM-2270	NIST	35.34 mg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
Simazine	P	SRM-3070	NIST	49.4 mg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
Trichloromethane (Chloroform)	P	7288-96	GUP TSIKV, Russia	99.88 %	http://www.comar.bam.de/
		SRM-1639	NIST	6235 ng/µL	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm

Table 3: Certified reference materials related to the WFD priority substances
Matrix: S – Sediment; W – Water; A – Aquatic plant or animal

Priority substance	Matrix	CRM-Identifier	Producer	Certified value	Reference
Anthracene	S	EC-1	National Water Research Institute, Canada	1.2 µg/g	http://www.comar.bam.de
	S	EC-8	National Water Research Institute, Canada	41 µg/kg	http://www.comar.bam.de
	S	IAEA-383	IAEA Analytical Quality Control Services	0.03 mg/kg	http://www.comar.bam.de
	S	IAEA-408	IAEA Analytical Quality Control Services	0.0098 mg/kg	http://www.comar.bam.de
	S	IAEA-417	IAEA Analytical Quality Control Services	630 ng/g	http://www.comar.bam.de
	S	HS-3B	NRC-CNRC, Canada	2.76 µg/g	http://www.comar.bam.de
	S	HS-4B	NRC-CNRC, Canada	0.46 µg/g	http://www.comar.bam.de
	S	HS-5	NRC-CNRC, Canada	0.38 µg/g	http://www.comar.bam.de
	S	HS-6	NRC-CNRC, Canada	1.1 µg/g	http://www.comar.bam.de
	S	SRM-1941b	NIST	184 µg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	S	SRM-1944	NIST	1.77 mg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	A	SRM-1974b	NIST	0.527 µg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	A	IAEA-140/OC	IAEA Analytical Quality Control Services	0.014 mg/kg	http://www.comar.bam.de
A	IAEA-432	IAEA Analytical Quality Control Services	1.5 ng/g	http://www.comar.bam.de	
Benzene	S	PR 9584	RIZA QA and Interlaboratory studies	7.62 µg/kg	http://www.comar.bam.de/
Cadmium and its compounds	W	BCR-505	EC-JRC-IRMM	0.80 nmol/kg	http://http://www.irmm.jrc.be/html/reference_materials_catalogue/index.htm/html/reference_materials_catalogue/index.htm
	W	BCR-403	EC-JRC-IRMM	0.175 nmol/kg	http://http://www.irmm.jrc.be/html/reference_materials_catalogue/index.htm/html/reference_materials_catalogue/index.htm
	W	BCR-609	EC-JRC-IRMM	0.164 µg/kg	http://http://www.irmm.jrc.be/html/reference_materials_catalogue/index.htm/html/reference_materials_catalogue/index.htm
	W	BCR-610	EC-JRC-IRMM	2.94 µg/kg	http://http://www.irmm.jrc.be/html/reference_materials_catalogue/index.htm/html/reference_materials_catalogue/index.htm
	W	BCR-713	EC-JRC-IRMM	5.1 µg/L	http://http://www.irmm.jrc.be/html/reference_materials_catalogue/index.htm
	W	BCR-714	EC-JRC-IRMM	19.9 µg/L	http://www.irmm.jrc.be/html/reference_materials_catalogue/index.htm
	W	BCR-715	EC-JRC-IRMM	40 µg/L	http://www.irmm.jrc.be/html/reference_materials_catalogue/index.htm
	W	QC LL2	EUROFINS (DK)	2 µg/L	http://www.eurofins.dk
	W	CASS-4	NRC-CNRC, Canada	0.026 µg/L	http://inms-ienm.nrc-cnrc.gc.ca
	W	LGC-6016	LGC-Promochem	101 µg/kg	http://www.comar.bam.de/
	W	LGC-6017	LGC-Promochem	0.13 µg/L	http://www.comar.bam.de/
	W	LGC-6019	LGC-Promochem	0.11 µg/L	http://www.comar.bam.de/
	W	NASS-5	NRC-CNRC, Canada	0.023 µg/L	http://inms-ienm.nrc-cnrc.gc.ca
	W	SLEW-3	NRC-CNRC, Canada	0.048 µg/L	http://inms-ienm.nrc-cnrc.gc.ca
	W	SLRM-12-3-10	Research Institute for Irrigation, Slovakia	0.005 µg/g	http://www.comar.bam.de
	W	SLRS-4	NRC-CNRC, Canada	0.012 µg/L	http://inms-ienm.nrc-cnrc.gc.ca
	W	SRM-1640	NIST	22.79 µg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	W	SRM-1643e	NIST	6.408 µg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	W	TM-23.2	NRC-CNRC, Canada	2.6 µg/kg	http://www.comar.bam.de/
	W	TM-24	NRC-CNRC, Canada	12.5 µg/kg	http://www.comar.bam.de/
	W	TM-26.2	NRC-CNRC, Canada	6.8 µg/kg	http://www.comar.bam.de/
	W	TM-27	NRC-CNRC, Canada	1.0 µg/kg	http://www.comar.bam.de/
	W	TM-27.2	NRC-CNRC, Canada	1.2 µg/kg	http://www.comar.bam.de/
	W	TM-28	NRC-CNRC, Canada	1.2 µg/kg	http://www.comar.bam.de/
	W	TMRAIN-51.2	NRC-CNRC, Canada	25.1 µg/kg	http://www.comar.bam.de/
	W	TMRAIN-52.2	NRC-CNRC, Canada	91.4 µg/kg	http://www.comar.bam.de/
	W	TMRAIN-53.2	NRC-CNRC, Canada	122 µg/kg	http://www.comar.bam.de/
	W	TMRAIN-54.2	NRC-CNRC, Canada	185 µg/kg	http://www.comar.bam.de/
	W	TMRAIN-95	NRC-CNRC, Canada	0.48 µg/kg	http://www.comar.bam.de/
	S	GBW-07314	NRCCRM, China	0.20 µg/g	http://www.comar.bam.de/
	S	GBW-08301	Institute of Environmental Chemistry, China	2.45 µg/g	http://www.comar.bam.de/
	S	HISS-1	NRC-CNRC, Canada	0.024 mg/kg	http://inms-ienm.nrc-cnrc.gc.ca
	S	IAEA-SL-1	IAEA, Austria	0.26 mg/kg	http://www.comar.bam.de/
	S	MESS-3	NRC-CNRC, Canada	0.24 mg/kg	http://inms-ienm.nrc-cnrc.gc.ca
	S	NIES-2	NIES, Japan	0.82 µg/g	http://www.comar.bam.de/
	S	NIES-9	NIES, Japan	0.15 µg/g	http://www.comar.bam.de/
	S	PACS-2	NRC-CNRC, Canada	2.11 mg/kg	http://inms-ienm.nrc-cnrc.gc.ca
	S	SRM-1646a	NIST	0.148 mg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	S	SRM-1944	NIST	8.8 mg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	S	SRM-2702	NIST	0.817 mg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	A	DORM-2	NRC-CNRC, Canada	0.043 mg/kg	http://inms-ienm.nrc-cnrc.gc.ca
A	LUTS-1	NRC-CNRC, Canada	2.12 mg/kg	http://inms-ienm.nrc-cnrc.gc.ca	
A	DOLT-3	NRC-CNRC, Canada	19.4 mg/kg	http://inms-ienm.nrc-cnrc.gc.ca	
A	TORT-2	NRC-CNRC, Canada	26.7 mg/kg	http://inms-ienm.nrc-cnrc.gc.ca	
A	GBW-08571	Institute of Environmental Chemistry, China	4.5 µg/g	http://www.comar.bam.de/	
A	LGC-7160	LGC-Promochem	1.85 mg/kg	http://www.comar.bam.de/	

Priority substance	Matrix	CRM-Identifier	Producer	Certified value	Reference
	A	SLRM-12-2-02	Institute of Radioecology and Applied Nuclear Techniques, Slovakia	44.8 µg/kg	http://www.comar.bam.de/
	A	SRM-1566b	NIST	2.48 mg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	A	SRM-2976	NIST	0.179 mg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	A	SRM-2977	NIST	0.82 mg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	A	ERM-CE278	EC-JRC-IRMM	0.348 mg/kg	http://www.irmm.jrc.be/html/reference_materials_catalogue/index.htm
	A	BCR-279	EC-JRC-IRMM	0.274 mg/kg	http://www.irmm.jrc.be/html/reference_materials_catalogue/index.htm
	A	BCR-060	EC-JRC-IRMM	2.20 mg/kg	http://www.irmm.jrc.be/html/reference_materials_catalogue/index.htm
	A	BCR-414	EC-JRC-IRMM	0.383 mg/kg	http://www.irmm.jrc.be/html/reference_materials_catalogue/index.htm
	A	BCR-422	EC-JRC-IRMM	0.017 mg/kg	http://www.irmm.jrc.be/html/reference_materials_catalogue/index.htm
Hexachlorobenzene	S	EC-2	National Water Research Institute, Canada	200.6 µg/kg	http://www.comar.bam.de
	S	EC-3	National Water Research Institute, Canada	279 µg/g	http://www.comar.bam.de
	S	EC-8	National Water Research Institute, Canada	98 µg/kg	http://www.comar.bam.de
	S	SRM-1941b	NIST	5.83 µg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	S	SRM-1944	NIST	6.03 µg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	A	SRM-1945	NIST	32.9 µg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	A	SRM-1946	NIST	7.25 µg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	A	BCR-598	EC-JRC-IRMM	55.7 µg/kg	http://www.irmm.jrc.be/html/reference_materials_catalogue/index.htm
	A	IAEA-432	IAEA Analytical Quality Control Services	0.2 ng/g	http://www.comar.bam.de
A	SRM-1588	NIST	157.8 µg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm	
Hexachlorobutadiene	S	EC-2	National Water Research Institute, Canada	21.3 µg/kg	http://www.comar.bam.de
	S	EC-3	National Water Research Institute, Canada	61 µg/g	http://www.comar.bam.de
	S	EC-8	National Water Research Institute, Canada	21 µg/kg	http://www.comar.bam.de
	A	SRM-1945	NIST	32.9 µg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
Hexachlorocyclohexane gamma-isomer	S	IAEA-408	IAEA Analytical Quality Control Services	0.00019 mg/kg	http://www.comar.bam.de
	S	IAEA-417	IAEA Analytical Quality Control Services	0.54 ng/g	http://www.comar.bam.de
	A	BCR-598	EC-JRC-IRMM	23.0 µg/kg	http://www.irmm.jrc.be/html/reference_materials_catalogue/index.htm
	A	SRM-1588	NIST	24.9 µg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	A	SRM-1945	NIST	3.30 µg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	A	SRM-1946	NIST	1.14 µg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
Lead and its compounds	W	7272-96	GUP TSIKV	0.103 g/L	http://www.comar.bam.de/
	W	BCR-403	EC-JRC-IRMM	0.117 nmol/kg	http://www.irmm.jrc.be/html/reference_materials_catalogue/index.htm
	W	BCR-609	EC-JRC-IRMM	1.63 µg/kg	http://www.irmm.jrc.be/html/reference_materials_catalogue/index.htm
	W	BCR-610	EC-JRC-IRMM	7.78 µg/kg	http://www.irmm.jrc.be/html/reference_materials_catalogue/index.htm
	W	BCR-713	EC-JRC-IRMM	47 µg/L	http://www.irmm.jrc.be/html/reference_materials_catalogue/index.htm
	W	BCR-714	EC-JRC-IRMM	145 µg/L	http://www.irmm.jrc.be/html/reference_materials_catalogue/index.htm
	W	BCR-715	EC-JRC-IRMM	0.49 µg/L	http://www.irmm.jrc.be/html/reference_materials_catalogue/index.htm
	W	QC LL2	EUROFINS (DK)	20 µg/L	http://www.eurofins.dk
	W	CASS-4	NRC-CNRC, Canada	0.0098 µg/L	http://inms-ienm.nrc-cnrc.gc.ca
	W	NASS-5	NRC-CNRC, Canada	0.008 µg/L	http://inms-ienm.nrc-cnrc.gc.ca
	W	SLEW-3	NRC-CNRC, Canada	0.0090 µg/L	http://inms-ienm.nrc-cnrc.gc.ca
	W	SLRS-4	NRC-CNRC, Canada	0.086 µg/L	http://inms-ienm.nrc-cnrc.gc.ca
	W	GBW-08601	NRCCRM, China	1.0 µg/g	http://www.comar.bam.de/
	W	GBW-08607	National Institute of Metrology, China	1.0 µg/g	http://www.comar.bam.de/
	W	GBW-08608	National Institute of Metrology, China	50 µg/kg	http://www.comar.bam.de/
	W	LGC-6016	LGC-Promochem	196 µg/kg	http://www.comar.bam.de/
	W	LGC-6017	LGC-Promochem	1.0 µg/L	http://www.comar.bam.de/
	W	LGC-6019	LGC-Promochem	5.2 µg/L	http://www.comar.bam.de/
	W	ERML-CA010a	LGC	95 mg/L	http://www.lgcpromochem.com
	W	SIRM 12-3-10	Research Institute for Irrigation, Slovakia	0.029 µg/g	http://www.comar.bam.de/
	W	SLRM-12-3-10	Research Institute for Irrigation, Slovakia	0.029 µg/g	http://www.comar.bam.de
	W	SRM-1640	NIST	22.79 µg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	W	SRM-1643e	NIST	19.45 µg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
W	TM-23.2	NRC-CNRC, Canada	3.8 µg/kg	http://www.comar.bam.de/	
W	TM-24	NRC-CNRC, Canada	7.3 µg/kg	http://www.comar.bam.de/	
W	TM-26.2	NRC-CNRC, Canada	9.9 µg/kg	http://www.comar.bam.de/	
W	TM-27	NRC-CNRC, Canada	4.9 µg/kg	http://www.comar.bam.de/	
W	TM-27.2	NRC-CNRC, Canada	3.2 µg/kg	http://www.comar.bam.de/	
W	TM-28	NRC-CNRC, Canada	3.0 µg/kg	http://www.comar.bam.de/	
W	TMRAIN-51.2	NRC-CNRC, Canada	72.9 µg/kg	http://www.comar.bam.de/	
W	TMRAIN-52.2	NRC-CNRC, Canada	368 µg/kg	http://www.comar.bam.de/	

Priority substance	Matrix	CRM-Identifier	Producer	Certified value	Reference
	W	TMRAIN-53.2	NRC-CNRC, Canada	360 µg/kg	http://www.comar.bam.de/
	W	TMRAIN-54.2	NRC-CNRC, Canada	531 µg/kg	http://www.comar.bam.de/
	W	TMRAIN-95	NRC-CNRC, Canada	0.29 µg/kg	http://www.comar.bam.de/
	S	GBW-07314	NRCCRM, China	25 µg/g	http://www.comar.bam.de/
	S	GBW-08301	Institute of Environmental Chemistry, China	79 µg/g	http://www.comar.bam.de/
	S	HISS-1	NRC-CNRC, Canada	3.13 mg/kg	http://inms-ienm.nrc-cnrc.gc.ca
	S	MESS-3	NRC-CNRC, Canada	21.1 mg/kg	http://inms-ienm.nrc-cnrc.gc.ca
	S	PACS-2	NRC-CNRC, Canada	183 mg/kg	http://inms-ienm.nrc-cnrc.gc.ca
	S	IAEA-SL-1	IAEA, Austria	37.7 mg/kg	http://www.comar.bam.de/
	S	NIES-2	NIES, Japan	105 µg/g	http://www.comar.bam.de/
	S	NIES-9	NIES, Japan	1.35 µg/g	http://www.comar.bam.de/
	S	SRM-1646a	NIST	11.7 mg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	S	SRM-1944	NIST	330 mg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	S	SRM-2702	NIST	132.8 mg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	A	BCR-060	EC-JRC-IRMM	63.8 mg/kg	http://www.irmm.jrc.be/html/reference_materials_catalogue/index.htm
	A	BCR-279	EC-JRC-IRMM	13.48 mg/kg	http://www.irmm.jrc.be/html/reference_materials_catalogue/index.htm
	A	BCR-414	EC-JRC-IRMM	3.97 mg/kg	http://www.irmm.jrc.be/html/reference_materials_catalogue/index.htm
	A	BCR-422	EC-JRC-IRMM	0.085 mg/kg	http://www.irmm.jrc.be/html/reference_materials_catalogue/index.htm
	A	ERM-CE278	EC-JRC-IRMM	2.00 mg/kg	http://www.irmm.jrc.be/html/reference_materials_catalogue/index.htm
	A	DOLT-3	NRC-CNRC, Canada	0.319 mg/kg	http://inms-ienm.nrc-cnrc.gc.ca
	A	DORM-2	NRC-CNRC, Canada	0.065 mg/kg	http://inms-ienm.nrc-cnrc.gc.ca
	A	GBW-08571	Institute of Environmental Chemistry, China	1.96 µg/g	http://www.comar.bam.de/
	A	SLRM-12-2-02	Institute of Radioecology and Applied Nuclear Techniques, Slovakia	1.23 µg/g	http://www.comar.bam.de/
	A	SRM-1566b	NIST	0.308 mg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	A	SRM-2976	NIST	1.19 mg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	A	SRM-2977	NIST	2.27 mg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	A	LUTS-1	NRC-CNRC, Canada	0.010 mg/kg	http://inms-ienm.nrc-cnrc.gc.ca
	A	TORT-2	NRC-CNRC, Canada	0.35 mg/kg	http://inms-ienm.nrc-cnrc.gc.ca
Mercury and its compounds	W	8004-93/1	GUP TSIKV	1.01 g/L	http://www.comar.bam.de/
	W	BCR-579	EC-JRC-IRMM	1.85 ng/kg	http://www.irmm.jrc.be/html/reference_materials_catalogue/index.htm
	W	ORMS-3	NRC-CNRC, Canada	12.6 pg/g	http://inms-ienm.nrc-cnrc.gc.ca
	W	SIRM 12-3-10	Research Institute for Irrigation, Slovakia	0.0011 µg/g	http://www.comar.bam.de/
	W	SRM-1641d	NIST	1.590 mg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	W	QC LL3	EUROFINS (DK)	5 µg/L	http://www.eurofins.dk
	W	QC LL3A	EUROFINS (DK)	0.5 µg/L	http://www.eurofins.dk
	S	ERM-CC580	EC-JRC-IRMM	132 mg/kg	http://www.irmm.jrc.be/html/reference_materials_catalogue/index.htm
	S	GBW-07314	NRCCRM, China	0.20 µg/g	http://www.comar.bam.de/
	S	GBW-08301	Institute of Environmental Chemistry, China	0.048 µg/g	http://www.comar.bam.de/
	S	MESS-3	NRC-CNRC, Canada	0.091 mg/kg	http://inms-ienm.nrc-cnrc.gc.ca
	S	PACS-2	NRC-CNRC, Canada	3.04 mg/kg	http://inms-ienm.nrc-cnrc.gc.ca
	S	SRM-2702	NIST	0.4474 mg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	S	WQB-1	NRC-CNRC, Canada	1.09 µg/g	http://www.comar.bam.de/
	S	WQB-3	NRC-CNRC, Canada	2.75 µg/g	http://www.comar.bam.de/
	A	BCR-060	EC-JRC-IRMM	0.34 mg/kg	http://www.irmm.jrc.be/html/reference_materials_catalogue/index.htm
	A	BCR-414	EC-JRC-IRMM	0.276 mg/kg	http://www.irmm.jrc.be/html/reference_materials_catalogue/index.htm
	A	BCR-422	EC-JRC-IRMM	0.559 mg/kg	http://www.irmm.jrc.be/html/reference_materials_catalogue/index.htm
	A	BCR-463	EC-JRC-IRMM	2.85 mg/kg	http://www.irmm.jrc.be/html/reference_materials_catalogue/index.htm
	A	DOLT-3	NRC-CNRC, Canada	3.37 mg/kg	http://inms-ienm.nrc-cnrc.gc.ca
	A	DORM-2	NRC-CNRC, Canada	4.64 mg/kg	http://inms-ienm.nrc-cnrc.gc.ca
	A	ERM-CE278	EC-JRC-IRMM	0.196 mg/kg	http://www.irmm.jrc.be/html/reference_materials_catalogue/index.htm
	A	ERM-CE464	EC-JRC-IRMM	5.24 mg/kg	http://www.irmm.jrc.be/html/reference_materials_catalogue/index.htm
	A	GBW-08571	Institute of Environmental Chemistry, China	0.067 µg/g	http://www.comar.bam.de/
	A	LGC-7160	LGC-Promochem	0.096 mg/kg	http://www.comar.bam.de/
	A	SRM-1566b	NIST	0.0371 mg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	A	SRM-1946	NIST	0.433 µg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	A	SRM-1974b	NIST	17.0 µg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	A	SRM-2976	NIST	61.0 µg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	A	TORT-2	NRC-CNRC, Canada	0.27 mg/kg	http://inms-ienm.nrc-cnrc.gc.ca
Naphthalene	S	EC-8	National Water Research Institute, Canada	10 µg/kg	http://www.comar.bam.de/
	S	IAEA-383	IAEA Analytical Quality Control Services	0.096 mg/kg	http://www.comar.bam.de/
	S	IAEA-408	IAEA Analytical Quality Control Services	0.027 mg/kg	http://www.comar.bam.de/
	S	HS-3B	NRC-CNRC, Canada	2.14 µg/g	http://www.comar.bam.de/
	S	HS-4B	NRC-CNRC, Canada	0.22 µg/g	http://www.comar.bam.de/
	S	HS-5	NRC-CNRC, Canada	0.25 µg/g	http://www.comar.bam.de/
	S	HS-6	NRC-CNRC, Canada	4.1 µg/g	http://www.comar.bam.de/
	S	SRM-1941b	NIST	848 µg/kg	http://ts.nist.gov/MeasurementServices/Ref

Priority substance	Matrix	CRM-Identifier	Producer	Certified value	Reference
	S	SRM-1944	NIST	1.65 mg/kg	erenceMaterials/232.cfm http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	A	IAEA-140/OC	IAEA Analytical Quality Control Services	0.017 mg/kg	http://www.comar.bam.de
	A	SRM-1974b	NIST	2.43 µg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
Nickel and its compounds	W	7272-96	GUP TSIKV, Russia	0.102 g/L	http://www.comar.bam.de/
	W	8001-93/1	GUP TSIKV, Russia	1.00 g/L	http://www.comar.bam.de/
	W	SIRM 12-3-10	Research Institute for Irrigation, Slovakia	0.061 µg/g	http://www.comar.bam.de/
	W	BCR-403	EC-JRC-IRMM	4.4 nmol/kg	http://www.irmm.jrc.be/html/reference_materials_catalogue/index.htm
	W	BCR-505	EC-JRC-IRMM	24.1 nmol/kg	http://www.irmm.jrc.be/html/reference_materials_catalogue/index.htm
	W	BCR-713	EC-JRC-IRMM	30 µg/L	http://www.irmm.jrc.be/html/reference_materials_catalogue/index.htm
	W	BCR-714	EC-JRC-IRMM	108 µg/L	http://www.irmm.jrc.be/html/reference_materials_catalogue/index.htm
	W	BCR-715	EC-JRC-IRMM	1.20 µg/L	http://www.irmm.jrc.be/html/reference_materials_catalogue/index.htm
	W	QC LL1	EUROFINS (DK)	15 µg/L	http://www.eurofins.dk
	W	SRM-1643e	NIST	60.89 µg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	W	GBW-08607	National Institute of Metrology, China	0.500 µg/g	http://www.comar.bam.de/
	W	GBW-08608	National Institute of Metrology, China	60 µg/kg	http://www.comar.bam.de/
	W	LGC-6016	LGC-Promochem	186 µg/kg	http://www.comar.bam.de/
	W	LGC-6017	LGC-Promochem	1.6 µg/L	http://www.comar.bam.de/
	W	LGC-6019	LGC-Promochem	2.6 µg/L	http://www.comar.bam.de/
	W	ERML-CA010a	LGC	48 mg/L	http://www.lgc-promochem.com
	W	CASS-4	NRC-CNRC, Canada	0.314 µg/L	http://inms-ienm.nrc-cnrc.gc.ca
	W	SLEW-3	NRC-CNRC, Canada	1.23 µg/L	http://inms-ienm.nrc-cnrc.gc.ca
	W	SLRS-4	NRC-CNRC, Canada	0.67 µg/L	http://inms-ienm.nrc-cnrc.gc.ca
	W	NASS-5	NRC-CNRC, Canada	0.253 µg/L	http://inms-ienm.nrc-cnrc.gc.ca
	W	TM-23.2	NRC-CNRC, Canada	5.3 µg/kg	http://www.comar.bam.de/
	W	TM-24	NRC-CNRC, Canada	3.5 µg/kg	http://www.comar.bam.de/
	W	TM-26.2	NRC-CNRC, Canada	9.9 µg/kg	http://www.comar.bam.de/
	W	TM-27	NRC-CNRC, Canada	2.7 µg/kg	http://www.comar.bam.de/
	W	TM-27.2	NRC-CNRC, Canada	2.5 µg/kg	http://www.comar.bam.de/
	W	TM-28	NRC-CNRC, Canada	19.3 µg/kg	http://www.comar.bam.de/
	W	TMRAIN-51.2	NRC-CNRC, Canada	66.7 µg/kg	http://www.comar.bam.de/
	W	TMRAIN-52.2	NRC-CNRC, Canada	268 µg/kg	http://www.comar.bam.de/
	W	TMRAIN-53.2	NRC-CNRC, Canada	319 µg/kg	http://www.comar.bam.de/
	W	TMRAIN-54.2	NRC-CNRC, Canada	325 µg/kg	http://www.comar.bam.de/
	W	TMRAIN-95	NRC-CNRC, Canada	0.80 µg/kg	http://www.comar.bam.de/
	S	SRM-1944	NIST	76.1 mg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	S	SRM-2702	NIST	75.4 mg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	S	GBW-07314	NRC-CNRC, China	34.3 µg/g	http://www.comar.bam.de/
	S	HISS-1	NRC-CNRC, Canada	2.16 mg/kg	http://inms-ienm.nrc-cnrc.gc.ca
	S	IAEA-SL-1	IAEA, Austria	44.9 mg/kg	http://www.comar.bam.de/
	S	MESS-3	NRC-CNRC, Canada	46.9 mg/kg	http://inms-ienm.nrc-cnrc.gc.ca
	S	NIES-2	NIES, Japan	40 µg/g	http://www.comar.bam.de/
	S	PACS-2	NRC-CNRC, Canada	39.5 mg/kg	http://inms-ienm.nrc-cnrc.gc.ca
	S	WQB-3	NRC-CNRC, Canada	52.0 µg/g	http://www.comar.bam.de/
	A	DOLT-3	NRC-CNRC, Canada	2.72 mg/kg	http://inms-ienm.nrc-cnrc.gc.ca
	A	DORM-2	NRC-CNRC, Canada	19.4 mg/kg	http://inms-ienm.nrc-cnrc.gc.ca
A	LUTS-1	NRC-CNRC, Canada	0.2 mg/kg	http://inms-ienm.nrc-cnrc.gc.ca	
A	TORT-2	NRC-CNRC, Canada	2.50 mg/kg	http://inms-ienm.nrc-cnrc.gc.ca	
A	GBW-08571	Institute of Environmental Chemistry, China	1.03 µg/g	http://www.comar.bam.de/	
A	BCR-414	EC-JRC-IRMM	18.8 mg/kg	http://www.irmm.jrc.be/html/reference_materials_catalogue/index.htm	
A	SRM-2977	NIST	6.06 mg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm	
A	LGC-7160	LGC-Promochem	0.23 mg/kg	http://www.comar.bam.de/	
Pentachlorobenzene	S	EC-2	National Water Research Institute, Canada	48.6 µg/kg	http://www.comar.bam.de
	S	EC-3	National Water Research Institute, Canada	65 µg/g	http://www.comar.bam.de
	S	EC-8	National Water Research Institute, Canada	30 µg/kg	http://www.comar.bam.de
Pentachlorophenol	S	BCR-530	EC-JRC-IRMM	0.47 mg/kg	http://www.irmm.jrc.be/html/reference_materials_catalogue/index.htm
PAHs benzo[a]pyrene	S	BCR-535	EC-JRC-IRMM	1.16 mg/kg	http://www.irmm.jrc.be/html/reference_materials_catalogue/index.htm
	S	EC-1	National Water Research Institute, Canada	5.3 µg/g	http://www.comar.bam.de
	S	EC-2	National Water Research Institute, Canada	1.21 µg/g	http://www.comar.bam.de
	S	EC-3	National Water Research Institute, Canada	386 µg/g	http://www.comar.bam.de
	S	EC-5	National Water Research Institute, Canada	449 µg/kg	http://www.comar.bam.de/
	S	EC-8	National Water Research Institute, Canada	207 µg/kg	http://www.comar.bam.de
	S	IAEA-383	IAEA Analytical Quality Control Services	0.12 mg/kg	http://www.comar.bam.de
	S	IAEA-408	IAEA Analytical Quality Control Services	0.048 mg/kg	http://www.comar.bam.de
	S	IAEA-417	IAEA Analytical Quality Control Services	2800 ng/g	http://www.comar.bam.de
	S	HS-3B	NRC-CNRC, Canada	5.80 µg/g	http://www.comar.bam.de
	S	HS-4B	NRC-CNRC, Canada	1.55 µg/g	http://www.comar.bam.de
	S	HS-5	NRC-CNRC, Canada	1.7 µg/g	http://www.comar.bam.de
	S	HS-6	NRC-CNRC, Canada	2.2 µg/g	http://www.comar.bam.de
S	SRM-1941b	NIST	358 µg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm	

Priority substance	Matrix	CRM-Identifier	Producer	Certified value	Reference
	S	SRM-1944	NIST	4.30 mg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	A	IAEA-140/OC	IAEA Analytical Quality Control Services	0.02 mg/kg	http://www.comar.bam.de
	A	IAEA-432	IAEA Analytical Quality Control Services	0.9 ng/g	http://www.comar.bam.de
	A	SRM-2977	NIST	8.35 µg/g	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	A	SRM-1974b	NIST	2.80 µg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
fluoranthene	S	EC-1	National Water Research Institute, Canada	23.2 µg/g	http://www.comar.bam.de
	S	EC-2	National Water Research Institute, Canada	3.55 µg/g	http://www.comar.bam.de
	S	EC-3	National Water Research Institute, Canada	558 µg/g	http://www.comar.bam.de
	S	EC-8	National Water Research Institute, Canada	462 µg/kg	http://www.comar.bam.de
	S	HS-3B	NRC-CNRC, Canada	25.33 µg/g	http://www.comar.bam.de
	S	HS-4B	NRC-CNRC, Canada	3.33 µg/g	http://www.comar.bam.de
	S	HS-5	NRC-CNRC, Canada	8.4 µg/g	http://www.comar.bam.de
	S	HS-6	NRC-CNRC, Canada	3.54 µg/g	http://www.comar.bam.de
	S	IAEA-383	IAEA Analytical Quality Control Services	0.29 mg/kg	http://www.comar.bam.de
	S	IAEA-408	IAEA Analytical Quality Control Services	0.084 mg/kg	http://www.comar.bam.de
	S	SRM-1941b	NIST	651 µg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	S	SRM-1944	NIST	8.92 mg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	A	IAEA-140/OC	IAEA Analytical Quality Control Services	0.088 mg/kg	http://www.comar.bam.de
	A	IAEA-432	IAEA Analytical Quality Control Services	12 ng/g	http://www.comar.bam.de
A	SRM-1974b	NIST	17.1 µg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm	
A	SRM-2977	NIST	38.7 µg/g	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm	
benzo[<i>b</i>]fluoranthene	S	BCR-535	EC-JRC-IRMM	2.29 mg/kg	http://www.irmm.jrc.be/html/reference_materials_catalogue/index.htm
	S	IAEA-383	IAEA Analytical Quality Control Services	0.15 mg/kg	http://www.comar.bam.de
	S	IAEA-408	IAEA Analytical Quality Control Services	0.046 mg/kg	http://www.comar.bam.de
	S	IAEA-417	IAEA Analytical Quality Control Services	4100 ng/g	http://www.comar.bam.de
	S	SRM-1941b	NIST	453 µg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	S	SRM-1944	NIST	3.87 mg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	S	EC-8	National Water Research Institute, Canada	208 µg/kg	http://www.comar.bam.de
	S	EC-1	National Water Research Institute, Canada	7.9 µg/g	http://www.comar.bam.de
	S	EC-2	National Water Research Institute, Canada	2.48 µg/g	http://www.comar.bam.de
	S	HS-5	NRC-CNRC, Canada	2.0 µg/g	http://www.comar.bam.de
	S	HS-6	NRC-CNRC, Canada	2.8 µg/g	http://www.comar.bam.de
	A	IAEA-432	IAEA Analytical Quality Control Services	4.8 ng/g	http://www.comar.bam.de
	A	SRM-1974b	NIST	6.46 µg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	A	SRM-2977	NIST	11.01 µg/g	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
benzo[<i>k</i>]fluoranthene	S	BCR-535	EC-JRC-IRMM	1.09 mg/kg	http://www.irmm.jrc.be/html/reference_materials_catalogue/index.htm
	S	IAEA-383	IAEA Analytical Quality Control Services	0.073 mg/kg	http://www.comar.bam.de
	S	IAEA-408	IAEA Analytical Quality Control Services	0.046 mg/kg	http://www.comar.bam.de
	S	IAEA-417	IAEA Analytical Quality Control Services	2000 ng/g	http://www.comar.bam.de
	S	SRM-1941b	NIST	225 µg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	S	EC-8	National Water Research Institute, Canada	294 µg/kg	http://www.comar.bam.de
	S	EC-1	National Water Research Institute, Canada	4.4 µg/g	http://www.comar.bam.de
	S	EC-2	National Water Research Institute, Canada	1.93 µg/g	http://www.comar.bam.de
	S	HS-5	NRC-CNRC, Canada	1.0 µg/g	http://www.comar.bam.de
	S	HS-6	NRC-CNRC, Canada	1.43 µg/g	http://www.comar.bam.de
	S	SRM-1944	NIST	2.30 mg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	A	IAEA-432	IAEA Analytical Quality Control Services	1.9 ng/g	http://www.comar.bam.de
	A	SRM-1974b	NIST	3.16 µg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	indeno[1,2,3- <i>cd</i>]pyrene	S	BCR-535	EC-JRC-IRMM	1.56 mg/kg
S		EC-1	National Water Research Institute, Canada	5.7 µg/g	http://www.comar.bam.de
S		EC-2	National Water Research Institute, Canada	1.55 µg/g	http://www.comar.bam.de
S		EC-8	National Water Research Institute, Canada	34 µg/kg	http://www.comar.bam.de
S		IAEA-417	IAEA Analytical Quality Control Services	2700 ng/g	http://www.comar.bam.de
S		HS-5	NRC-CNRC, Canada	1.3 µg/g	http://www.comar.bam.de

Priority substance	Matrix	CRM-Identifier	Producer	Certified value	Reference
	S	HS-6	NRC-CNRC, Canada	1.95 µg/g	http://www.comar.bam.de
	S	SRM-1941b	NIST	341 µg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	S	SRM-1944	NIST	2.78 mg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	A	IAEA-140/OC	IAEA Analytical Quality Control Services	0.033 mg/kg	http://www.comar.bam.de
	A	SRM-1974b	NIST	2.14 µg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	A	SRM-2977	NIST	4.84 µg/g	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
benzo[<i>g,h,i</i>]perylene	S	EC-1	National Water Research Institute, Canada	4.9 µg/g	http://www.comar.bam.de
	S	EC-2	National Water Research Institute, Canada	1.47 µg/g	http://www.comar.bam.de
	S	EC-8	National Water Research Institute, Canada	176 µg/kg	http://www.comar.bam.de
	S	IAEA-383	IAEA Analytical Quality Control Services	0.19 mg/kg	http://www.comar.bam.de
	S	IAEA-408	IAEA Analytical Quality Control Services	0.038 mg/kg	http://www.comar.bam.de
	S	IAEA-417	IAEA Analytical Quality Control Services	2300 ng/g	http://www.comar.bam.de
	S	HS-3B	NRC-CNRC, Canada	3.88 µg/g	http://www.comar.bam.de
	S	HS-4B	NRC-CNRC, Canada	1.23 µg/g	http://www.comar.bam.de
	S	HS-5	NRC-CNRC, Canada	1.3 µg/g	http://www.comar.bam.de
	S	HS-6	NRC-CNRC, Canada	1.78 µg/g	http://www.comar.bam.de
	S	SRM-1941b	NIST	307 µg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	S	SRM-1944	NIST	2.84 mg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	A	SRM-1974b	NIST	3.12 µg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	A	SRM-2977	NIST	9.53 µg/g	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
A	IAEA-140/OC	IAEA Analytical Quality Control Services	0.02 mg/kg	http://www.comar.bam.de	
Tributyltin compounds	S	BCR-462	EC-JRC-IRMM	54 ug/kg	http://www.irmm.jrc.be/html/reference_materials_catalogue/index.htm
	S	BCR-646	EC-JRC-IRMM	480 µg/kg	http://www.irmm.jrc.be/html/reference_materials_catalogue/index.htm
	S	HIP-1	NRC-CNRC, Canada	78 ng/g	http://inms-ienm.nrc-cnrc.gc.ca
	S	PACS-1	NRC-CNRC, Canada	890 ng/g	http://inms-ienm.nrc-cnrc.gc.ca
	S	PACS-2	NRC-CNRC, Canada	0.890 mg/kg (Tri-)	http://inms-ienm.nrc-cnrc.gc.ca
	S	SOPH-1	NRC-CNRC, Canada	125 ng/g	http://inms-ienm.nrc-cnrc.gc.ca
	A	NIES-11	NIES, Japan	1.3 µg/g	http://www.comar.bam.de/
Trichlorobenzenes (1,2,4-trichlorobenzene)	S	EC-2	National Water Research Institute, Canada	80.7 µg/kg	http://www.comar.bam.de
	S	EC-8	National Water Research Institute, Canada	67 µg/kg	http://www.comar.bam.de

**Table 4: Certified reference materials related to other pollutants
P - Pure compounds or solutions**

Priority substance	Matrix	CRM-Identifier	Producer	Certified value	Reference
DDT p,p'-DDT	P	SRM 1492	NIST	302 µg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	P	SRM 2261	NIST	3.004 mg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	P	SRM 2273	NIST	2.862 mg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	P	SRM 2275	NIST		http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
Dieldrin	P	SRM 1492	NIST	307 µg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	P	SRM 2261	NIST	3.012 mg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
Endrin	P	SRM 2275	NIST	2.908 mg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
Carbontetrachloride	P	SRM 3006	NIST	0.010099 g/g	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
Tetrachloroethylene	P	SRM 3010	NIST	0.009772 g/g	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm

**Table 5: Certified reference materials related to other pollutants
Matrix: S – Sediment; W – Water; A – Aquatic plant or animal**

Priority substance	Matrix	CRM-Identifier	Producer	Certified value	Reference
DDT p,p'-DDT	S	IAEA-408	IAEA Analytical Quality Control Services	0.0014 mg/kg	http://www.comar.bam.de
	S	SRM-1944	NIST	199 µg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	A	SRM-1974b	NIST	3.91 µg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	A	IAEA-140/OC	IAEA Analytical Quality Control Services	0.0022 mg/kg	http://www.comar.bam.de
	A	SRM-1945	NIST	245 µg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	A	SRM-1946	NIST	37.2 µg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	A	SRM-1588b	NIST	570 µg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	A	SRM-2977	NIST	1.28 mg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	A	BCR-598	EC-JRC-IRMM	179 µg/kg	http://www.irmm.jrc.be/html/reference_materials_catalogue/index.htm
Dieldrin	S	IAEA-408	IAEA Analytical Quality Control Services	0.0003 mg/kg	http://www.comar.bam.de
	A	IAEA-140/OC	IAEA Analytical Quality Control Services	0.0017 mg/kg	http://www.comar.bam.de
	A	SRM-1588b	NIST	156 µg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	A	SRM-2977	NIST	6.04 mg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	A	BCR-598	EC-JRC-IRMM	59 µg/kg	http://www.irmm.jrc.be/html/reference_materials_catalogue/index.htm

ANNEX IV: Case Studies

Background information
<p>Title/Name of case study: Pesticides in Surface Water Bodies from Agricultural Sources (Pesticide Program).</p>
<p>Type of case study: Monitoring to check the chemical and ecological status compliance (operational and investigative monitoring).</p>
<p>Reporting Institution: Ministry of the Environment (Spain).</p>
<p>Web-Link: www.mma.es</p>
<p>Main sources for further information; literature: <i>Analysis of pesticides and metabolites in Spanish surface waters by isotope dilution gas chromatography/mass spectrometry with previous automated solid-phase extraction. Estimation of the uncertainty of the analytical results.</i> Planas et al. Journal of Chromatography A, 1131 (2006) 242-252.</p>
<p>Objective of case study - background information: Development of the methodology for monitoring the pollution caused by pesticides from agricultural sources. Analysing pesticides is necessary to check the good chemical and ecological status compliance. The pesticides included in the monitoring program must be all the priority substances discharged and “other pesticides” discharged in significant quantities. It is not easy to select the “other pesticides” to analyse due to high number of possible compounds, changes in pesticides use, pesticide fate, etc. To solve this, the surveillance of pesticide pollution from agricultural activities may combine 2 types of analytical methodologies. Type 1: Standardized techniques with high level of QA/QC to monitor EQS compliance (legally binding EQSs or calculated EQSs). Type 2: MS characterization to determine new pesticides not included in common lists in order to incorporate them in the selected compounds to monitor in the future. This combined methodology is used to monitor pesticides in water bodies potentially at risk of failing to meet the pesticides EQS due to pressure from agricultural sources.</p>
Contribution to...
<p>Specific contribution linked to WFD monitoring programmes Operational and investigative monitoring design.</p>
<p>Description <i>Monitoring points:</i> water bodies potentially at risk of pesticides pollution from agricultural sources. <i>Matrix:</i> Water <i>Frequency:</i> 8 sampling/year <i>Methodology and substances</i> Using Isotope dilution GC/MS with previous automated SPE 10 pesticides from Priority Substances List , 04 pesticides from List II with national legally binding EQSs 05 metabolite pesticides 13 pesticides commonly used or detected in waters Using MS characterization of the all the pollutants present in the sample Unknown pesticide presents in the sample</p>

Experiences gained - Conclusions - Recommendations**Experience gained:**

Determination of the level of pollution from pesticides of water bodies at risk due to agricultural pressures.
Development of a Methodology with high QA/QC data.
Determination of new pollutants to be included in the Pesticides Program.

Conclusion:

A method based on isotope dilution GC/MS with automated SPE extraction was developed for the analysis of 32 pesticides and metabolites in surface water samples. Trueness was in the range 80-120% for 29 pesticides, precision below 15% for 25 compounds, method detection limit ranged from 1 to 9 ng/g and expanded uncertainties were < 40% for 24 pesticides.

93 Spanish surface water samples collected during summer and autumn 2004. Highest concentration and occurrence were found for atrazine, simazine, alachlor, terbutylazine and metoachlor included in the Priority List and/or Spanish Relevant List.

New pesticides were detected using MS characterization technique, the pollutant molinate and imazalil and are included in the future pesticide program.

Pesticides concentrations and occurrence are higher in the summer than in the autumn period. In summer, four pesticides were found in more than 50% of the analysed samples and four compounds were detected above the concentration level of 1 µg/l (atrazine, terbutylazine, 3,4-dichloroaniline and fenitrothion), while in autumn percentage of detection was bellow 50% for all pesticides, only one compound (terbutylazine) exceeded 1 µg/l.

Recommendations:

The surveillance of pesticides in water from agricultural activities needs the combination of 2 types of techniques. Standardized analytical methods with a high level of QA/QC to monitor specific pesticides, at least all the pollutants included in the Priority List and/or other National Relevant List in order to monitor the EQS compliance, and hence Chemical status. And the application of screening techniques to detect new pesticides from diffuse sources not included in common Lists in order to monitor ecological status compliance.

Outlook - Next steps – Accessibility of results/information

Background information
<p>Title/Name of case study:</p> <p>Conversion of pollutant concentrations measured in suspended particulate matter (SPM) into total concentrations in the whole water sample.</p>
<p>Type of case study:</p> <p>Routine operation since 1990 in the water quality monitoring program of the international Rhine Commission (ICPR) for compliance checking of annual data of lipophilic pollutants with water quality targets.</p>
<p>Reporting Institution:</p> <p>International Commission for the Protection of the Rhine (ICPR)</p>
<p>Web-Link:</p> <p>http://www.iksr.de/fileadmin/user_upload/Dokumente/Berichte/IKSR_Bericht_Nr_143d.pdf</p>
<p>Objective of case study - background information –</p> <p>In surface waters a number of the priority substances are adsorbed to SPM from 50 close to 100 percent. The water quality targets of the ICPR (analogous the EQS) for organic priority substances are expressed as total concentrations, that is the dissolved portion plus adsorbed portion of the substance in the whole water sample. For some organic priority substances the AA-EQS are very low, and the respective detection limits of the recommended analytical methods are insufficient. The objective is to support compliance checking with whole water EQS (or ICPR water quality targets) by conversion of SPM determinand concentration.</p>
<p>Contribution to <u>support</u> compliance checking with EQS</p>
<p>Specific contribution linked to WFD monitoring programmes</p> <p>Surveillance monitoring design; specific monitoring of pollutants adsorbed to suspended particulate matter; compliance checking of SPM determinand concentration with whole water EQS.</p>
<p>Characterisation</p> <p>For organic micropollutants like PCB, TBT, PAH or hexachlorobenzene, the ICPR had developed water quality targets for whole water. For reasons of the analytical method, surveillance of the quality targets was performed by sampling and analyzing these pollutants in suspended particles. Sampling by centrifuge allows collecting the suspended material from several 1,000 litres of water within a few hours. Thus, a sufficient amount of SPM can be gained for chemical analysis, what corresponds to an enrichment from several 100 (or 1,000) litres of water. The amount of water centrifuged is recorded.</p> <p>Course of procedure:</p> <p>The concentration of contaminants is determined in µg/kg dw and converted to whole water by means of the SPM content (in mg/L):</p> $C_{Ti} = (S_i \times C_{si}) \times 10^{-6}$ <p> C_{Ti} = total contaminant content on the day of sampling in µg/L S_i = SPM content on the day of sampling in mg/L C_{si} = contaminant content in SPM on the day of sampling in µg/kg. </p> <p>This applies to substances that are adsorbed at SPM by more than 90 %. For substances that are adsorbed by 50 % at SPM, the value is multiplied by the factor 2:</p> $C_{Ti} = 2 (S_i \times C_{si}) \times 10^{-6}$

Other factors might be selected for a particular substance, if the partition coefficient is known.

The mean value (50- or 90-percentile in ICPR procedure) is calculated from the C_{Ti} values. Values below the limit of detection (limit of quantification) are included in the mean-value calculation (arithmetic mean) by the numerical value of the limit of detection. Then, the value of the arithmetic mean is indicated as “less than”.

Experiences gained - Conclusions - Recommendations

Experience gained:

The ICPR member states have successfully applied this method at selected sampling sites since 1990. The error that results from the arbitrary definition of the conversion factor for adsorption between 50 and 90 percent is negligible against the other errors in trace analyses. But for EQS compliance checking procedure it is possible to define the adsorbed portion for each priority substance in 10-percent steps (50, 60, 70, 80, 90 or 100 percent).

Conclusion:

The collection of the SPM from several 100 (or 1,000) litres of surface water allows the compliance checking of the EQS for priority substances, which are partially or not dissolved in the water because of their hydrophobic and lipophilic properties. Sampling by centrifuge is time- and labour-intensive and should be applied in surveillance monitoring only at selected sampling sites at large rivers. But it is no problem to meet the minimum performance criteria for the quality of analytical results – also for low EQS values (e.g. tributyl tin). The results of the contaminant concentrations in SPM can be used for comparisons with the EQS, and - after a hydrological interpretation - they are also suitable for trend analyses.

Recommendations:

- For selected priority substances and for selected monitoring sites at large rivers the described procedure is suitable for compliance checking with EQS and for trend analyses. Special attention should be given to the following micropollutants: Pentabromodiphenylether, C10-13 chloroalkanes, Fluoranthene, Hexachlorobenzene, Pentachlorobenzene, PAH (Benzo(a)pyrene, Benzo(b)fluoranthene, Benzo(k)fluoranthene, Benzo(g,h,i)perylene, Indeno(1,2,3-cd)pyrene), Tributyltin and Trifluralin.
- the result of each measurement (spot sample) is converted into the total determinand concentration by means of the SPM content of the water and according to the percent factor of the adsorbed portion of contaminants;
- No further effort is necessary for analytical techniques to obtain a limit of quantification half of the EQS.

Outlook - Next steps – Accessibility of results/information

Background information
<p>Title/Name of case study: Comments Concerning the National Swedish Contaminant Monitoring Programme in Marine Biota</p>
<p>Type of case study: Monitoring activities within the Swedish contaminant programme in marine biota</p>
<p>Reporting Institution: Environmental Protection Agency (Sweden)</p>
<p>Web-Link: www.naturvardsverket.se</p>
<p>Main sources for further information; literature: Comments Concerning the National Swedish Contaminant Monitoring Programme in Marine Biota, 2006</p>
<p>Objective of case study - background information: The data of concern in this report represent the bioavailable part of the investigated contaminants i.e. the part that has virtually passed through the biological membranes and may cause biological effects. The main objectives of the monitoring program in marine biota could be summarised as follows:</p> <ul style="list-style-type: none"> - to estimate the levels and the normal variation of various contaminants in marine biota from several representative sites, uninfluenced by local sources, along the Swedish coasts. The goal is to describe the general contaminant status and to serve as reference values for regional and local monitoring programmes - to monitor long term time trends and to estimate the rate of found changes. - to estimate the response in marine biota of measures taken to reduce the discharges of various contaminants - to detect incidents of regional influence or widespread incidents of 'Chernobyl'- character and to act as watchdog monitoring to detect renewed usage of banned contaminants. - to indicate large scale spatial differences - to explore the development and regional differences of the composition and pattern of e.g. PCB's, HCH's and DDT's as well as the ratios between various contaminants.
Contribution to...
<p>Specific contribution linked to WFD monitoring programmes Surveillance monitoring design and operational monitoring design as soon as EQS are developed for biota.</p>
<p>Description <u>Substances monitored:</u> Metals, for example Hg, Cd, Pb and Cu and organic substances, for example PCB, DDT, Lindane, brominated flameretardants and dioxins.</p> <p><u>Sampling area:</u> The sampling sites are located in areas regarded as locally uncontaminated and, as much as possible, uninfluenced by major river outlets or ferry routes and not too close to heavy populated areas.</p> <p><u>Collected specimens:</u> For many species adult specimens are less stationary than sub-adults. To increase comparability between years, young specimens are generally collected. Only healthy looking specimens with undamaged skin are selected. The collected specimens are placed individually in polyethene plastic bags, deep frozen as soon as possible and transported to the sample preparation laboratory.</p>

Number of samples and frequency: In general 20 individual specimens from the Baltic sites (reported to HELCOM) and 25 from the Swedish westcoast sites (reported to OSPARCOM) are analysed annually from each site/species. For guillemot eggs and perch, 10 individual specimens are analysed. Organochlorines in blue mussels are analysed in pooled samples containing about 50 individual specimens in each pool. Since 1996, samples from 12 individual specimens are analysed which is proposed in the revised guidelines for HELCOM and OSPARCOM.

Experience gained:

Continuous development of design for both a spatial and temporal monitoring programme and also increased knowledge of choice of matrix. The importance of quantifying objectives.

Conclusion:

Herring is the most commonly used indicator species for monitoring contaminants in biota within the BMP (Baltic Monitoring Programme) in the HELCOM convention area and is sampled by Finland, Estonia, Poland and Sweden. Herring muscle tissue is fat and thus very appropriate for analysis of fat-soluble contaminants i.e. hydrocarbons.

Cod is among the ‘first choice species’ recommended within the JAMP (Joint Assessment and Monitoring Programme) and BMP (Baltic Monitoring Programme). The cod liver is fat and organic contaminants are often found in relatively high concentrations. For that reason, it is also a very appropriate matrix for screening for ‘new’ contaminants.

Mussels are one of the most common used organisms for monitoring contaminants in biota. Adult mussels are sessile and hence it is easier to define the area the samples represent, compared to fish.

Blue mussel is among the ‘first choice species’ recommended within the JAMP (Joint Assessment and Monitoring Programme).

Recommendations:

It is very important that the objectives of the monitoring are quantified before designing a monitoring programme. When the objectives are defined the choice of sampling location, matrix, sampling method and analytical procedure could cause problems if the proper guidelines are not followed.

Outlook - Next steps – Accessibility of results/information

Background information
Title/Name of case study: Screening of Industrial and Consumer Chemicals in Finland (VESKA 1)
Type of case study: Screening to select sites and substances for surveillance monitoring of WFD
Reporting Institution: Finnish Environment Institute SYKE
Web-Link: http://www.ymparisto.fi
Main sources for further information; literature:
Objectives of case study: To study the occurrence and concentrations of the substances chosen by risk assessment in the aquatic environment close to emission sources To produce information for the purpose of emission source identification. To develop the analytics used to examine harmful substances and to build up cooperation network between laboratories. To develop a risk assessment method that can be used to estimate the circulation of the studied compounds in nature and to minimize the expenses needed for their monitoring. To set a criterion that could be used to preclude or add substances to a more detailed monitoring plan.
Contribution to...
Specific contribution linked to WFD monitoring programmes Supply data for national surveillance monitoring programme 2006-2008
Description The study was carried out in the vicinity of twelve industrialized cities in Finland, in water systems downstream municipal sewage treatment plants. Concentrations were measured in sludge and waste water samples (1-3 occasions) and surface water (1-3 occasions), sediment (once, surface 2-3 cm) and fish (4-10 specimen pooled, Northern pike, <i>Esox lucius</i>) muscle samples. Organotin compounds (both butyl and phenyl –forms) were found in all matrices, often exceeding EQS or "benchmark" values. This will trigger more research, monitoring and management activities MBT and DBT were found in sediments also below inland sewage treatment plants, indicating sources other than antifouling paints (stabilizer in plastics). TPhT indicated bioaccumulation: found less than TBT in sediments but more in fish Alkylphenols, phthalates, organotin compounds, HCH, HCB and VOC-compounds were found in treated sewage water. Out of these, only DEHP and alkylphenols were found in excess of surface water EQS proposals. In surface waters, only nonylphenol ethoxylates were found at the (national) EQS-level. Several substances were not detected (other alkylphenols, chlorobenzenes and volatile organic compounds). PAHs, PBDE, organotins and phthalates were, however, not measured in surface water phase. In sediments, organotins, PAHs, HCHs and dibutylphthalate were most commonly found.
Experience gained:

Conclusion:

Simultaneous screening of several substance groups might not be cost-efficient for industrial and household chemicals with several, poorly known sources.

On national level, surveillance monitoring will be started for alkylphenols, phthalates and PAHs in water (10 sites/year). First year (mid 2007- mid 2008) results will determine the need of continuation (rotation, cessation). Sediment and biota monitoring continues (5-15 sites, 2-6 yr rotation) for lipophilic substances.

Recommendations:

In addition to analytical problems at low concentrations, natural conditions in Northern Europe (lake-richness, low temperature, low particulate matter, low degradation, low population/water volume) would favour sediment and/or biota over water, in monitoring many industrial and household chemicals presently on the Priority Substances list (e.g. PBDE, HCB, SCCP, some PAHs, DEHP, TBT).

Effect-based monitoring should be developed and brought into the guidance for impact monitoring locations.

Outlook - Next steps – Accessibility of results/information

New groups of substances will be screened in sewage effluents and waste deposit leachates. The impact monitoring of selected compounds will start gradually along source identification and the renewal process of the permissions (industrial and municipal STPs) with statutory monitoring.

Background information
Title/Name of case study: Pesticide Screening in Finnish Surface Waters (VESKA 2)
Type of case study: Screening to select sites and substances for surveillance monitoring of WFD
Reporting Institution: Finnish Environment Institute (SYKE)
Web-Link: http://www.ymparisto.fi/download.asp?contentid=49817&lan=EN
Main sources for further information; literature:
Objectives of case study: To study the occurrence and concentrations of agricultural pesticides in Finnish surface waters. To produce information for identification of emission source. To develop a risk assessment method that can be used to minimize the expenses of later monitoring.
Contribution to...
Specific contribution linked to WFD monitoring programmes Supply data for national surveillance monitoring programme 2006-2008
Description <i>Monitoring points:</i> water bodies (streams and rivers) potentially at risk of pesticide pollution from agricultural sources <i>Matrix:</i> surface water and the top of bottom sediment (0-1 cm) <i>Duration:</i> 2004 - 2005 <i>Frequency</i> <ul style="list-style-type: none"> - at one intensive site: weekly (May-Oct 2004) + monthly in winter (2004-2005) - intermediate sites: monthly (Apr/May-Sep/Oct) - areal screening sites: twice (Jun/Jul + Jul/Aug in 2005). <i>Analysed substance:</i> <ul style="list-style-type: none"> - 100 compounds from water samples using multi-residue methods (GC-MS and LC-MS-MS) (including all pesticides in the EU Priority list and four of the six pesticides in the national list of pesticides) - Tribenuronmethyl (a low-dose herbicide in the national list) from part of water samples using a specific analysing method - The 14 pesticides analysed from sediment samples were selected basing on partitioning coefficients (from the EU and national lists of priority substances and other potential pesticides). <i>Number of samples:</i> 190 water samples + 31 sediment samples The study was carried out in two parts. The objective of the pilot year 2004 was to find the best timing for surface water sampling and to assist in the selection of the sampling sites for a survey for following year. In the second year (2005) the main objective was areal representativeness, but most of the sites were sampled only twice at the time of expected high concentrations. In 2004 the focus was in upstream sites (catchment areas: 1-100 km ²) close to fields. Surface water was collected in an intensive site and in 6 other agricultural streams. Additional samples were collected once from 6 rivers (Sep/Oct). The pilot year indicated that agricultural land use percent was more important factor to explain pesticide detections than catchment area. In 2005, sampling sites were selected from watershed register using agricultural land use percent as the

main criterion: 35 agricultural sites and five reference sites from non-agricultural areas (catchment areas of the sampling points: .50 - 37 000 km²). In addition, six rivers and two of the smaller streams sampled during the pilot year were sampled monthly (May-Oct) in 2005.

Pesticides in water samples (70 (in 2004) + 120 (in 2005) + quality assurance samples):

The number of different pesticides detected was 24 in 2004 and 46 in 2005. Detected concentrations were mainly low (traces). In 2005, one or more herbicides were detected in 90% of water samples. Phenoxy acid herbicides were most frequently found compounds. This may be explained by the volume of their use in Finland. Only following few exceedings of EQS values were observed during the screening, although the sampling was focused in the expected concentration peaks and in the areas of high pesticide loadings:

- Endosulfansulphate was detected in one site (3 detections /3 sampling times) (max 0.02 µg/l = quantification limit), while suggested EQS-value is 0.005 µg/l.
- The detected peaks of MCPA concentration exceed national EQS value (1.6 µg/l) in several sites (max 8.8 µg/l), but concentrations were still lower than MacQS (15 µg/l).
- In single samples the concentrations of low-dose herbicides (thifensulfuronmethyl, tribenuronmethyl) were higher than Swedish "target values". However, the Finnish national EQS of tribenuronmethyl was not exceeded.
- Insecticides were detected seldom, which is inline with the sold amounts of them. Pirimicarb was found in one site and its concentration was higher than Norwegian limit value.

Pesticides in sediment samples (31 + a parallel sample):

In 2005, the top of bottom sediment (in all sites where possible) was sampled and 14 substances were analysed and 6 detected from sediment samples. Atrazine (forbidden in 1991) was detected in more than half of the sediment samples, prochloraz in every third sample, and the others in single samples. Currently there are no confirmed sediment EQS values for pesticides, but the earlier proposed values were exceeded in case of atrazine, prochloraz, endosulfan and its metabolite endosulfansulphate.

Conclusion:

Simultaneous screening of several substances was cost-efficient for pesticides. High number of different pesticide compounds, mainly herbicides and their metabolites were detected. Concentrations exceeded seldom levels of potential environmental threat.

The time and site of sampling have significant effects on the results. No watershed specific information about pesticide usage is available. Agricultural land use percent was a good tool in selecting sampling sites, but further information about the type of agriculture (e.g. typical crops) would help in finding the risky sites.

The intensive agricultural land use fraction is usually rather low in big Finnish catchments and pesticides are diluted in water from non-agricultural areas in big rivers while pesticides may occasionally pose local problems in some small streams close to fields.

Outlook - Next steps – Accessibility of results/information

For year 2007 the statutory pesticide monitoring is planned to be performed in 8 rivers and in one stream (10-12 samples/site). Later (in 2008-) it will be reasonable to include some upstream sites to monitoring program.

Background information
<p>Title/Name of case study: French National Monitoring Network (RNO) Réseau National d'Observation de la qualité du milieu marin</p>
<p>Type of case study: A 30 years Chemical monitoring network (surveillance and operational monitoring)</p>
<p>Reporting Institution: IFREMER (Institut français de recherche pour l'exploitation de la mer) French Research Institute for Exploitation of the Sea</p>
<p>Web-Link: www.ifremer.fr and www.ifremer.fr/envlit/surveillance/rno.htm</p>
<p>Main sources for further information; literature: Annual bulletin may be downloaded at : www.ifremer.fr/envlit/surveillance/rnopublis.htm</p>
<p>Objective of case study - background information:</p> <ol style="list-style-type: none"> 1. Assessment of the levels and trends of the chemical contamination of the French coastal seas. 2. To meet OSPAR and Barcelona Conventions monitoring obligations
Contribution to...
<p>Specific contribution linked to WFD monitoring programmes Surveillance and Operational Monitoring</p>
<p>Description</p> <p>Chemical contaminants monitored :</p> <ul style="list-style-type: none"> - metals : Ag, Cd, Cr, Cu, Hg, Ni, Pb, V, Zn - organochlorinated compounds: DDT compounds, HCH isomers, PCB congeners - PAH's : 16 US-EPA PAH's and some alkylated PAH's <p>Strategy of monitoring :</p> <p>The RNO is largely based on bivalve molluscs (mussels and oysters) which are used as quantitative indicators of contamination. Some 90 sampling points are sampled twice a year for metals and once a year for organic contaminants. Analyses are carried out at a single laboratory, the Ifremer Center of Nantes. An aliquot of the samples is systematically archived for possible controls at a later date or the retrospective search of other contaminants (the bank contains more than 8000 samples, since 1981).</p> <p>The contaminants are also measured in the sediments. The first centimetre of the surface sediments can integrate several years of contamination. A yearly sampling cruise is carried on 1/10 of the French maritime frontage, the whole French littoral being covered every 10 years. The contaminants measured are the same than in biota, in addition to descriptive and normalization parameters (grain size, organic carbon, carbonates, aluminium, iron, lithium and manganese). Some sediment cores are collected to reconstruct the history of the contamination over several decades.</p>
<p>Experience gained:</p> <p>Direct monitoring in water is not used any longer because it is too expensive and not reliable. Indeed, the operational difficulties to collect valid samples (i.e. uncontaminated and representative) for analyses of substances present in water at trace levels are too great. First, collecting uncontaminated samples needs a care difficult to reach in routine monitoring. Secondly, the spatial and temporal representativeness of samples collected in Water Bodies affected by tides and currents, are too low. This is our first-hand</p>

experience of direct measurements of contaminants in water which was carried out between 1979 and 1984 and abandoned for the reasons above. This is coherent with the OSPAR Convention monitoring programme which is also based on biota and sediment.

Conclusion:

To assess the levels of contamination by metals and organic hydrophobic substances, it is highly preferable to use accumulative matrixes that present higher levels and allow temporal integration of the natural water variability.

Recommendations:

Within the frame of the WFD, Surveillance Monitoring should be advantageously carried out in sediments for the metals and hydrophobic substances. One survey by Management Plan (6 years) would be sufficient to assess the quality of the Water Bodies.

Operational Monitoring needs to assess temporal trends of the contamination and should be carried out in biota (mussels as a first choice). One survey per year (synchronous with biological life cycle of the biota) would make possible to evaluate the trends.

Outlook - Next steps – Accessibility of results/information

Ifremer developed a Web site including a broad section devoted to marine monitoring (www.ifremer.fr/envlit/surveillance). It is possible to view and to download the data of contaminants in molluscs for each sampling point.

Background information
<p>Title/Name of case study: What Concentrations of Hazardous Substances Do We Find in the Environment? Results from the Swedish Screening Programme 2003-2004</p>
<p>Type of case study: Screening</p>
<p>Reporting Institution: Environmental Protection Agency (Sweden)</p>
<p>Web-Link: www.naturvardsverket.se</p>
<p>Main sources for further information; literature: What concentrations of hazardous substances do we find in the environment? Results from the Swedish Screening Programme 2003-2004 Report 5524, February 2006.</p>
<p>Objective of case study - background information: For the purpose of obtaining information regarding the concentrations of newly discovered persistent organic pollutants (POPs), as well as other potential problem substances used in society, the national environmental monitoring scheme was supplemented by a screening programme a few years ago. In this programme, one or more selected substances are measured on one or more occasions during a single year and in different media, such as sewage, fish or air. Screening was initiated on a small scale in 1996-97 and has gradually increased in scope since then. The reason for including a substance in the screening programme may be that it is used on a large scale, that it has been prioritized in various international contexts, or that it has attracted national attention for other reasons.</p>
Contribution to...
<p>Specific contribution linked to WFD monitoring programmes Data for substances those are not included in the regular monitoring programme.</p>
<p>Description The screening studies have been modelled on the DPSIR strategy. This strategy analyses environmental problems based on Drivers such as those created by industry, Pressures on the environment such as polluting discharges that harm the State of the environment, which in turn results in an Impact on human health and the environment, whereby we try to find Responses or actions to deal with the problems.</p> <p><i>A screening study consists of the following closely-connected parts:</i> Choice of substance Preparatory theoretical study Measurement study Evaluation</p>
<p>Experience gained: The primary purpose of the screening is not to support research on new POPs, but to comply with requirements on reporting of certain substances in various EU directives and international conventions. Many of these substances are of no relevance for Sweden, and the screening could help to show this so that resources do not have to be wasted on measurement of these substances.</p>

Draw attention to new environmental pollutants. Informing the public without frightening them is important, but perhaps even more important is furnishing data to those who work with chemical risk reduction, i.e. various public authorities.

Conclusion:

Further studies should be made of the following substance groups

Organophosphates

Bisphenol A

α - and β -endosulfan

Siloxanes

Chloro- and bromostyrenes

The following substance group should be subjected to another screening study in a few years

Adipates

The following substance groups do not have to be followed regularly

Chlorinated paraffins

Limonene

Mirex

Isocyanates

Recommendations:

Will be based on the results obtained for each substance/group.

Outlook - Next steps – Accessibility of results/information

Data are available on the Internet from the environmental monitoring scheme's data host for screening.
<http://www.ivl.se/english/ivlstartpage/rightmenu/environmentaldata.4.360a0d56117c51a2d30800064209.html>

Background information
<p>Title/Name of case study: Monitoring Using Passive Sampling Devices to Improve Trace Metal-Related Risk Assessments</p>
<p>Type of case study: Complementary monitoring by <i>in-situ</i> deployment of passive sampling to help reduce the uncertainty associated with infrequent grab sampling for compliance monitoring</p>
<p>Reporting Institution: University of Portsmouth (UK), Bureau de Recherche Géologique et minière (Fr) As part of the EU-funded FP6 project <i>Screening Methods for Water Data information in support of the implementation of the WFD (SWIFT-WFD)</i></p>
<p>Web-Link: none</p>
<p>Main sources for further information; literature: <i>Evaluation of the performance of the Chemcatcher and DGT passive sampling devices for monitoring heavy metals in water</i> Allan IJ, Knutsson J, Guigues N, Mills GA, Fouillac A-M and Greenwood R, (in preparation) (2007)</p>
<p>Objective of case study - background information: Demonstration of the applicability of passive sampling to increase confidence in measures of water quality provided by infrequent spot (bottle) sampling campaigns. Grab or bottle sampling followed by filtration at 0.45µm is to be used for compliance checks (AA-EQS & MAC-EQS). Whilst monthly spot samples provide a precise estimate of concentrations of contaminants at the time of sampling, there is uncertainty concerning conditions prevailing in the periods between sampling events. This is of particular concern where concentrations are known to fluctuate or where there are significant or potential natural or anthropogenic pressures. One possible solution to this problem is to deploy passive samplers to provide time-weighted average (TWA) concentrations of concentrations of contaminants in the period between grab samples. This may confirm or contradict the data from the routine monitoring campaigns, and should help to reduce the possibility of making erroneous decisions in risk assessments required in the implementation of the WFD. In this application the TWA concentrations of metals estimated using DGT and Chemcatcher samplers were compared with estimates based on spot sampling in the Meuse River (Eijsden, The Netherlands). In this trial 2 different grab sampling procedures were used at relatively high frequencies (one to three times per week) and metal analyses conducted in two different laboratories in a pilot-scale inter-organisational comparison that incorporated both the analytical determination and the sampling step.</p>
Contribution to...
<p>Specific contribution linked to WFD monitoring programmes Surveillance and operational monitoring tasks</p>
<p>Description <i>Matrix:</i> Water <i>Passive sampling:</i> Use of the Diffusive Gradient in Thin Film (DGT) and Chemcatcher sampling devices following guidelines provided in the BSI Publicly Available Specification 61, and analysis of sampler extracts by ICP-MS in an university research laboratory. <i>Sampler exposure:</i> Consecutive and/or overlapping 7, 14, 21 and 28 day periods <i>Grab sampling protocol 1:</i> Routine weekly sampling, transport of the sample to the laboratory followed by filtration (0.45 µm) and ICP-MS analysis. <i>Grab sampling protocol 2:</i> Sampling every two or three days, on-site filtration (0.45 µm) and analysis by ICP-OES in an accredited laboratory.</p>

Experience gained:

There was good agreement between the results for cadmium, copper, nickel and zinc provided by the two types of samplers, despite differences in their working principles. High and fluctuating concentrations of cadmium (between proposed MAC-EQS and AA-EQS thresholds) were detected by passive sampling during the first 14 day exposure period. This was confirmed by the relatively high frequency of grab sampling used in this trial, but may have been missed if only conventional sampling rates had been used. Extra information, on speciation of the metals, was provided by the samplers, and this was consistent with predictions obtained using equilibrium speciation modelling with visual MINTEQ (NICA-Donnan model).

Conclusion:

Reliability and consistency of TWA metal concentrations measured by passive sampling were shown when compared with 2 distinct grab sampling protocols in a procedure that included uncertainty both on the sampling and analytical measurement steps. This provided representative information on average concentrations. On the other hand an estimate based on a single grab sample could have provided misleading information since for instance levels of Cd varied over a factor of five during the trial.

Recommendations:

Passive sampling devices should be deployed following BS PAS 61 guidelines and manufacturer's specifications for period up to 14 to 20 days to achieve representative sampling. This should be combined with grab sampling to reduce monitoring uncertainty to manageable levels.

Outlook - Next steps – Accessibility of results/information

These results will be published in detail in a peer-reviewed scientific journal.

A desirable extension of this work would be to increase the duration of the trial to two or three years in order to provide a reliable, long-term comparison between the average concentrations of contaminants estimated by routine grab sampling, and passive sampling. This would establish the utility of the two methods either on their own or in combination to quantify trends in trace metal concentrations over time. Since the two methods measure different (operationally defined, and water body specific) fractions of metals, relationships between the concentrations in filtered bottle samples and those measured by passive samplers need to be established.

Other future developments may include testing and optimising combinations of grab and passive sampling in order to improve sampling representativeness while ensuring a reduction in monitoring costs.

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