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Title: **GUIDANCE ON SURFACE WATER CHEMICAL MONITORING UNDER THE WATER FRAMEWORK DIRECTIVE**

Version no.: 10 (final version) Date: 15 October 2008

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Circulation and received comments:
This document provides the final draft of the guidance, which takes into account the latest comments received from Member States.

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GUIDANCE FOR CHEMICAL MONITORING UNDER THE WATER FRAMEWORK DIRECTIVE

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.

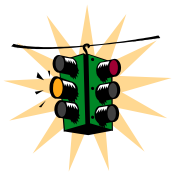
Member States have expressed the need for more guidance on implementation details of the monitoring for chemical substances. In-line with previous documents under the WFD Common Implementation Strategy (WFD CIS) this guidance document has therefore been developed, as mandated through the Chemical Monitoring 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 C[1].

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.

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

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

	**Look out!** Issues of compliance, statistical treatment and reporting of monitoring data are not within the mandate of this guidance document

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 the provisions regarding the monitoring of chemical substances in the surface water are laid down in Article 8 and the Annex V.

	**Look in:** Water Framework Directive 2000/60/EC Article 8 and Annex V *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.*

The Directive sets the Environmental Quality Standards and the basic provisions for compliance checking.

	**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))

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.

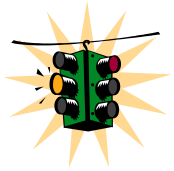
	**Look in:** Guidance document No. 3 - ANALYSIS OF PRESSURES AND IMPACTS

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 gain 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 compliance[2] with respect to EQS is whole water, or for metals, the liquid fraction obtained by filtration of the whole water sample. However, as regards mercury, hexachlorobenzene, and hexachlorobutadiene it is not possible to ensure protection against indirect effects and secondary poisoning by EQSs for surface water alone. Hence, EQSs referring to concentrations in biota have been established for these compounds at Community level. In order to allow Member States flexibility depending on their monitoring strategy, they may either monitor and apply those EQSs for biota, or establish stricter EQSs for surface water providing the same level of protection. 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, waters samples may be taken in different depths to give a better

[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 environmental quality standards 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.

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.

In general, reliable data on emission sources reduces 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.

Look in:
Water Framework Directive 2000/60/EC Article 16(7)

The Commission shall submit proposals for quality standards applicable to the concentrations of the priority substances in surface water, sediments ***or*** *biota.*

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 the 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 Biota[3]

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 assessement, 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 Water Framework Directive

[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

- assess long-term changes in natural conditions and to the assess the long term changes resulting from widespread anthropogenic activity.
- monitor the progressive reduction in the contamination of priority substances (PS) and 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 gives an integrated measure of the contaminant burden over a longer time period and hence a less variable measure 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 speciments 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 of monitoring programs. 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 SEDFLEX[6]. 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 = $CHEMICAL_{Animal}/CHEMICAL_{Water}$. 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 European Union (European Commission 2004), the Canadian Environmental Protection Act (CEPA)'s Domestic Substances List (DSL) (ENVIRONMENT

[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.

CANADA 2003)[9], and the US EPA high production chemicals assessments (WALKER et al. 2004)[10].

The mechanistic model SEDFLEX is a model composed of one dispersion part simulating the sources, sinks and transports 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 water[6]. 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 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 to 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 identify areas of concern and where effort can be directed, such as a follow up with water samples and direct measurements. This process provides good grounds for using models where appropriate.

[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.

4.4. Monitoring frequency

Look in:
Water Framework Directive 2000/60/EC Annex V 1.3.4

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.

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.

Guidance document No. 7 - MONITORING UNDER THE WATER FRAMEWORK DIRECTIVE, 2.1

The monitoring frequencies given in WFD, Annex V 1.3.4 of once-a-month for priority substances or 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 load 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 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 which is transferred 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, 26 samples a year may be justified. Flow-proportional or time-proportional samples 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 surveillance monitoring makes use of monitoring data which have to be reported according to other European directives, international river and sea conventions for the purpose of surveillance monitoring (e.g. 76/464/EWG, 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.

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

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 been 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 against 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 have to be taken into account. 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 the aquatic system 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 program. 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 selection 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 involved 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 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 guidance may be found in the ISO Standard on Water Quality – Sampling 5667 (www.iso.org), the OSPAR Convention (www.ospar.org) for the Joint Assessment and Monitoring Programme (JAMP) or the HELCOM COMBINE (http://www.helcom.fi/groups/monas/CombineManual/en_GB/main/).

5.2. Water Sampling

	**Look in:** ISO Standard Series 5667, Part 1, 3, 4, 6 and 9 OSPAR JAMP Guidelines: Chlorophyll a in Water, Nutrients and Oxygen Manual for Marine Monitoring in the COMBINE Programme of HELCOM

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).

The selection of the sample containers and their subsequent transport and storage arrangements should not lead to contamination or other changes in the relevant chemical properties of the sample. Some precautions, depending on the nature of analysed contaminants, 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, many of the chemical parameters in unpolluted waters 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. Also, it is 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.

Look in:
ISO Standard Series 5667 Part 17

OSPAR JAMP Guidelines for the Estimation of Riverine PAH Inputs into the North Sea and the North-East Atlantic

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 Sampling[3]

Look in:
ISO Standard Series 5667, Part 12, 15 and 19

OSPAR JAMP Guidelines for Monitoring Contaminants in Sediments

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 compete 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 visual 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 Sampling[3]

Look in:
OSPAR JAMP Guidelines for Monitoring Contaminants in Biota

Manual for Marine Monitoring in the COMBINE Programme of HELCOM

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. Fish are not selected for analysis if they are visibly damaged, in bad condition or show any indication of disease. 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 validated 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 project[11].

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, other pollutants and physico-chemical parameters. Available certified reference materials relevant to WFD monitoring[12] are listed in Annex III. The Annex III was elaborated within the EU-project EAQC-WISE[11] .

6.1. Method performance criteria

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"

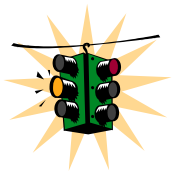
Minimum performance criteria have been defined for the limit of quantification (LOQ) and the measurement uncertainty U (expanded uncertainty of measurement). They are, where

[11] EAQC-WISE project, funded under the 6th RTD Framework Programme, European Commission, http://www.eaqc-wise.net/

[12] 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.

possible, linked to the Environmental Quality Standards where possible. 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.



Look out!
The mandate M/424 for standardisation adressed 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.

6.1.1. Uncertainty of measurement[13,14,15,]

According to the International Vocabulary of Basic and General Terms in Metrology VIM ISO 1993 measurement uncertainty has been defined as *'a parameter associated with the result of a measurement that characterises the dispersion of the values that could reasonably be associated to the measurand'*.

Measurement uncertainty (U_m) is typically expressed as a laboratory result ± 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 %.

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. A 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.

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[13] Nordtest Report TR537. Handbook for calculation of measurement uncertainty in environmental laboratories, 2nd Edition, 2004.
[14] EURACHEM/CITAC Guide: "Quantifying Uncertainty in Analytical Measurement", 2nd Edition, 2000
[15] ISO/IEC "GUM" (with BIPM, IFCC, IUPAC, IUPAP, OIML): "Guide to the expression of uncertainty in measurement", 1993.

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 total 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 Quantification[16]

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.

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

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.

Calculating an Estimate of the Limit of Detection
The limit of detection may be calculated as follows :

$$LOD = 3 * sbl$$

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.

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, trichlorbenzene, 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 (< 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.

Bioavailability and natural background concentrations of metals can be taken into account when assessing the monitoring results against EQS. For the assessment of priority metals compulsory calculation methods will be developed and adopted by the comitology procedure.

6.3. Sediment/SPM Analysis[3]

With the exception of PBDE, there are no standardised methods specifically developed for the analhysis 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.

Look in:
OSPAR JAMP Guidelines for Monitoring Contaminants in Sediments

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 techniques[17].

[17] 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

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 in preparation in the EU EQS Technical Guidance – Metals section.

6.4. Biota Analysis[3]

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.

Look in:
OSPAR JAMP Guidelines for Monitoring Contaminants in Biota

Manual for Marine Monitoring in the COMBINE Programme of HELCOM

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 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 ß-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	*p,p'*-DDT, *o,p'*-DDT, *p,p'*-DDE, *p,p*'-DDD	Total concentration and concentration of *p,p'*-DDT to be reported.

The CAS number 608-73-1 refers to technical HCH, hence, all relevant isomers have to 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 anaual 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.

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"

7. COMPLEMENTARY METHODS[18,19]

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.

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-

[18] This chapter was elaborated in close cooperation with the EU-project SWIFT (www.swift-wfd.com).
[19] 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.

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 sampling[20]. 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 protocols[21] 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 project[22] (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 Environmental Quality standards (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.

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

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

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

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

Technique	**Analytical Methods**			***In-situ* Sampling Techniques**		**Biological Methods**		
	Lab	**On-site**	***In-situ***	**Biomonitoring**	**Passive sampling**	**Direct toxicity assessment**	**Biological Early warning system**	**Biomarkers**
Examples	Immunoassay (e.g. atrazine), test kits, hand-held sensors (e.g. Palmsens)			MusselWatch programmes	Semi-permeable membrane device (SPMD), Chemcatcher	Daphtoxkit®	Mosselmonitor®, multi-species freshwater biomonitor	Measurement of metallothionein synthesis
Measurement	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
Type of information obtained	Qualitative, semi-quantitative, quantitative			Semi-quantitative, Qualitative	Qualitative, semi-quantitative or quantitative	Qualitative	Qualitative	Qualitative
Performance criteria	- LOD - LOQ - Calibration, quantification range				- LOD, LOQ (field) - Bias - Sensitivity		- Levels of false positives and negatives	
Implementation	- 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
Applicable to:	operational & investigative monitoring			operational & investigative monitoring	surveillance, operational & investigative monitoring	operational & investigative monitoring	operational & investigative monitoring	operational & investigative monitoring

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 non-priority substances 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 temporalvariation 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 water[21]. 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 $LogK_{oc}$-$logK_{ow}$ 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.