UNDP/GEF Danube Regional Project
Strengthening the Implementation Capacities for Nutrient
Reduction and Transboundary Cooperation
in the Danube River Basin

Development of the Danube List of Priority Substances and SOPs for newly included determinands

Project Component 2.2: Development of operational tools for monitoring, laboratory and information management with particular attention to nutrients and toxic substances

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Abbreviations

DRPS	Danube River Priority Substances
TNMN	Trans-National Monitoring Network
JDS	Joint Danube Survey
EMIS	Emission Sources Expert Group
MLIM	Monitoring and Laboratory Information Management
ICPDR	International Commission for the Protection of the Danube River
WFD	Water Framework Directive
DRB	Danube River Basin
EG	Expert Group
AMPS	Expert Group on Analysis and Monitoring of Priority Substances

Executive Summary

The main objective of this activity was to develop the Danube List of Priority Substances, based on the EU List of Priority Substances, determinands of TNMN and JDS; and taking into account the results of Phare project ZZ-97-25 Component VI in line with work of EMIS EG on this topic. However, the activities concerning developing the Danube List of Priority Substances had started long time before the Danube Regional Project began and the list was finalized by the ICPDR during course of the project. Therefore, a summary is provided of the activities performed and milestones achieved. Moreover, general recommendations are given for the follow-up actions.

In line with the Decision No 2455/2001/EC of the European Parliament and of the Council of 20 November 2001 establishing the list of priority substances in the field of water policy and amending Directive 2000/60/EC, and taking into account determinands analysed within TNMN and JDS as well as the results of Phare project ZZ-97-25 Component VI, the EMIS EG prepared the draft Danube List of Priority Substances. At the 1st Meeting of the Joint MLIM/EMIS Working Group in February 2003 this draft was discussed and it was suggested to keep the Annex A as prepared by the EMIS EG (identical with the EU WFD list). The Annex B was proposed to be divided into two groups – General Parameters (COD, NH4, N, P) and Danube Specific Priority Substances (As, Co, Zn, Cr). The ICPDR at its 1st Standing Working Group meeting in June 2003 agreed with the proposed Danube List of Priority Substances but considered it only as provisional. To arrive at a final list the national targeted screenings for EU WFD Priority Substances will have to be performed to prove their relevance for the specific area/region.

For the determinands, which newly appeared in the proposed Danube List of Priority Substances it was necessary to make available the respective standard operational procedures (SOPs). The overview of SOPs provided in the technical report takes into account the results of the review on possibilities to analyze the EU WFD priority substances in the Danube countries, which was performed by the MLIM EG in 2002. An attention was also paid to the activities of the Expert Group on Analysis and Monitoring of Priority Substances (AMPS) working under the "EU Expert Advisory Forum on Priority Substances and Pollution Control". The recommended standard operational procedures are divided into two groups - priority substances from the DECISION No. 2455/2001/EC and geneneral parameters and priority substances specific for the Danube River Basin.

1. Development of the Danube List of Priority Substances

1.1 Introduction

The main objective of this activity was to develop the Danube List of Priority Substances, based on the EU List of Priority Substances, determinands of TNMN and JDS; and taking into account the results of Phare project ZZ-97-25 Component VI in line with work of EMIS EG on this topic. However, the activities concerning developing the Danube List of Priority Substances had started long time before the Danube Regional Project began and the list was finalized by the ICPDR during course of the project. Therefore, the authors could only provide a summary of the activities performed, milestones achieved and a general recommendation for the follow-up actions.

1.2 Summary of activities and recommendations

In line with the Decision No 2455/2001/EC of the European Parliament and of the Council of 20 November 2001 establishing the list of priority substances in the field of water policy and amending Directive 2000/60/EC, and taking into account determinands analysed within TNMN and JDS as well as the results of Phare project ZZ-97-25 Component VI, the EMIS EG prepared the draft Danube List of Priority Substances. They recommended to the Contracting Parties that the substances and groups of substances they had put on the list should be Priority Substances for the Danube River Basin and should be subject for the following measures:

- Introduce subsequently these substances into the monitoring programmes for discharges wherever the possibility exists that those substances might occur.
- Introduce subsequently these substances into the monitoring programmes for the in-stream chemical status. Parameter No. 34 (Chemical Oxygen Demand) might be substituted by the parameter BOD (Biological Oxygen Demand).
- Introduce subsequently these substances into permits for discharge of waste waters, which contain those substances regulate or their use via other relevant national legislation.

They also recommended that this list should be reviewed in 2004 considering further development of the EU List of Priority Substances, especially, concerning the identification of priority hazardous substances of which emissions, discharges and losses will have to be finished within a time frame of 20 years.

With respect to the substances in the Annex IA of the proposed Danube list the MLIM EG at its 29th meeting had reservations about the automatic inclusion of all EU WFD priority substances into the Danube list. MLIM EG recommended that further investigation in this area should be performed from the emission and in-stream standpoint. The MLIM EG decided to proceed with the evaluation of the in-stream measurements and the EMIS EG was asked to provide information on estimated emissions of the substances on the WFD list. With respect to the substances in the Annex IB of the proposed Danube list the MLIM EG discussed the parameters 34 – 41 and because of the lack of clarity in the used terminology doubts were expressed if the parameters 34 – 37 may be looked upon as the priority substances, especially, in the view of in-stream water quality. It was stated that for priority substances the quality objectives were necessary to be set. At the ICPDR Chairpersons meeting in October 2002 it was agreed that a Joint MLIM/EMIS Working Group should further deal with finalization of the Danube List of Priority Substances. At the 1st Meeting of the Joint MLIM/EMIS Working Group in February 2003 it was suggested to keep the Annex A as prepared by the EMIS EG (identical with the EU WFD list). The Annex B was proposed to be divided into two groups – General Parameters (COD, NH4, N, P) and Danube Specific Priority Substances (As, Co, Zn, Cr). The MLIM EG and the EMIS EG accepted this amendment to the first version of the Danube List of Priority Pollutants and agreed that this version should be revised after the national surveys on priority substances as well as an update of the industrial discharges inventory would be carried out.

The ICPDR at its 1st Standing Working Group meeting in June 2003 agreed with the proposed Danube List of Priority Substances but considered it only as provisional. To arrive at a final list the national targeted screenings for EU WFD Priority Substances will have to be performed to prove their relevance for the specific area/region.

Therefore, it is recommended to summarize within the MLIM EG time plans for the national screenings for priority substances and based on this data to agree the deadline for reporting on results of these screenings and for preparation of amendment to the Danube List of Priority Substances. The national screenings should be focused on the in-stream quality as well as on the emission sources (the latter part should be carried out under supervision of the EMIS EG).

2. Development of SOPs for newly included determinands

2.1 Introduction

The objective of this activity was to make available SOPs for newly included determinands. It was planned that after reaching an agreement on the final version of the Danube List of Priority Substances the standard operational procedures in form of a brief description of recommended analytical methods would be developed for all relevant substances. This precondition, however, could not be met as the final version of the Danube List was not available in the course of this assignment. Therefore a brief method description refers to the provisional list.

The overview of SOPs takes into account the results of the review on possibilities to analyze the EU WFD priority substances in the Danube countries, which was performed by the MLIM EG in 2002. As stated in the Inception Report an attention was paid also to the activities of the Expert Group on Analysis and Monitoring of Priority Substances (AMPS) working under the "Expert Advisory Forum on Priority Substances and Pollution Control".

The term newly included determinands is understood in this report as those substances, which are new to the current analytical practice within the TNMN activities. For this purpose the provisional Danube List of Priority Substances will be discussed in two separate chapters – one dedicated to general parameters and priority substances specific for the Danube River Basin (Annex B of the Danube List) and the second referring to the substances from the Decision No 2455/2001/EC (Annex A of the Danube List).

2.2 Results and assessment of needs

2.2.1 General parameters and priority substances specific for the Danube River Basin

COD, NH_4, N and P are considered as general parameters while As, Co, Zn and Cr has been identified as substances specific for the Danube. They are all included in the TNMN (nitrogen is expressed in terms of organic N and its inorganic forms - NH_4, NO_3, NO_2). For all these parameters appropriate analytical methods were agreed upon for the Phase I of the TNMN as follows:

Determinand	**Agreed method**
Ammonium (NH_4^+-N)	**ISO 7150-1:1984** Water quality. Determination of ammonium. Part 1: Manual spectrometric method.
Nitrite (NO_2^--N)	**ISO 6777:1984** Water quality. Determination of nitrite. Molecular absorption spectrometric method.
Nitrate (NO_3^- -N)	**ISO 7890-3:1988** Water quality. Determination of nitrate. Part 3: Spectrometric method using sulfosalicylic acid.
Organic Nitrogen	Kjeldahl-N, or instrumental Total-N (minus inorganic-N)
Total Nitrogen	**EN ISO 11905-1:1998** "Water quality – Determination of nitrogen – Part 1: Method using oxidative digestion with peroxodisulfate", and, **ISO 11261:1995** Soil quality – Determination of total nitrogen – Modified Kjeldahl method (Total N in the sediment)
Orthophosphate (PO_4^{3-} -P)	**ISO 1189:1996** Water quality. Determination of phosphorus. Ammonium molybdate spectrometric methods.
Total Phosphorus	**ISO 1189:1996** Water quality. Determination of phosphorus. Ammonium molybdate spectrometric methods.
COD_{Cr}	**ISO 6060:1989** Water quality. Determination of chemical oxygen demand. This ISO method was replaced by the DIN low level COD method.
Arsenic (As)	**ISO 11969:1996** Determination of arsenic. Atomic absorption spectrometric method (hydride technique).
Copper (Cu)	Atomic absorption spectrophotometric method
Zinc (Zn)	Atomic absorption spectrophotometric method
Chromium (Cr) – total	**ISO 9174:1990** Water quality. Determination of total chromium. Atomic absorption spectrometric method.

More detailed description of these methods can be found in the Guidance Notes for MLIM that were prepared within the EU Phare project “Strengthening Sustainability of Water Quality Management in the Danube River Basin” in 2000.

2.2.2 Priority substances from the DECISION No. 2455/2001/EC

The recommendations for the standard operational procedures provided in this chapter will primarily reflect current opinions and developments in the Expert Group on Analysis and Monitoring of Priority Substances (AMPS) working under the Expert Advisory Forum on Priority Substances (EAF PS).

In principle the authors of this chapter share the opinion of those AMPS experts stating that it is better not to set a predetermined specific methodology to analyze the priority substances since a flexibility in choosing the appropriate analytical method is necessary. As it was pointed out during AMPS discussions, usually the development of analytical chemistry is faster than the promulgation of a Directive. Thus, it may happen that the proposed methodology is not the best technique for all the laboratories. Therefore, the methods indicated in this paper should be considered as recommended procedures and the use of an alternative technique should not be excluded.

An excellent tabled overview of the current status of availability of SOPs for the analysis of the priority substances from the Decision No. 2455/2001/EC (Table of existing standard methods and proposed quality standards for priority substances in water) was prepared by EU JRC and is available in Annex 1. This overview served as a basis for the methods recommended for the application within the TNMN activities. Additional sources for these recommendations were the remarks done by the CEN TC 230 and the inquiry on availability of standard methods for EU WFD priority substances in the Danube countries done by the ICPDR Secretariat in 2002. Even though the data for this ICPDR questionnaire came only from Germany, Austria, Czech Republic, Slovakia, Slovenia and Romania, it represents a good overview of the situation in the ICPDR countries.

At this point it must be emphasized that the following overview covers all substances from the Decision No. 2455/2001/EC. However, in future, an attention will be given at the ICPDR level (i.e., adding parameters to the TNMN list) only to those determinands, which will be selected for the final version of the Danube List of Priority Substances after carrying out national screenings. This means that some of the methods discussed below may not be necessary for application at the ICPDR level in the future.

Alachlor

EN ISO 6468 (Determination of certain organochlorine insecticides, polychlorine biphenyls and chlorobenzenes - Gas chromatographic method after liquid-liquid extraction) is a recommended technique. This method is applicable for drinking, ground, surface and wastewater; detection limit: 1 ng/l to 10 ng/l.

It prevails the ISO 11 370 because of the lower LOD. The ICPDR questionnaire indicates that there are applicable methods in the Danube countries.

Anthracene

ISO 17993: 2002 (Water quality – Determination of 15 polynuclear aromatic hydrocarbons (PAH) in water by HPLC with fluorescence detection is a recommended SOP. This method is suitable for drinking and ground water for mass concentrations > 0,005 µg/l; and for surface water for mass concentrations > 0,01 µg/l. The ICPDR questionnaire indicates that there are applicable methods for anthracene in the Danube countries.

Atrazine

Atrazine belongs to the TNMN determinands. The ICPDR questionnaire indicates that there are applicable methods for analysis of atrazine in the Danube countries. Guidance Notes for MLIM recommended the ISO 6468:1996 “Water quality. Determination of certain organochlorine insecticides, polychlorinated biphenyls and chlorobenzenes. Gas chromatographic method after liquid-liquid extraction” as a method of choice.

However, in line with the AMPS and CEN TC 230, the EN ISO 11369 and the EN ISO 10695 are recommended for the use in the Danube countries in the future. EN ISO 11369 (Water quality – Determination of selected plant treatment agents) is based on high performance liquid chromatography with UV detection after solid-liquid extraction and is suitable for drinking and ground water for concentrations >0,05 - 0,1 µg/l. EN ISO 10695 (Water quality – Determination of selected organic nitrogen and phosphorus compounds - Gas chromatographic methods) is suitable method for drinking, ground, surface and wastewater and its detection limit depends on the matrix and the compound to be determined; lowest limit of application (without optimisation of analysis): 0,05 µg/l.

Benzene

ISO 15680 (Water quality – Gas-chromatographic determination of a number of monocyclic aromatic hydrocarbons, naphthalene and several chlorinated compounds using purge and trap and thermal desorption) is the preferred method owing to the high sensitivity. This method for drinking, ground, surface, sea and (diluted) wastewater has a detection limit of 10 ng/l and a working range: up to 100 µg/l.

The head-space technique (ISO 11 423), which is also considered by AMPS, does not have sufficiently low LOD to cope with the quality standards.

The ICPDR questionnaire indicates that there are applicable methods for analysis of benzene in several Danube countries, however, some countries still require methodological support.

Brominated diphenylethers

There are 209 theoretical congeners of polybrominated diphenylethers (PBDE), out of which only few are present in technical mixtures. In this respect the analysis of PBDE resembles that of PCBs and requires a widely agreed approach based on the consensus. The agreement on the analysis of groups of substances is probably the major obstacle to be coped with during selection of suitable SOPs for the EU WFD priority substances. According to the ICPDR questionnaire in 2002 only Germany, Slovakia and Austria (expected in 2003) reported availability of SOP for PBDE, the other Danube countries still required methodological support. In this respect PBDE belong to problematic substances for the TNMN as far as their analysis is concerned.

AMPS recommends for analysis of PBDE in sludge and sediment the ISO WD 22032 method employing gas chromatography with mass spectrometric detection.

Recently, a background paper on Indicator Substances and Analytical Methods for the determination of groups of substances was elaborated by Peter LEPOM, Robert LOOS and Alfred RAUCHBÜCHL to support the AMPS activities. This document provides very good review of the present possibilities in analysis of polybrominated diphenylethers, alkylphenols and short-chain chlorinated paraffins and is attached to this report as Annex 2. We recommend to use this background paper at the ICPDR level.

Cadmium and its compounds

Cadmium belongs to the TNMN determinands. The ICPDR questionnaire indicates that there are applicable methods for analysis of cadmium in the Danube countries. Guidance Notes for MLIM recommend the ISO 5861 "Water quality. Determination of cadmium by atomic absorption spectrometry" as a method of choice. The same method is recommended by AMPS.

C_{10-13}- Chloroalkanes

C_{10-13}- Chloroalkanes (short-chain chlorinated paraffins, SCCPs) are polychlorinated n-alkanes with chlorine content ranging from 49 to 70% by weight. The theoretical maximum number of positional isomers calculated for $n\text{-}C_nH_{2n+2-z}Cl_z$, assuming no more than one bound chlorine atom on an carbon atom, for SCCPs is 7820. However, the complexity of mixture of C_{10-13}- chloroalkanes is further enhanced because chlorine substitution at a secondary carbon atom usually produces a chiral carbon atom so that enantiomers and diastereomers are generated. Furthermore, although the source hydrocarbon skeletons are primarily *n*-alkanes, they can contain branched alkanes and also other hydrocarbons, which increase the complexity of mixtures. Hence, it can be expected that commercial mixtures of C_{10-13}- chloroalkanes contain several thousands of compounds. According to the ICPDR questionnaire in 2002 only Czech Republic and Austria (expected in 2004) reported availability of SOP for SCCPs, the other Danube countries still require methodological support. SCCPs are the only substances, for which AMPS reports no standard method available. In this respect SCCPs can probably be considered as the most problematic substances to be included into TNMN from the methodological point of view.

Therefore, similarly to PBDE, the background paper on Indicator Substances and Analytical Methods for the determination of groups of substances given in Annex 2 is recommended as the best reference for considerations on analysis of C_{10-13}- chloroalkanes.

Chlorfenvinphos, Chlorpyrifos

EN 12918 (Water quality – Determination of parathion, parathion-methyl and some other organophosphorus compounds in water by dichlormethane extraction and gas chromatographic analysis) is recommended by AMPS for both pesticides. This method for drinking, surface and waste water has reported LOD of about >0,05 µg/l for drinking water.

According to the ICPDR questionnaire most of the countries do not report any method available. Thus, the analysis of chlorfenvinphos and chlorpyrifos will require methodological support in the ICPDR countries provided these pesticides will be found relevant for the Danube River Basin.

1,2-Dichloroethane, Dichloromethane

ISO 15680 using gas chromatography after purge & trap preconcentration with thermal desorption is the preferred method owing to the high sensitivity. The head-space technique, which is also considered by AMPS does not have sufficiently low LOD to cope with the quality standards. The ICPDR questionnaire indicates that there are applicable methods for analysis of benzene in the Danube countries; however, some may still require methodological support.

Di(2-ethylhexyl)phthalate (DEHP)

According to the ICPDR questionnaire in 2002 only Germany reported availability of a method for analysis of DEHP, Slovakia and Austria expected to have it developed by the end of 2002 and in 2003, respectively.

AMPS recommends an ISO DIS 18856 (Water quality – Determination of selected phthalates by gas chromatography/mass spectrometry), which is suitable for drinking, ground, surface and waste water having an application range between 0,02 µg/l to 0,15 µg/l, depending on the individual substance.

Diuron

EN ISO 11369 (Water quality – Determination of selected plant treatment agents - Method using high performance liquid chromatography with UV detection after solid-liquid extraction) is a recommended method. It is applicable for drinking and ground water for concentrations >0,05 - 0,1 µg/l.

The ICPDR questionnaire indicates that there are applicable methods only in some Danube countries.

Endosulfan (alpha-endosulphan)

EN 6468 (Water quality – Determination of certain organochlorine insecticides, polychlorine biphenyls and chlorobenzenes - Gas chromatographic method after liquid-liquid extraction) is a recommended technique. It is applicable for drinking, ground, surface and waste water having detection limit of 1 ng/l to 10 ng/l.

The ICPDR questionnaire indicates that there are applicable methods in the Danube countries.

Fluoranthene

ISO 17993: (Water quality – Determination of 15 polynuclear aromatic hydrocarbons (PAH) in water by HPLC with fluorescence detection) is a recommended method. It is suitable for drinking and ground water for mass concentrations > 0,005 µg/l and for surface water for mass concentrations > 0,01 µg/l.

The ICPDR questionnaire indicates that there are applicable methods in the Danube countries.

Hexachlorobenzene

EN 6468 based on gas chromatographic separation with ECD detection after liquid-liquid extraction is a recommended technique. The ICPDR questionnaire indicates that there are applicable methods in most of the responding Danube countries. For those reporting no method for HCB but using an analogous procedure to EN 6468 for other chlorinated pesticides (e.g., lindane) the verification of this procedure for HCB is recommended.

Hexachlorobutadiene

EN ISO 10301 (Water quality – Determination of highly volatile halogenated hydrocarbons – Gas-chromatographic methods) is a recommended technique. There are two optional procedures available:

a) liquid-liquid extraction; method for drinking, ground, bathing, surface and waste water; typical "quantification" limits between 0,01 µg/l and 50 µg/l, depending on the compound,

b) head-space method; method for drinking, ground and surface, typical "quantification" limits between 0,1 µg/l and 200 µg/l, depending on the compound.

The ICPDR questionnaire indicates that there are applicable methods only in some Danube countries.

Hexachlorocyclohexane (Lindane)

Lindane belongs to the TNMN determinands. The ICPDR questionnaire indicates that there are applicable methods for analysis of lindane in the Danube countries. Guidance Notes for MLIM recommend the ISO 6468:1996 "Water quality. Determination of certain organochlorine insecticides, polychlorinated biphenyls and chlorobenzenes. Gas chromatographic method after liquid-liquid extraction" as a method of choice. This method is also recommended by AMPS.

Isoproturon

The ICPDR questionnaire indicates that there are applicable methods for analysis of isoproturon in Danube countries, however, some countries still require methodological support. EN ISO 11369 (Water quality – Determination of selected plant treatment agents) that is based on high performance liquid chromatography with UV detection after solid-liquid extraction is recommended for the use in the Danube countries. This method is suitable for drinking and ground water for concentrations >0,05 - 0,1 µg/l.

Lead and its compounds

Lead belongs to the TNMN determinands. The ICPDR questionnaire indicates that there are applicable methods for analysis of lead in all reporting countries. Guidance Notes for MLIM recommend atomic absorption spectrometric method as a method of choice. In line with CEN TC 230 and AMPS it is recommended to use EN ISO 11 885 (Water quality – Determination of 33 elements by inductively coupled plasma atomic emission spectroscopy) that is applicable for raw, drinking and waste water having detection limit between 0,0005 mg/l to 2mg/l, depending on sample and matrix; (for lead: 0,07/0,2 mg/l). In case of absence of an ICP AES unit the laboratories can apply ISO 15 586 (Water quality – Determination of trace elements by atomic absorption spectrometry with graphite furnace), which is applicable for fresh waters (e.g,. lake and river water, precipitation, ground water, drinking water, waste water) and sediments with detection limit between 0,1 µg/l to 2 µg/l, depending on the element (1 µg/l for lead).

Mercury and its compounds

Mercury belongs to the TNMN determinands. The ICPDR questionnaire indicates that there are applicable methods for analysis of mercury in the Danube countries. Guidance Notes for MLIM recommend the ISO 1483 "Water quality – Determination of mercury) as a method of choice. This method is suitable for analysis of ground, waste and surface water having a working range of 0,1 µg/l - 10 µg/l. The same method is recommended by AMPS.

Naphthalene

ISO 17993: 2002 (Water quality – Determination of 15 polynuclear aromatic hydrocarbons (PAH) in water by HPLC with fluorescence detection) is a recommended SOP. This method is suitable for drinking and ground water for mass concentrations > 0,005 µg/l; and for surface water for mass concentrations > 0,01 µg/l. The ICPDR questionnaire indicates that there are applicable methods for naphthalene in the Danube countries.

Nickel and its compounds

Nickel belongs to the TNMN determinands. The ICPDR questionnaire indicates that there are applicable methods for analysis of nickel in all reporting countries. Guidance Notes for MLIM recommend atomic absorption spectrometric method as a method of choice. In line with CEN TC 230 and AMPS it is recommended to use EN ISO 11 885 (Water quality – Determination of 33 elements by inductively coupled plasma atomic emission spectroscopy) that is applicable for raw, drinking and waste water having detection limit between 0,0005 mg/l to 2 mg/l, depending on sample and matrix. In case of absence of an ICP AES unit the laboratories can apply ISO 15 586 (Water quality – Determination of trace elements by atomic absorption spectrometry with graphite furnace), which is applicable for fresh waters (e.g., lake and river water, precipitation, ground water, drinking water, waste water) and sediments with detection limit between 0,1 µg/l to 2 µg/l, depending on the element (1 µg/l for nickel).

Nonylphenols

Commercially produced nonylphenols contain predominantly 4-nonylphenol with a varied and undefined degree of branching in the alkyl group. According to product data sheets of some nonylphenol manufacturers the two most important impurities in commercial 4-nonylphenol are 2-nonylphenol (up to 10 % w) and 2,4-dinonylphenols (up to 1 % w).

According to the ICPDR questionnaire in 2002 only Germany, Czech Republic Slovakia (expected by the end of 2002) and Austria (expected in 2003) reported availability of SOP for nonylphenols, the other Danube countries still require methodological support. AMPS recommends for analysis of nonylphenols ISO 18 857 (Water quality – Determination of selected alkylphenols – Part 1: Method for non-filtered samples using liquid extraction and gas chromatography with mass selective detection). This method is applicable for selected alkylphenols (octyl- and nonylphenols) in non-filtered samples from drinking, ground, and surface water in a concentration range from 0,005 µg/l to 0,2 µg/l.

For considerations on analysis of nonylphenols, the background paper on Indicator Substances and Analytical Methods for the determination of groups of substances given in Annex 2 can serve as an excellent reference.

Octylphenols

The case for octylphenols is analogous to that for nonylphenols. According to the ICPDR questionnaire in 2002 only Germany, Czech Republic, Slovakia (expected by the end of 2002) and Austria (expected in 2003) reported availability of SOP for octylphenols; the other Danube countries still require methodological support. AMPS recommends for analysis of octylphenols ISO 18 857 (Water quality – Determination of selected alkylphenols – Part 1: Method for non-filtered samples using liquid extraction and gas chromatography with mass selective detection). This method is applicable for selected alkylphenols (octyl- and nonylphenols) in non-filtered samples from drinking, ground, and surface water in a concentration range from 0,005 µg/l to 0,2 µg/l.

For considerations on analysis of octylphenols, the background paper on Indicator Substances and Analytical Methods for the determination of groups of substances given in Annex 2 can serve as an excellent reference.

Pentachlorobenzene

EN 6468 based on gas chromatographic separation with ECD detection after liquid-liquid extraction is a recommended technique. The ICPDR questionnaire indicates that there are applicable methods in most of the responding Danube countries. For those reporting no method for pentachlorobenzene but using an analogous procedure to EN 6468 for other chlorinated pesticides (e.g., lindane), a verification of this procedure for pentachlorobenzene is recommended.

Pentachlorophenol

EN 12 673 (Water quality – Gas chromatographic determination of some selected chlorophenols in water) is a recommended SOP. It is applicable method for drinking, ground, rain, waste, sea and surface water having a working range of 0,1 µg/l - 1 mg/l. The ICPDR questionnaire indicates that there are appropriate methods in most of the responding Danube countries, methodological support will be necessary in certain national laboratories.

Polyaromatic hydrocarbons

PAHs belong to the TNMN determinands. The ICPDR questionnaire indicates that there are applicable methods for analysis of PAHs in the Danube countries. ISO 17993: 2002 (Water quality – Determination of 15 polynuclear aromatic hydrocarbons (PAH) in water by HPLC with fluorescence detection is a recommended SOP. This method is suitable for drinking and ground water for mass concentrations > 0,005 µg/l; and for surface water for mass concentrations > 0,01 µg/l.

Simazine

Simazine belongs to the TNMN determinands. The ICPDR questionnaire indicates that there are applicable methods for analysis of simazine in the Danube countries.

In line with the AMPS and CEN TC 230 the EN ISO 11369 and the EN ISO 10695 are recommended for the use in the Danube countries. EN ISO 11369 (Water quality – Determination of selected plant treatment agents) is based on high performance liquid chromatography with UV detection after solid-liquid extraction and is suitable for drinking and ground water for concentrations >0,05 - 0,1 µg/l. EN ISO 10695 (Water quality – Determination of selected organic nitrogen and phosphorus compounds - Gas chromatographic methods) is suitable method for drinking, ground, surface and waste water and its detection limit depends on the matrix and the compound to be determined; lowest limit of application (without optimization of analysis): 0,05 µg/l.

Tributyltin compounds (Tributyltin cation)

According to the ICPDR questionnaire in 2002 only Germany and Austria reported availability of a method for analysis of DEHP, Slovakia expected to have it developed by the end of 2002.

AMPS recommends an ISO DIS 17 353 (Water quality – Determination of selected organotin compounds – Gas-chromatographic method). This method is suitable for drinking, surface and wastewater with a maximum of 2 g/l of suspended material; Method working range is between 10 ng/l to 1000 ng/l, depending on the individual substance.

Trichlorobenzenes (1,2,3-TCB; 1,2,4-TCB; 1,3,5-TCB)

EN 6468 based on gas chromatographic separation with ECD detection after liquid-liquid extraction is a recommended technique. The ICPDR questionnaire indicates that there are applicable methods for trichlorobenzenes only in Germany, Czech Republic and Slovakia; Austria should have a method available in 2003. For those reporting no method for trichlorobenzenes but using an analogous procedure to EN 6468 for other chlorinated pesticides (e.g., lindane) the verification of this procedure for trichlorobenzenes is recommended.

An optional SOP is ISO 15680 (Water quality – Gas-chromatographic determination of a number of monocyclic aromatic hydrocarbons, naphthalene and several chlorinated compounds using purge and trap and thermal desorption). This method is applicable for drinking, ground, surface, sea and (diluted) waste water having detection limit of 10 ng/l and working range up to 100 µg/l.

Trichloromethane

Trichloromethane belongs to the TNMN determinands. The ICPDR questionnaire indicates that there are applicable methods for analysis of trichloromethane in most of the Danube countries, however, some countries report no method available (possibly caused by missing equipment). This also causes a data gap in the TNMN database.

Guidance Notes for MLIM recommend for the analysis of chloroform EN ISO 10301 (Water quality – Determination of highly volatile halogenated hydrocarbons – Gas-chromatographic methods). There are two optional procedures available:

liquid-liquid extraction; method for drinking, ground, bathing, surface and wastewater; typical "quantification" limits between 0,01 µg/l and 50 µg/l, depending on the compound.

head-space method; method for drinking, ground and surface, typical "quantification" limits between 0,1 µg/l and 200 µg/l, depending on the compound.

EN ISO 10301 is also one of the methods recommended by AMPS, the other option is ISO 15680 (Water quality – Gas-chromatographic determination of a number of monocyclic aromatic hydrocarbons, naphthalene and several chlorinated compounds using purge and trap and thermal desorption). This method is applicable for drinking, ground, surface, sea and (diluted) waste water having detection limit of 10 ng/l and working range up to 100 µg/l. In case of chloroform there is no apparent prevalence of the purge & trap method over the head-space procedure regarding the LODs. Presence of three chlorine atoms enables sensitive detection by the ECD detector even in the case of the low-recovery head-space.

Trifluralin

EN ISO 10695 (Water quality – Determination of selected organic nitrogen and phosphorus compounds - Gas chromatographic methods) is suitable method for drinking, ground, surface and waste water and its detection limit depends on the matrix and the compound to be determined; lowest limit of application (without optimization of analysis): 0,05 µg/l.

The ICPDR questionnaire indicates that there are applicable methods for analysis of Trifluralin in several Danube countries, however, some countries still require methodological support.

2.3 Conclusions

To summarize visually all the above-mentioned methodological recommendations for the Danube-specific substances as well as for the EU WFD priority substances, a summary table, derived from the original AMPS table, was drafted and is presented in Annex 3. It must be stressed that this table reflects the current situation (i.e., the provisional Danube List of Priority Substances). In future, methodological demands will be influenced by final changes of the Danube List.

Annexes

Annex 1

Table of existing standard methods and proposed QS for PS in water (as of 14 January 2003)

Priority Substance	**Available standard method (Ref.)**			**Specific ring trial data for surface water**			**Method-Applicability**	**Proposals for Quality standards for PS of the WFD**			**76/464/EEC**
	Standard	**Year**	**Principle**	**Lowest conc.** [3]	**S_R**[3]	**Application range**[2]	**Applicability in routine labs - (yes/no) or remarks**	**AA-QS**[7] **for inland (In) & transitional (Tr) waters**	**AA-QS**[7] **for coastal (Co) & territorial (Te) waters**	**MAC-QS**[7]	**Quality objective**
Alachlor	ISO 11370 2000	Jan-95	TLC, AMD-Technique				no (2), yes (2)	0.035 µg/l	n.a.	1.15 µg/l	
	US EPA 505	Jul-91	GC/ECD (MS for conf.)				--				
Anthracene	ISO 17993: 2002 or see PAH´s						yes (2)	0.063 µg/l	0.0063 µg/l	0.01 µg/l	
	US EPA 8100		GC/FID				yes (1)				
Atrazine	EN ISO 11369	Nov-97	HPLC/UV				no (1), yes (1)	0.34 µg/l	0.34 µg/l	2 µg/l	
	EN ISO 10695: 2000	Nov-00	GC/NPD (MS for conf.)				no (1), yes (2)				
	ISO 11370 2000	Jan-95	TLC, AMD-Technique	0,13 µg/l	38%	³ 0.13 µg/l	no (1)				
	US EPA 505	Jul-91	GC/ECD (MS for conf.)				--				
Benzene	DIN 38407-9	May-91	Headspace-GC/FID	ca. 5,9 µg/l	16-29%	³ 5,9 µg/l	no (1), yes (1)	16 µg/l*	1.6 µg/l*	49 µg/l	
	Draft ISO 15680	Sep-01	Purge/Trap + Therm. Desorp.	0.2 µg/l	15%	³ 0.2 µg/l	no (1), yes (1)				
	ISO 11423-1	Sep-97	Headspace-GC/FID	6 µg/L	16%	³ 6 µg/l	yes (1)				
Brominated diphenylethers	ISO WD 22032	Mar-02	GC/MS				no (3), yes (1)				
Bis(pentabromophenyl)ether	*ISO WD 22032*	Mar-02	GC/MS				--	n.a.	n.a.	not required	
Diphenyl ether, octabromo derivate	*ISO WD 22032*	Mar-02	GC/MS				--	33.8 µg/l (1217 µg/kg seafood, 1513 mg/kg SPM)	not required		
Diphenyl ether, pentabromo derivate	*ISO WD 22032*	Mar-02	GC/MS				--	0.0005 µg/l	0.00018 µg/l	1.4 µg/l	
Cadmium and its compounds	EN ISO 5961	May-95	ET-AAS				yes (4)	0.08 µg/l	n.a.		5 µg/l (2.5-0.5 µg/l)
	DIN 38406-16	Mar-90	Voltametry	0,81 µg/l	29%	³ 0,81 µg/l	no (1)				
	ISO/DIS 17294-2	Nov-02	ICP-MS	5,75 µg/l	8.5%	³ 5,75 µg/l	yes (1)				
	EN ISO 11885	Apr-98	ICP-AES				yes (1)				
	ISO DIS 15586 [5]	May 01	ET-AAS				--				
C10-13-chloroalkanes	**no Standard available**	--	--				no (3)	0.41 µg/l	0.1 µg/l	1.4 µg/l	

Priority Substance	**Available standard method (Ref.)**			**Specific ring trial data for surface water**			**Method-Applicability**	**Proposals for Quality standards for PS of the WFD**			**76/464/EEC**
	Standard	**Year**	**Principle**	**Lowest conc.** ^{3}	**S_R^3**	**Application range**^{2}	**Applicability in routine labs - (yes/no) or remarks**	**AA-QS^7 for inland (In) & transitional (Tr) waters**	**AA-QS^7 for coastal (Co) & territorial (Te) waters**	**MAC-QS^7**	**Quality objective**
Chlorfenvinphos	DIN EN 12918	Nov-99	GC	0,081 µg/l	13%	³ 0,081 µg/l	no (3), yes (1)	0.01 µg/l	0.01 µg/l	0.01 µg/l	
	ISO 11370 2000	Jan-95	TLC, AMD-Technique				no (1)				
Chlorpyrifos *(-ethyl, -methyl)*	DIN EN 12918	Nov-99	GC				no (3), yes (1)	0.00046 µg/l	0.00046 µg/l	0.001 µg/l	
1,2-Dichloroethane	EN ISO 10301	Aug-97	GC or Headspace-GC				yes (4)	1060 µg/l*	1060 µg/l*	1080 µg/l	**10 µg/l**
	Draft ISO 15680 ^{5}	Sep-01	Purge/Trap + Therm. Desorp.	0.2 µg/l	35%	³ 0.2 µg/l	--				
Dichloromethane	EN ISO 10301	Aug-97	GC or Headspace-GC-ECD or other				no (1), yes (3)	8.2 µg/l	8.2 µg/l	162 µg/l	
	Draft ISO 15680 ^{5}	Sep-01	Purge/Trap + Therm. Desorp.	0.2 µg/l	35%	³ 0.2 µg/l	--				
Di(2-ethylhexyl)phthalate (DEHP)	ISO DIS 18856	Mar-02	GC/MS				no (2), yes (2)	0.33 µg/l	0.17 µg/l	not required	
Diuron	EN ISO 11369	Nov-97	HPLC/UV				no (2), yes (2)	0.046 µg/l	0.046 µg/l	1.1 µg/l	
Endosulfan	EN ISO 6468	Feb-97	GC/ECD	0.194 µg/l	68% (10% recovery!)	³ 0.194 µg/l	no (2), yes (1)	0.004 µg/l	0.004 µg/l	0.004 µg/l	
	US EPA 8081		GC/ECD				yes (1)				
Fluoranthene	ISO 17993: 2002 or see PAH´s						no (1), yes (1)	0.12 µg/l	0.12 µg/l	0.9 µg/l	
	US EPA 8270		GC/MS				yes (1)				
Hexachlorobenzene	EN ISO 6468	Feb-97	GC/ECD	0.058 µg/l	34%	³ 0.058 µg/l	yes (3)	0.008 µg/l*	0.008 µg/l*	0.05 µg/l	0.03 µg/l
	US EPA 8081		GC/ECD				yes (1)				
	US EPA 505	Jul-91	GC/ECD (MS for conf.)				--				
Hexachlorobutadiene	EN ISO 10301	Aug-97	GC or Headspace-GC-ECD or other				no (2), yes (2)	= 0.003 µg/l	= 0.003 µg/l	0.59 µg/l	0.1 µg/l
Hexachlorocyclohexane	EN ISO 6468	Feb-97	GC/ECD	0.039 µg/l	38%	³ 0.039 µg/l	yes (4)	0.042 µg/l	0.01 µg/l	0.9 µg/l	
gamma-HCH (Lindane)	*EN ISO 6468*	Feb-97	GC/ECD	0.039 µg/l	38%	³ 0.039 µg/l	--	0.02 µg/l	0.002 µg/l	0.03 µg/l	
Isoproturon	EN ISO 11369	Nov-97	HPLC/UV				no (2), yes (2)	0.32 µg/l	0.32 µg/l	1.3 µg/l	
Lead and its compounds	DIN 38406-6	Jul-98	ET-AAS	29,5 µg/l	11-16%	³ 29,5 µg/l	yes (3)	1 µg/l	1 µg/l	2 µg/l	
	ISO 8288		flame AAS				yes (1)				
	US EPA 7421		ET-AAS				yes (1)				
	DIN 38406-16	Mar-90	Voltametry	2,9 µg/l	53%	³ 2,9 µg/l	no (1)				
	ISO/DIS 17294-2	Nov-02	ICP-MS	13,6 µg/l	8.3%	³ 13,6 µg/l	yes (2)				

Priority Substance	**Available standard method (Ref.)**			**Specific ring trial data for surface water**			**Method-Applicability**	**Proposals for Quality standards for PS of the WFD**			**76/464/EEC**
	Standard	**Year**	**Principle**	**Lowest conc.** [3]	**S_R**[3]	**Application range**[2]	**Applicability in routine labs - (yes/no) or remarks**	**AA-QS**[7] **for inland (In) & transitional (Tr) waters**	**AA-QS**[7] **for coastal (Co) & territorial (Te) waters**	**MAC-QS**[7]	**Quality objective**
	EN ISO 11885	Apr-98	ICP-AES				yes (2)				
	ISO DIS 15586 [5]	May 01	ET-AAS				--				
Mercury and its compounds	EN 1483	Aug-97	Cold Vapour-AAS	1,474 µg/l	27%	³ 1,474 µg/l	no (1), yes (3)	0.036 µg/l*	0.036 µg/l*	0.07 µg/l	1 µg/l (0.3 µg/l)
	EN 12338	Oct-98	CV-AAS with Amalgamation	0,283 µg/l	19%	³ 0,283 µg/l	yes (2)				
	EN 13506	Nov-01	Atomic fluor. spectrometry	0,05 µg/l	11.6% (25.9% ?)	³ 0,05 µg/l [4]	--				
Naphthalene	ISO 17993: 2002 or see PAH´s						yes (2)	2.4 µg/l	1.2 µg/l	80 µg/l	
	Draft ISO 15680 [5]	Sep-01	Purge/Trap + Therm. Desorp.	0.2 µg/l	32%	³ 0.2 µg/l	--				
	US EPA 8270		GC/MS				yes (1)				
Nickel and its compounds	DIN 38406-11	Sep-91	ET-AAS				yes (3)	0.6 µg/l	0.6 µg/l	1.3 µg/l	
	ISO 8288		flame AAS				yes (1)				
	US EPA 7521		ET-AAS				yes (1)				
	DIN 38406-16	Mar-90	Voltametry	3.2 µg/l	30%	³ 3,2 µg/l	no (1)				
	ISO/DIS 17294-2	Nov-02	ICP-MS	5,44 µg/l	14.5%	³ 5,44 µg/l	yes (2)				
	EN ISO 11885	Apr-98	ICP-AES				yes (2)				
	ISO DIS 15586 [5]	May 01	ET-AAS				--				
Nonylphenols	ISO CD 18857-1	Jul-01	GC/MS	0,023 µg/l	57.20%	³ 0,023 µg/l	no (1), yes (2)	0.33 µg/l	0.033 µg/l	2.1 µg/l	
	Sweedish EPA Raport 3829-1990		GC/ECD				yes (1)				
Octylphenols	ISO CD 18857-1	Jul-01	GC/MS	0,019 µg/l	25.10%	³ 0,019 µg/l	no (3), yes (1)	0.1 µg/l	0.01 µg/l	0.133 µg/l	
Pentachlorobenzene	EN ISO 6468	Feb-97	GC/ECD				yes (3)	< 0.05 µg/l	< 0.05 µg/l	1 µg/l	
	US EPA 8081		GC/ECD				yes (1)				
Pentachlorophenol	EN 12673	May-99	GC/ECD/MS after Deriv.	0,25 µg/l	37%	³ 0,25 µg/l	yes (4)	0.1 µg/l	0.1 µg/l	1 µg/l	2 µg/l
	ISO 8165-2	Jul-99	GC/ECD after Deriv.				no (1), yes (1)				
Polyaromatic Hydrocarbons (PAH´s)	ISO 17993: 2002		HPLC/Fluo				yes (1)				
	US EPA 8270		GC/MS				yes (3)				
	DIN 38414-23	Feb-02	HPLC/Fluo				no (1), yes (1)				

Priority Substance	**Available standard method (Ref.)**			**Specific ring trial data for surface water**			**Method-Applicability**	**Proposals for Quality standards for PS of the WFD**			**76/464/EEC**
	Standard	**Year**	**Principle**	**Lowest conc. [3]**	**S_R[3]**	**Application range[2]**	**Applicability in routine labs - (yes/no) or remarks**	**AA-QS[7] for inland (In) & transitional (Tr) waters**	**AA-QS[7] for coastal (Co) & territorial (Te) waters**	**MAC-QS[7]**	**Quality objective**
	XP X33-012	Mar-00	HPLC/UV or GC/MS				--				
Benzo(a)pyrene	*ISO 17993: 2002 or see PAH´s*		HPLC/Fluo				--	0.05 µg/l*	0.005 µg/l*	0.05 µg/l	
Benzo(b)fluoroanthene	*ISO 17993: 2002 or see PAH´s*		HPLC/Fluo				--	n.a.	n.a.	n.a.	
Benzo(g,h,i)perylene	*ISO 17993: 2002 or see PAH´s*		HPLC/Fluo				--	n.a.	n.a.	n.a.	
Benzo(k)fluoroanthene	*ISO 17993: 2002 or see PAH´s*		HPLC/Fluo				--	0.0054 µg/l*	0.00054 µg/l*	n.a.	
Indeno(1,2,3-cd)-pyrene	*ISO 17993: 2002 or see PAH´s*		HPLC/Fluo				--	n.a.	n.a.	n.a.	
Simazine	EN ISO 11369	Nov-97	HPLC/UV				no (1), yes (1)	< 1 µg/l (In)	1.1 µg/l (Tr, Co, Te)	4.2 µg/l	
	EN ISO 10695: 2000	Nov-00	GC/MS or GC/NPD				no (1), yes (1)				
	ISO 11370 2000	Jan-95	TLC, AMD-Technique				no (1)				
	US EPA 505	Jul-91	GC/ECD (MS for conf.)				--				
Tributyltin compounds	ISO/DIS 17353		GC/MS - FPD - AES	0.39 µg/l	24%	³ 0.39 µg/l	no (1), yes (3)	0.0001 µg/l	0.0001 µg/l	0.0015 µg/l	
	WD DIN 38414-XX	??					no (1), yes (1)				
	NF T 90-250	Jul-01	GC				--				
	ISO/AWI 23161	Apr-02	GC/MS				--				
Trichlorobenzenes	EN ISO 6468	Feb-97	GC/ECD	0.182 µg/l	35%	³ 0.182 µg/l	no (1), yes (3)	1.8 µg/l	0.4 µg/l	50 µg/l	**0.4 µg/l**
	US EPA 8081		GC/ECD				yes (1)				
	Draft ISO 15680 [5]	Sep-01	Purge/Trap + Therm. Desorp.	0.2 µg/l	35%	³ 0.2 µg/l	--				
Trichloromethane	EN ISO 10301	Aug-97	GC or Headspace-GC-ECD or other				yes (4)	3.85 µg/l	3.85 µg/l	38.5 µg/l	12 µg/l
	Draft ISO 15680 [5]	Sep-01	Purge/Trap + Therm. Desorp.	0.2 µg/l	35%	³ 0.2 µg/l	--				
Trifluralin	EN ISO 10695: 2000	Nov-00	GC/MS or GC/ECD or GC/NPD				no (2), yes (2)	0.03 µg/l	0.03 µg/l	0.42 µg/l	
	ISO 11370 2000	Jan-95	TLC, AMD-Technique				no (1)				

Priority Substance	**Available standard method (Ref.)**			**Specific ring trial data for surface water**			**Method-Applicability**	**Proposals for Quality standards for PS of the WFD**			**76/464/EEC**
	Standard	**Year**	**Principle**	**Lowest conc.** [3]	**S_R**[3]	**Application range**[2]	**Applicability in routine labs - (yes/no) or remarks**	**AA-QS[7] for inland (In) & transitional (Tr) waters**	**AA-QS[7] for coastal (Co) & territorial (Te) waters**	**MAC-QS[7]**	**Quality objective**
DDT	*EN ISO 6468*		GC/ECD	0.015 µg/l	37%	[3] 0.015 µg/l	--	n.a. (proposal at a later date)			10 µg/l (25 µg/l total)
Aldrin	*EN ISO 6468*		GC/ECD				--	n.a. (proposal at a later date)			**10 µg/l**
Endrin	*EN ISO 6468*		GC/ECD	0.051 µg/l	22%	[3] 0.051 µg/l	--	n.a. (proposal at a later date)			**5 µg/l**
Isodrin		--	--				--	n.a. (proposal at a later date)			**5 µg/l**
Dieldrin	*EN ISO 6468*		GC/ECD	0.031 µg/l	52%	[3] 0.031 µg/l	--	n.a. (proposal at a later date)			**10 µg/l**
Tetrachloroethene	*EN ISO 10301*		GC or Headspace-GC-ECD or other				--	10 µg/l	5.1 µg/l	36 µg/l	10 µg/l
Tetrachloromethane	*EN ISO 10301*		GC or Headspace-GC-ECD or other				--	7.2 µg/l	7.2 µg/l	24.6 µg/l	12 µg/l
Trichloroethene	*EN ISO 10301*		GC or Headspace-GC-ECD or other				--	10 µg/l	10 µg/l	210 µg/l	10 µg/l

EN = European Standard
ISO = International Standard
DIN = German Standard
DIN V = German Pre-standard
WD = Working Draft

Format code :
black = conc. ≤ AA-QS
red (normal) = conc. ≤ AA-QS for In & Tr
but > AA-QS for Co & Te
red bold = conc. > both AA-QS

[1] The proposed application range derives from chapter "Scope of the method"
[2] The application range for surface water corresponds to the lowest concentrations for which tests of precision and bias have been carried out, according to the definition in ISO/TR 13530, 1997-09
[3] Concentrations of the analyte(s) in the intercomparison samples used for the determination of repeatability and reproducibility; S_R = relative reproducibility standard deviation
[4] Performance data according to ISO 5725
[5] Standard is part of CEN working programm (2001-11)
[6] ≥ 0,01 µg/l for surface water, ≥ 0,005 µg/l for drinking water
[7] Two kinds of quality standards are proposed, referring to (1) annual average concentration **AA-QS** and (2) short term concentration peaks, maximum admissible concentration **MAC-QS**

Format code:
Priority Substance normal format = WFD priority substance
Priority Substance italic format = 76/464/EEC priority substance or quality standard proposed
Priority substance in black = at least one method with application range ≤ AA-QS or 76/464/EEC quality objective
Priority Substance red (normal) = available methods with application range ≤ AA-QS for In & Tr but > AA-QS for Co & Te
Priority Substance red & bold = no standard method available at all or no available method with application range £ AA-QS for In & Tr nor for Co & Te

values in red are lower than propsed QS

- "specific QS"

[D] = Drinking water
[G] = Ground water
[S] = Surface water
[W] = Waste water
[Std.] = standard solution
[Dist.] = distilled water

Annex 2

Water Framework Directive / Priority Substances

Analytical determination of groups of substances
New analytical methods

- Proposal for Indicator Substances and Analytical Methods –

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Introduction and problem identification

Article 16 of the Water Framework Directive (2000/60/EC) sets out the Community strategy against pollution of water by dangerous substances. According to the provisions of this article, a list of priority substances was established which represent a significant risk to or via the aquatic environment at Community level. Following the proposals of the European Commission in February 2000 and January 2001 and the first Parliament's reading, Council and European Parliament agreed to a list of 33 substances on 7 June 2001. The list of priority substances was finally published in December 2001 (Decision No 2455/2001/EC).

Four priority substances, namely polybrominated diphenyl ethers (PBDEs), C_{10}-C_{13}-chloroalkanes (short-chain chlorinated paraffins, SCCPs), nonylphenols and octylphenols (the last two summarized as alkylphenols in this paper) comprise groups of chemicals consisting of a few to several thousands of positional isomers. For the time being, only an ISO committee draft for the determination of alkylphenols in surface water (ISO/CD18857-1) and a first working draft for the determination of polybrominated diphenyl ethers in sludge and sediments (ISO/WD 22032) are available. For SCCPs, there is neither an agreed analytical reference method nor does a well-defined set of „indicator substances“ exist as for other pollutants e.g. PAH or PCB. For this reason, monitoring data, which are available for SCCPs often, relate to different quantification methods and calibration substances (e.g. different technical mixtures). This makes the comparison and assessment of published data difficult if not impossible.

Comparability of analytical data clearly is a prerequisite for the assessment of monitoring results as well as for the establishment of harmonised environmental quality standards at Community level. Therefore, it is suggested, that the expert advisory forum EAF may attempt to make strong efforts to identify indicator substances for each of the three groups to be analysed obligatory or to define reference methods for the determination of the total content of the priority chemicals as sum parameter.

At present, a variety of different high-sophisticated analytical methods for the determination of the three groups of substances are available on research level often lacking proper validation by interlaboratory studies. At the moment, it seems to be difficult to recommend one or the other of the published analytical procedures. The identification of single reference methods would probably exclude a number of methods with similar performance characteristics and therefore, not be approved on Community level. Hence, it is proposed to favour the identification of indicator substances which shall be analysed obligatory associated with proper calibration standards and the definition of minimum performance criteria for analytical methods rather than to focus on single reference methods for each of the three priority chemicals.

In order to inspire the discussion at European level, this paper sets out in the annex a number of concrete proposals based on background information, found in the literature as well as on recent experience in the analysis of the priority substances under discussion gained during pilot studies which have been carried out by the German and Austrian Federal Environmental Agencies, respectively. It is organised as follows.

„Information on composition and production volume of technical mixtures “
„Indicator substances"
„Standard material”
„Analytical method“

Under section „Information on composition and production volume of technical mixtures” some information is provided regarding the individual compounds of each group of substances under discussion contained in technical products. On the basis of data on toxicity, production volumes and occurrence in environmental samples, most important representatives for each group of substances are identified.

In section „Indicator substances" a concrete proposal for individual substances to be analysed is provided.

Section „Standard material“ contains some details regarding the availability of analytical standards for identification and quantification purposes with emphasis on the compounds proposed for analysis in the previous section as well as information on certified reference materials (CRMs) as far as available.

In section „Analytical method“ the literature on analytical methods is summarised, advantages and limitations of the different procedures will be discussed and proposals for analysis and quantification of the three priority chemicals will be given.

Finally, in section "Need for Action" problems are identified which need further consideration and/or research work to end up with analytical procedures which are capable to provide accurate and comparable results.

Short-chain chlorinated paraffins (C_{10}-C_{13})

Information on composition of technical mixtures and production volume

Short-chain chlorinated paraffins (SCCPs) are polychlorinated n-alkanes (C_{10}-C_{13}) with chlorine content ranging from 49 to 70% by weight. They are used mainly in metal working fluids for a variety of engineering and metal working operations such as drilling, machining/cutting, drawing and stamping. SCCPs are also used in sealants, as flame retardants in rubbers and textiles, in leather processing and in paints and coatings [1]. Production figures for SCCPs are hard to find in the literature. Based on EURO-Chlor information, the total EU production volume was 15,000 t/year or less in 1994 and about 4,000 t/year in 1998 [2]. It is thought that the current level is probably lower than this, particularly due to reduction in uses of SCCPs, especially in the metalworking industry. SCCPs are manufactured by chlorination of liquid n-paraffin. In Western Europe, major producers are INEOS CHLOR and CAFFARO.

Risk assessment for short chain chlorinated paraffins has been completed under Regulation 793/1993/EEC [1]. SCCPs are classified as dangerous to the environment, being very toxic to aquatic organisms and may cause long-term adverse effects in the aquatic environment. The Commission has adopted a recommendation to take measures to restrict the use of SCCPs, in particular in metal working fluids and leather finishing products in order to protect the aquatic environment [3].

Indicator substances

It seems not possible to identify indicator compounds for routine quantitative analysis of SCCPs.

Standard material

Until recently technical mixtures with known chlorine content have been used for calibration purposes. An international interlaboratory study [4] indicated that some of the observed variability in the analytical results may be introduced when different commercial formulations are used as external standards. These results were confirmed by [5] who investigated the influence of carbon chain length and chlorine content of the external standard used for quantification on the analytical results. In this study, SCCP concentrations of fish samples were quantified using several individual polychlorinated alkane standards and a commercial formulation. Results varied widely (by a factor of ten) depending on chlorine content of the standard used. These findings emphasise the importance of the choice of suitable standards for quantitative analysis. The authors showed that technical SCCP mixtures should not be used as standards in many cases because the SCCP carbon chain pattern in various fish species varied considerably and did not resemble that of the technical formulation.

Recently, numerous synthetic individual SCCPs of particular carbon chain length and different degree of chlorination have become available from Dr. Ehrenstorfer GmbH, Augsburg, Germany. These are:

Chloroparaffin C10, chlorine content 44.82%, 50.18%, 55.00%, 60.09% and 65.02%, respectively.

Chloroparaffin C11, chlorine content 45.50%, 50.21%,55.20%,60.53% and 65.25%, respectively.

Chloroparaffin C12, chlorine content 45.32%, 50.18%, 55.00%, 65.08% and 69.98%, respectively

Chloroparaffin C13, chlorine content 44.90%, 50.23%, 55.03%, 59.98% and 65.18%, respectively.

A final recommendation what standard to be used for quantification of SCCPs in environmental samples can not be given at the moment.

Analytical method

Extraction and clean-up techniques for the analysis of SCCPs in biological samples and sediments are quite similar to those developed for the analysis of other halogenated compounds such as PCBs and chlorinated pesticides. Most procedures are based on batch or Soxhlet extraction with organic solvents, clean-up of the extracts by adsorption and gel permeation chromatography and determination by gas chromatography electron capture [6] or mass spectrometric detection [7-11]. Another approach is carbon skeleton analysis by gas chromatography with flame ionisation detection after simultaneous dechlorination and hydrogenation [12,13]

An accurate chemical analysis of SCCPs in environmental samples is difficult to achieve due to the highly complex nature of commercial formulations, the impact of numerous physical, chemical and biological processes after use, and the lack of certified chemical standards. SCCPs are very complex mixtures containing many congener groups chlorinated to various degrees and positions on the carbon backbone. The theoretical maximum number of positional isomers calculated for n-$C_nH_{2n+2-z}Cl_z$, assuming no more than one bound chlorine atom on an carbon atom, for SCCPs is 7820 [14]. However, the complexity of SCCP mixture is further enhanced because chlorine substitution at a secondary carbon atom usually produces a chiral carbon atom so that enantiomers and diastereomers will be generated. Furthermore, although the hydrocarbon feedstocks used to prepare SCCPs are primarily *n*-alkanes, they do contain branched alkanes and probably other hydrocarbons which would also add to the complexity of the mixtures. Even if only a small percentage of the theoretically possible number of chloroalkanes are readily formed, it can be assumed that commercial SCCP formulations contain many thousand compounds.

There are three different approaches to analyse SCCPs in environmental samples, these are:

Carbon skeleton analysis after simultaneous catalytic dechlorination and hydrogenation by gas chromatography [12,13], gas chromatography with electron capture detection [6] and gas chromatography-mass spectrometry in the negative chemical ionisation mode [see e.g. 7-11].

Due to the lack in sensitivity and selectivity – no information on the degree of chlorination of the SCCPs can be achieved - the first approach will not be considered further. GC-ECD analysis of SCCPs is quite unspecific. Since the compounds of interest elute over a wide retention time range, an unequivocal identification is not possible due to interferences from other halogenated compounds, even when applying lengthy and expansive clean-up procedures and using several stationary phases of different polarity.

Therefore, electron capture negative ionisation mass spectrometry (ECNI-MS) at low or high resolution is generally favoured.

To obtain reliable results, the variability of the mass spectra of SCCPs in dependence on degree of chlorination and ion source temperature and to a lesser extent on chain length of the carbon skeleton has to be taken into consideration [15, 16]. At 250°C, mass spectra of higher chlorinated SCCPs are characterised by a peak cluster representing the $[M-Cl]^-$ fragment ion for all chlorination degrees with an relative intensity ranging from some 50 to 65%. The relative intensities of the $[M]^{-\cdot}$, $[M-HCl]^{-\cdot}$, $[M-2HCl]^-$ and $[M-HCl_2]^-$, are around or below 10%. At low ion source temperature (100°C), $[M-Cl]^-$ and $[M-HCl]^-$ are most prominent ion clusters with higher intensity of the latter for lower chlorinated SCCPs. Fragmentation is shifted to $[M-Cl]^-$ with increasing degree of chlorination. The relative response factors of SCCP mixtures vary by one order of magnitude depending on the degree of chlorination with lowest response factors for the low chlorinated mixtures (chlorine content 45 to 50%). Compared to the influence of chlorination degree on the fragmentation, that of carbon skeleton chain length is less important [15].

$[M+Cl]^-$ as well as $[M-Cl]^-$ ions were reported in the ECNI mass spectra of synthesised lower chlorinated SCCPs [16]. Their abundances decreased with increasing ion source temperature, while the abundances of the structurally non-characteristic ions, $[Cl_2]^{-\cdot}$ and $[HCl_2]^-$, increased.

Jansson et al. [7, 8] analysed environmental samples using GC-ECNI-MS in the selected ion monitoring mode after selective clean-up. Structurally non-characteristic $[Cl_2]^{-\cdot}$ and $[HCl_2]^-$ ions at m/z = 70 to 73 that predominate in the mass spectra of SCCPs at high ion source temperatures were recorded. A similar approach was used by Nicholls et al. [11]. They analysed SCCPs and MCCPs in water, sediment, sewage sludge and biota samples from selected industrial areas in England and Wales. SCCPs were determined in sample extracts using GC-ion trap mass spectrometry operated in the negative chemical ionisation mode.

Three technical products were chosen for reference calibration purposes. The analysis and quantification of formulations identified in sample extracts was undertaken by a two-step GC-MS process:

1. qualitative identification of formulation type
2. quantitative analysis based on the response characteristics summed across the mass region m/z = 70 to 75 corresponding to $[Cl_2]^{-\cdot}$ (70, 72, 74) and $[HCl_2]^-$ (71,73,75) for most appropriate calibration standard

Average recoveries of SCCPs from spiked sediments (1-2 mg/kg, n=8) were 84%. The limit of determination was equivalent to a SCCP formulation containing 1 ng/µl in solution. Within batch repeatability for the GC-MS measurement using the internal standard method was in the range 6-10% RSD (n=10) for SCCP.

Procedures based on monitoring structurally non-characteristic fragment ions corresponding to $[Cl_2]^{-\cdot}$ and $[HCl_2]^-$ present the problem that many other halogenated compounds fragment to yield such ions, e.g. p,p'-DDT, p,p'-DDE, lindane, dieldrin, aldrin and endrin. Thus, if these contaminants are not completely removed from the sample matrix during extraction and clean-up, they ultimately contribute to the response of the quantification ions $[Cl_2]^{-\cdot}$ (m/z = 70, 72, 74) and $[HCl_2]^-$ (m/z = 71, 73, 75) and lead to an overestimation of SCCPs.

Recently, Tomy et al. [9] published a method for quantifying SCCPs in environmental samples by high-resolution gas chromatography/electron capture negative ion high-resolution mass spectrometry in the selected ion monitoring mode at an ion source temperature of 120°C. The molecular compositions of commercial SCCPs and of SCCP-containing extracts were determined by monitoring the two most intensive ions in the $[M-Cl]^-$ cluster, one for quantification and the other for confirmation for the following formula groups: C_{10} (Cl_5 to Cl_{10}), C_{11} (Cl_5 to Cl_{10}), C_{12} (Cl_6 to Cl_{10}), and C_{13} (Cl_7 to Cl_9), and assuming that integrated signals are proportional to molar concentrations weighted by the number of chlorine atoms in the formula group. Quantification was achieved by selecting the biggest peak corresponding to $[M-Cl]^-$ ion in the most abundant formula group present in the sample and correcting for variations in the formula group abundances between standard and sample. It has been shown that high-resolution mass spectrometry eliminates self-interferences between SCCPs and potential interferences from chlordanes, toxaphenes, PCBs and other organochlorine pesticides. Recoveries of SCCPs from fish averaged >80%. The analytical detection limit was 60 pg of injected SCCP at a signal-to-noise ratio of 4:1, while method detection limit was 23 ng/g.

Although the proposed method seems to be a suitable approach to analyse SCCPs in environmental samples on the research level, its application for routine analysis is questionable due to the use of a high-resolution mass spectrometer for detection that is not available in most environmental laboratories responsible for routine monitoring, its complexity and the observed variability in results as shown in a recent interlaboratory study [4].

Coelhan [10] proposed a short-column GC-ECNI-MS method for the determination of SCCPs in fish samples that dispenses with chromatographic separation. Only a short capillary column of 62 cm length (thereof 42 cm in the interface) is coupled to a low resolution mass spectrometer operated in the negative ionisation mode at an ion source temperature of 100°C using methane as reagent gas. SCCPs in fish samples were identified by comparison of mass spectra of sample extracts with those of synthesised polychlorinated alkanes and of CERECLOR 63L. The quantification was performed by reintegration of selected ions from full-scan spectra. Without chromatographic separation, all SCCPs elute from the column as only one peak. Consequently, this leads to an enormous increase in sensitivity and makes it more easy to survey the mass spectra. If the SIM mode is used, an additional enhancement in sensitivity is possible. Detection limits in the full- scan mode ranged from 10 to 100 pg depending on carbon chain length of the n-alkane and on the degree of chlorination. Recoveries of SCCPs from spiked herring oil averaged to 112% for the low spiking level (200 ng/g) and to 102% for the high dose (800 ng/g). Since no chromatographic separation has to be achieved, time of analysis is only one minute. Due to dispensing with chromatographic separation complete removal of all other halogenated compounds, which might interfere with the determination of SCCPs is a fundamental requirement.

Methods that monitor ions at nominal mass present the primary problem that interferences from higher chlorinated PCBs, toxaphenes and chlordane-related compounds, all of which elute in the retention time range of SCCPs and have similar molecular masses to SCCPs, can not be excluded of a certainty.

Although some work has been conducted on development of selective and sensitive methods for SCCP analysis in recent years no validated procedure is available at present that meets the specific requirements of WFD and which could be recommended for routine monitoring of SCCPs in environmental samples. Taking into account all information available GC-ECNI-MS seems to be the most appropriate technique for quantitative analysis of SCCPs at the required low concentration levels.

Need for Action

Preparation of certified reference materials (standard solutions, sediment and biota samples)

Methods for the analysis of SCCPs require the use of surrogate standards (usually ^{13}C- labelled) and certified or standard reference materials (CRMs or SRMs). For the time being, there are neither standard reference materials for calibration purposes nor isotopically labelled reference standards, and no reference materials have yet been certified for SCCP content. However, SCCPs were found in two SRMs from the National Institute for Standards and Technology (NIST). SRM 1588, a cod liver oil extract and SRM 1945 a whale blubber extract contained 49 and 172 ng/g of ΣSCCPs, respectively [14]. These SRMs are, therefore, possible candidates for future certification.

Development of analytical methodologies for the determination of SCCPs in environmental samples

As outlined in section "Analytical method" there is no validated analytical procedure available for routine monitoring of SCCPs in environmental samples. Method development should focus on appropriate calibration protocols, improvement in clean-up methods and optimisation of mass spectrometric detection preferably using electron capture negative ionisation low resolution mass spectrometry. Furthermore, in- house validation studies comparing the most promising approaches GC-ECNI-LRMS, GC-ECNI-HRMS and short-column GC-ECNI-LRMS are highly recommended.

Development of an European standard for the determination of SCCPs in sediments

The responsible ISO/TC 147 "Water quality" has not started any standardisation work on this issue yet, mainly due to the lack of validated analytical protocols from research laboratories which might be used as basis for standardisation work.

Establishment of Laboratory Performance Studies on the determination of SCCPs in sediments and biota in the near future.

Polybrominated Diphenyl Ethers

Information on composition of technical mixtures and production volume

There are 209 theoretical congeners of which only a few are present in technical formulations. The individual congeners are numbered according to the IUPAC system used for the numbering of PCBs based on the position of the halogen atoms on the rings. The major technical products are Penta-, Octa- and DecaBDE. The consumption of PBDEs for 1999 within the European Community was estimated to be 210, 450 and 7,500 tons, respectively [17]. Each product is a mixture of diphenyl ethers of varying degree of bromination. Although there is no guarantee that the composition of products from different manufacturers is the same, the proportion of the main components seems to be of the same order. According to information of BSEF the technical Penta-mix consists of 33.7 % tetraBDE, 54.6% pentaBDE and 11.7% hexaBDE whilst the Octa-Mix contains 35.5% hexaBDE, 42% heptaBDE, 36% octaBDE 13.9% nonaBDE and 2.1% decaBDE. Technical DecaBDE contains 3% nonaBDE and 97% decaBDE. For a typical commercial PentaBDE (Bromkal 70-5DE) Sjödin et al. [18] reported the following main constituents: 35% BDE-47, 37% BDE-99, 6.8% BDE-100, 3.9% BDE-153, 2,5% BDE-154, and 1.6% BDE-85. From this follows that five congeners contribute more than 80% to the technical mixture and should be considered when analysing for PentaBDE classified as priority hazardous chemicals. The main PBDEs reported in environmental samples are 2,2',4,4'-TetraBDE (BDE-47), 2,2',4,4',5-PentaBDE (BDE-99), 2,2',4,4',6-PentaBDE (BDE-100), 2,2',4,4',5,5'-HexaBDE (BDE-153), 2,2',4,4',5,6'-HexaBDE (BDE-154) and 2,2',3,3',4,4',5,5',6,6'-DecaBDE (BDE 209) [18]. 2,2',3,4,4',5',6-HeptaBDE (BDE183) may also be of importance as this is one of the main constituents of the technical OctaBDE formulation, but up to now only a limited number of data are available for this congener. A small number of other BDE congeners have been found in environmental samples occasionally including BDE-28, BDE-85, BDE-66, BDE-138, BDE-71, BDE-75 but only at low concentrations. Tetra- to hexabrominated congeners dominate in biota samples with highest concentrations for BDE 47 whilst DecaBDE is the most important BDE in sediment and solid particulate matter (SPM) with regard to frequency of occurrence and concentration level [17].

For pentabromodiphenyl ethers risk assessment under Regulation EEC No. 793/93 has been completed and identified unacceptable risks from use in polyurethane foams [19]. For octa- and decabromodiphenyl ether risk assessment is in progress.

Indicator substances

Technical Pentabromodiphenyl ether

2,2´,4,4´-Tetrabromodiphenyl ether (BDE-47)
2,2´,4,4´,5-Pentabromodiphenyl ether (BDE-99)
2,2´,4,4´,6-Pentabromodiphenyl ether (BDE-100)
2,2´,4,4´,5,5´-Hexabromodiphenyl ether (BDE-153)
2,2´,4,4´,5,6´-Hexabromodiphenyl ether (BDE-154)

Technical Octabromodiphenyl ether

2,2´,3,4,4´,5´,6-Heptabromodiphenyl ether (PDBE 183)

Technical Decabromodiphenyl ether

2,2',3,3',4,4',5,5',6,6'-Decabromodiphenyl ether (BDE-209)

Standard material

According to the increasing awareness of flame retardants as possible sources of environmental pollution two standard manufacturers (Cambridge Isotope Laboratories and Wellington Laboratories, Inc.) have reacted and offer now a wide range of unlabelled and ^{13}C-labelled polybrominated diphenyl ether standard solutions and standard mixtures as well as samples of technical products. The offered standard solutions include the proposed indicator substances. The most important suppliers for polybrominated diphenyl ethers are:

- Cambridge Isotope Laboratories, Andover. MA, U.S.A.
- Wellington Laboratories, Inc., Guelph, Ontario, Canada
- Dr. Ehrenstorfer GmbH, Augsburg, Germany
- Greyhound chromatography, Birkenhead, U.K.
- LGC Promochem GmbH, Wesel, Germany
- Accustandard, Inc., New Haven, CT, U.S.A.

Analytical method

Extraction and clean-up techniques for the analysis of PBDE residues in biological samples and sediments are quite similar to those developed for the analysis of other halogenated compounds such as PCBs and chlorinated pesticides. Most procedures are based on batch or Soxhlet extraction with organic solvents, purification of the extracts by adsorption and/or gel permeation chromatography and determination by gas chromatography with electron capture, atomic emission or mass spectrometric detection [see 20-24].

Both GC-MS with electron impact or electron capture negative ionisation may be used for final analysis of PBDEs. Another variety of GC-MS method is gas chromatography with high resolution mass spectrometric detection. Due to the fact that some of the individual compounds are very similar in their chemical and physical behaviour, a separation method with high resolution power is necessary. In a recent study retention times of 34 (Br_2-Br_7) BDE congeners on a 30 m 5% diphenyl-95%-dimethylsiloxane type column were compared to those of 131 commonly observed PCB congeners and 26 organochlorine pesticides. Results from this study indicate that there is a potential for co-elution of 10 PBDE, PCB's and organochlorine pesticides. Of particular concern is the interference of BDE-47 the predominant congener in biota samples with CB-180 [25]. The brominated biphenyl congener 153 and Tetrabromobisphenol A can co-elute with BDE-154 and BDE-153, respectively, when using non-polar capillary columns [20]. Therefore, mass spectrometric detection should be preferred. Since the ECD responds also to other halogenated compounds its use seems possible only for BDE-209. This congener has a very long retention time and no of the other environmental relevant halogenated compounds elute in this area of the chromatogram. The analysis of BDE-209 is considerably more complicated than that of most lower brominated diphenyl ethers. BDE-209 is subject to degradation when exposed to daylight in the laboratory, and at higher temperatures. Therefore, the use of amber glassware is recommended for analysis of DecaBDE. In addition it should not be exposed to high temperatures for long time periods. This implies that the final temperature of the oven programme should not exceed 320°C for more than a few minutes. Consequently, short GC columns should be used for the analysis of this compound. By separate instrumental analysis of BDE-209 on a short column and of all other congeners using e.g. a 50 m column, thermal degradation of BDE-209 is prevented while adequate resolution of the other BDEs is ensured. However, a recent intercomparison exercise between three laboratories showed that combined analysis of all BDEs on a single 25 m capillary columns resulted in reliable results for BDE 209 as well as the lower brominated congeners [26]. That approach offers the advantage of considerable reduction in time for gas chromatographic analysis.

Both high resolution (HRMS) and low resolution (LRMS) instruments are used for GC-MS analysis of PBDEs in environmental samples. In principle, HRMS is preferred because of its higher selectivity, however, it has not been demonstrated that in practice GC-HRMS is superior to GC-LRMS [23, 26]. Most often used LRMS technique is based on electron capture negative ionisation (ECNI) with methane or ammonia as reagent gas that offers a considerable higher sensitivity than electron impact ionisation (EI). A drawback of the ECNI technique is that for most BDE congeners only ions due to bromine can be monitored (m/z=79/81). BDE-209 is the only conger which forms intensive mass fragments in the higher mass range, such as m/z = 484.7; 486.7 and 488.7. These ions can be used for quantification. EI-MS offers more selectivity and the possibility to confirm identity of compounds from their full scan mass spectra, but with considerable lower sensitivity. A recent study indicated that by combining GC/EI-MS with large volume injection and narrow bore columns (I.D. 0.1mm) a sensitivity can be obtained which is comparable to that of ECNI-MS [27].

Unlabelled and ^{13}C-labelled analytical standards are now available for many congeners but the selection of appropriate internal standards is still problematic. When applying EI mass spectrometry ^{13}C-labelleld BDEs can be generally used but in case of ECNI technique labelled compounds are of little value as only bromine ions are usually being monitored. The only exception is BDE-209 where the labelled congener can be used successfully as internal standard.
The following compounds were used as internal standards for PBDE analysis:

^{13}C-labelled BDEs, BDEs not occurring in technical mixtures and never being found in environmental samples such as BDE-15, BDE-77, BDE-181, BDE-190, decabromobiphenyl, chlorinated biphenyls, ^{13}C-labelled chlorinated biphenyls, ^{13}C-labelled chlorinated diphenyl ethers, dechlorane and tetrachloro-p-terphenyl [22]

From reported environmental concentrations of PBDEs [17] it can be concluded that due to its low sensitivity GC-LRMS in the electron impact mode is not appropriate to monitor the concentrations of BDE congeners in sediments, suspended particulate matter and biota to be expected in European river systems in most cases. Therefore, GC-ECNI-LRMS and GC-HRMS seem to be the methods of choice for the analysis of PBDE in environmental samples. This is reflected in recent publications on analytical methodologies for the determination of PBDEs (19, 21-24) and in methods used by the participants of the first world-wide interlaboratory study on polybrominated diphenyl ethers [26]. Instrumentation for HRMS is much less common in routine environmental laboratories and more expensive than that for GC-ECNI-MS.

Taking into account all information available at the moment GC-ECNI-MS seems to be the most appropriate technique for quantitative analysis of PBDEs in environmental samples at the required low concentration levels.

In May 2002 a first working draft "Water quality - Determination of polybrominated diphenyl ethers in sediments and sewage sludge" (ISO/WD 22032) has been presented for discussion by ISO/TC 147 on its meeting at Orlando, Florida. Both GC-LRMS and GC-ECNI-MS are included but many of the technical details have not been agreed upon yet. Approval as committee draft can be expected in 2003 at the earliest.

Need for Action

Preparation of CRMs (biota and sediment)

No Certified reference materials for PBDEs are available at present. However, some analyses have been carried out on fish reference materials with certified concentrations for other organic contaminants, which indicated the presence of PBDEs in those materials [22]. These materials might be useful for QA/QC and method validation. Netherlands Institute for Fisheries Research (RIVO) is working on a feasibility study on the preparation of CRMs for PBDS in biological samples and sediments.

Further improvement of analytical methodologies for the determination of PBDEs with emphasis on the analysis of BDE-209

The first world wide inter-laboratory study on PBDEs was performed in 2000. It involved five biological samples, two sediments and two standard solutions. Results reported were acceptable for BDE-47 with a range of relative standard deviations (Rsd) of 17 to 40%, Results for BDE-99 (Rsd 25-77%), BDE-100 (Rsd 19-48%), BDE-153 (Rsd 30-48%) and BDE-154 (25-43%) showed a need for further improvement of the analysis of these congeners. The analysis of BDE-209 was not under control by the participating laboratories [26]. Results of the second international interlaboratory study on brominated flame retardants were reported, recently [28]. Progress was made with regard to reproducibility of analytical results for some BDE congeners, e.g. BDE-99, but analysis of BDE-209 is still not under control by the majority of laboratories. A coefficient of variation (CV) of 65% (n=13) was obtained for the analysis of a sediment sample.

Establishment of regular Laboratory Performance Studies on the determination of PBDE in biota and sediments

The QUASIMEME Laboratory Performance Studies (Aberdeen, UK) has organised a development exercise for brominated flame retardants in biota, sediment and milk in 2002 [28]. A new developing exercise is planned in 2003.

Alkylphenols (Nonylphenols/Octylphenols)

Information on composition of technical mixtures and production volume

Commercially produced nonylphenols contain predominantly 4-nonylphenol with a varied and undefined degree of branching in the alkyl group. According to product data sheets of some nonylphenol manufacturers the two most important impurities in commercial 4-nonylphenol are 2-nonylphenol (up to 10 % w) and 2,4-dinonylphenols (up to 1 % w). Due to the manufacturing process no 4-n-nonylphenol is present in commercial products. Therfore this isomer seems to be suitable as internal standard for analysis.

The most comprehensive source for production and usage data yet available seems to be the report of the risk assessment conducted under Regulation EEC No 793/93 [29]. According to this report 73500 t of production capacity within the EU, 3500 t exports and 8500 t of imports give 78500 t of nonylphenol used in 1997. Nonylphenol is a raw material for the manufacture of i.a. nonylphenol ethoxylates, modified phenolic resins, plastics, stabilisers and phenolic oximes. More than half of the nonylphenol production (some 60% in 1997) is used for manufacturing nonylphenol ethoxylates.

Production data for octylphenol are even scarcer. Although theoretically several isomers in the alkyl part are possible, only the 4(1,1,3,3-tetramethylbutyl)-phenol (4-tert-Octylphenol) seems to be of relevance due to the manufacturing process, that is the reaction of 2,2,4-trimethylpentane with phenol. Production in the EU is reported to be 6800 t in 1998, thereof 5000 t are estimated to be used for the production of octylphenoxy ethoxylates [30]. The use pattern seems to differ to some extent from nonylphenol.

Besides their high aquatic toxicity nonylphenols show endocrine disrupting effects but only alkylphenols with the alkylgroup in para-position have been identified as estrogenic active compounds. Octylphenols show a higher endocrine disrupting potential than nonylphenols [31].

Risk assessment for nonylphenol and 4-nonylphenol (branched) has been completed under Regulation 793/1993/EEC [29]. A need for limiting the risks to due to the toxicity and estrogen activity of nonylphenol has been idientified. The risks from other degradation products of alkylphenolethoxylates (see below) has not been adressed in this study.

Nonylphenols (NPs) and octylphenol (OP) found in the environment do not stem from the production process and use of NP and OP itself but are mainly degradation products of the non-ionic surfactants nonylphenol polyethoxylates (NPEOs) and octylphenol polyethoxylates (OPEOs).

Alkylphenol polyethoxylate (APEO) surfactants are used worldwide in various industry, agricultural, and household applications. Industrial uses include the manufacture of plastics, textiles, paper, and agricultural chemical products. Commercial blends of APEOs are polydisperse mixtures of isomers (alkyl chain branching) and oligomers (2 to 20 ethoxy units). The biodegradation pathway of APEOs to short-chain ethoxylate (APE$_{1-3}$O), and ethoxy carboxylate metabolites (APE$_{1-3}$C) is well established. The polyethoxylate chain of 1 to 20 ethoxy units is shortened during aerobic and anaerobic wastewater treatment processes, or in river waters if discharged directly (Figure 1). APECs are relatively water soluble, so that the concentrations of APECs in river water are typically higher than that of the short-chain ethoxylated APEOs or APs, which have lower water solubilities [33-37].

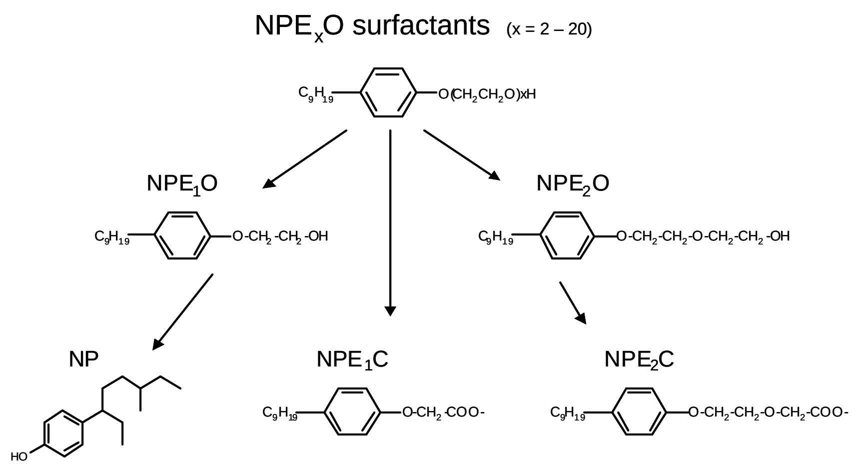

Figure 1: Endocrine disrupting metabolites of NPEO surfactants.

NP is lipophilic with reported octanol-water partition coefficients in a range of log Kow = 3.01 – 4.48. Thus, moderate to high adsorption potential to the soil matrix can be expected. NP behaves as a weak acid with a p_{ka} of 10.7. Ionisation under neutral to alkaline conditions influences its solubility and sorption to solid matrices; it accumulates in anaerobically digested sewage sludge [38].

APEOs are biodegradable materials that are effectively removed in well-functioning biological WWTPs. Biodegradation of APEOs occurs via ether cleavage which leads to the formation of short-chain APEOs, mostly mono- (APE_1O), di- (APE_2O), and triethoxylates (APE_3O). Under aerobic conditions carboxylation of the terminal alcoholic group with production of more persistent nonylphenol polyethoxycarboxylates (APECs) occurs. These APEO metabolites formed are more toxic than their parent compounds, and more bioaccumulative in aquatic organisms. APEOs with short ethoxy chains (1-3) are lipophilic, while those with long chains are hydrophilic [35,38].

Indicator substances

4-Nonylphenol
4-Nonylphenol mono-ethoxylate, NPE_1O
4-Nonylphenol di-ethoxylate, NPE_2O
4-Nonylphenoxy acetic acid, NPE_1C
4-Nonylphenoxyethoxy acetic acid, NPE_2C

4-Octylphenol
4-Octylphenol mono-ethoxylate, OPE_1O
4-Octylphenol di-ethoxylate, OPE_2O
4-Octylphenoxy acetic acid, OPE_1C
4-Octylphenoxyethoxy acetic acid, OPE_2C

Standard material	Supplier
4-Nonylphenol, technical mixture of isomers	Aldrich
4-Octylphenol	Aldrich
4-n-Nonylphenol	Dr. Ehrenstorfer
4-n-Nonylphenol, d8	Dr. Ehrenstorfer
4-Nonylphenol mono-ethoxylate, NPE_1O	Dr. Ehrenstorfer
4-Nonylphenol di-ethoxylate, NPE_2O	Dr. Ehrenstorfer
4-Nonylphenol mono-ethoxylate, d2, NPE_2O	Dr. Ehrenstorfer
4-Octylphenol mono-ethoxylate, OPE_1O	Dr. Ehrenstorfer
4-Octylphenol di-ethoxylate, OPE_2O	Dr. Ehrenstorfer
4-Nonylphenoxy acetic acid, NPE_1C	Dr. Ehrenstorfer
4-Nonylphenoxy acetic acid, d2, NPE_1C	Dr. Ehrenstorfer
4-Octylphenoxy acetic acid, OPE_1C	Dr. Ehrenstorfer

Analytical Methods

The substance example alkylphenols (APs) shows the difficulty in the establishment of a common agreed analytical method for their determination in environmental matrices.
A literature review on existing methods for the determination of nonyl-, and octylphenol was conducted, which points out that many different analytical methods are existing. Nearly every laboratory uses in general it’s own procedure.

The analytical determination of alkylphenolic compounds is dominated by chromatographic methods. The collected literature data (Tables 1-2) show that gas chromatographic (GC) and liquid chromatographic (LC) separation techniques for the analysis of APs are used more or less in the same extent. However, in the last 10 years LC-MS gained in popularity and partially substituted GC-MS methodologies [39].

Also included in the review and the tables are shorter APEO surfactant metabolites (APE$_{1-3}$O), and carboxylated APE$_{1-3}$C compounds because they are often analysed together with the APs and also have an endocrine disrupting potential.

The list of priority substances of the WFD will be constantly revised. Also additional substances which are relevant for individual water basins have to be measured by the Member States. Due to the endocrine disrupting potential of the APEO metabolites APE$_{1-3}$O and APE$_{1-3}$C and the often higher concentration values found for these compounds compared to NP itself, they might in the future become priority substances.

The main difference in the separation efficiency of GC- and LC-methods is that GC reveals the presence of the different isomers of the alkyl chain – NP is detected as an isomer cluster peak consisting of approx. 10 peaks which spans a retention time window of 1-2 minutes – whereas in LC NP elutes in 1-4 peaks (Figure #). Thus, both separation principles have their pros and cons.

A very good and comprehensive review article on APEOs and their metabolites was published by Thiele et al. [34] in the year 1997, and recently a review on endocrine disrupting compounds (EDCs) by Petrovic et al. [39].

Liquid Chromatography

LC is predominantly performed by reversed-phase (RP)-LC, but also in the normal-phase mode (Table 1). In normal-phase HPLC, the APEOs are separated according to the increasing number of ethylene oxide units, RP-HPLC separates the oligomers only slightly. RP-LC allows the separation of different alkyl-chain isomers. Detection is mostly conducted by electrospray ionization (ESI) mass spectrometry (MS), but also by fluorescence and UV. Another problematic fact for the comparison of the methods is that usually different LC eluants with diverse modifiers are used (Table 1).

Figure # shows the RP-HPLC separation of technical NP and 4n-NP. The isomers of the technical NP can be slightly separated, but it is normally more convenient to integrate and quantify only the first big peak. 4n-NP instead elutes as a single peak.

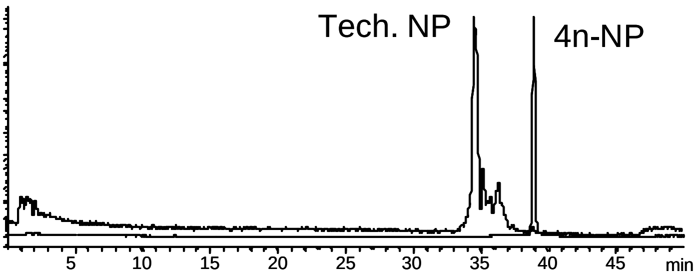

Figure: HPLC separation of technical NP and 4n-NP. Superspher 100 RP-18 column (250 x 2 mm, 4 µm particles), linear gradient from 20 to 90 % acetonitrile (water with 5 mM acetic acid) in 40 min and back to 20 % in 5 min at a flow rate of 0.4 ml/min. One results of the IES-JRC-Ispra (R. Loos).

Gas Chromatography

The main problem of the comparison of the GC methods is that APs are either analysed after derivatization of the hydroxy-group or without derivatization. The OH-group can be derivatized to e.g. acetyl-, methyl-, heptafluorobutyl-, pentafluorobenzoyl-, or trimethylsilyl ethers.

ISO-CEN [40] proposed a method for the determination of APs in water samples based on liquid extraction and GC analysis of the underivatized phenols. The water samples are acidified to pH 2 and are during 4 h extracted in a shaking device using toluene. Clean-up is performed with silica gel using n-hexane and toluene elution. NP is analysed by GC-MS in the SIM mode detecting the mass fragments m/z 135 and 107. These ions are formed during electron impact fragmentation of the alkyl-chain.

However, it has been reported that several problems are usually encountered with trace level analysis of phenolic compounds without derivatization. E.g., analyte losses due to adsorption in the GC inlet may occur. Moreover, peak tailing due to interaction of the analytes with active sites in the analytical column can be observed. With derivatization instead sharper peaks are obtained. Consequently, lower detection limits can be obtained. Another beneficial effect of derivatization is that much higher m/z values are formed, which increases analytical precision [41,42]. Meesters et al. [43] report that the application of a derivatization step – acetylation by acetic anhydride – led to a tremendous improvement in the SIM trace.

Problematic of the NP detection in its underivatized form is the detection of the small m/z fragment ions 107, 121, 135, and 149 (Table 2). This increases the probability of false positive responses due to interfering matrix constituents.

A problematic fact of the good separation efficiency of GC is that the NP isomer cluster of usually 12 peaks might complicate detection and quantification of “total NP” [42,43].

Extraction methods

Water extraction is mostly performed by liquid-liquid extraction (LLE) and solid-phase extraction (SPE). Also steam distillation, solvent sublation, and solid-phase microextraction (SPME) are used. SPE and SPME methodologies are gaining popularity due to simpler handling operations [38]. SPE is performed with C18, polymeric sorbents, or graphitized carbon blacks using different elution solvents (Table 3).

Solid samples like sediment, sewage sludge, fish, tissue, etc. are extracted by soxhlet, pressurized liquid extraction (PLE) also known as accelerated solvent extraction (ASE), steam distillation, supercritical hot-water extraction, supercritical fluid extraction (SFE), ultrasonic irradiation (sonication), microwave extraction, or SPE (Table 4).

All these extraction procedures yield different extraction efficiencies, also depending on the solvents and conditions used. Some scientists have compared different extraction methods. E.g., Meesters and Schroeder [43] performed a comparison of Soxhlet, steam distillation, supercritical fluid (SFE), and ASE extraction for the extraction of NP from sewage sludge and obtained the best results with ASE using ethylacetate-formic acid (9:1).

Pryor et al. [32] performed an analytical reference check of a soxhlet extraction procedure for sewage sludge samples with a SFE method and found apparent discrepancies in the NP concentration data using these 2 different extraction methods.

Thus, it can be concluded that the recoveries and resulting concentrations depend on the extraction procedure.

Some laboratories perform the extraction of NP at acidic pH which increases extraction efficiency due to reduced water-solubility. However, disadvantageous is that also interfering matrix substances such as humic acids are co-extracted at acidic pH and can complicate the analysis.

Clean-up

Another problem of the analysis of alkylphenolic compounds is that usually a clean-up step is necessary for a correct determination. It has been reported that without column clean-up, matrix compounds from sludge, sediment or polluted water samples interfere with the analytes and prevent a correct determination [39,43,45]. Table 4 shows that most of the extraction methods for solid samples are followed by a clean-up step. However, also solid sample extraction methods without clean-up are reported [32]. The conventional clean-up procedures are either based on solid-liquid adsorption chromatography in open columns using different adsorbents (silica, Florisil, Alumina, or carbon), or on SPE with C_{18}, NH_2, or CN modified silica [39].

Also contradictory clean-up results are reported in the literature. E.g., Meesters and Schroeder [43] report that methanol and acetone are not well suited for the ASE extraction of NP. Their optimized extraction conditions are ethylacetate-formic acid (9:1) at 170°C. Petrovic et al. [33] in contrast use acetone-methanol (1:1) at 50°C.

Need for action

Preparation of certified reference materials (standard solutions, sediment samples)

No certified reference material seems to be available for the time being. To improve comparability of monitoring data the production of reference material should be initated.

Establishment of Laboratory Performance Studies on the determination of NP/OP and further degradation products of APEOs

In conclusion of the analytical method section, monitoring data often relate to different extraction, sample clean-up, and quantification methods. This makes the comparison and assessment of published data difficult, if not impossible. Therefore there is a need for validation of different analytical methods by interlaboratory studies.

Further Studies on degradation of APEOs

To elucidate the environmental fate of NP/OP, also the differing behaviour of its various isomers should be respected in the future.

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Annex 3

Reduced summary table of the standard methods

Priority Substance	**Danube TNMN**	**Available standard method (Ref.)**			**Scope of method**		**Method-Applicability**
	agreed method	**Standard**	**Year**	**Principle**	**Proposed Range of Application**[1]	**Matrix**	**Applicability in routine labs - (yes/no) or remarks**
Alachlor		ISO 11370 2000	Jan-95	TLC, AMD-Technique	**? 50 ng/l**	Water	no (2), yes (2)
		EN 6468		GC, LLE	detection limit: 1 ng/l to 10 ng/l		
		US EPA 505	Jul-91	GC/ECD (MS for conf.)	**0,5-40 µg/L**	Water (D,G,S)	--
Anthracene		ISO 17993: 2002 or see PAH´s		HPLC/fluorescence	? 0,01 µg/l [6]		yes (2)
		US EPA 8100		GC/FID	? 0.1 or 0,01 µg/l	Water	yes (1)
Atrazine		EN ISO 11369	Nov-97	HPLC/UV	? ca. 0,1 µg/l	Water [D,G]	no (1), yes (1)
		EN ISO 10695: 2000	Nov-00	GC/NPD (MS for conf.)	? 50 ng/l	Water [D,G,S,W]	no (1), yes (2)
		ISO 11370 2000	Jan-95	TLC, AMD-Technique	? 50 ng/l	Water	no (1)
		US EPA 505	Jul-91	GC/ECD (MS for conf.)	**3-50 µg/L**	Water [D,G,S]	--
Benzene		DIN 38407-9	May-91	Headspace-GC/FID	? 5 µg/l	Water [D,G,S,W]	no (1), yes (1)
		Draft ISO 15680	Sep-01	Purge/Trap + Therm. Desorp.	10 ng/l - 100 µg/l	Water [D,G,S,W]	no (1), yes (1)
		ISO 11423-1	Sep-97	Headspace-GC/FID	? 2 µg/l	Water [D,G,S,W]	yes (1)
Brominated diphenylethers		ISO WD 22032	Mar-02	GC/MS	0.005 - 100 µg/kg	Sludge, Sediment	no (3), yes (1)
Bis(pentabromophenyl)ether		*ISO WD 22032*	Mar-02	GC/MS	0.03 - 100 µg/kg	Sludge, Sediment	--
Diphenyl ether, octabromo derivate		*ISO WD 22032*	Mar-02	GC/MS	0.005 - 25 µg/kg	Sludge, Sediment	--
Diphenyl ether, pentabromo derivate		*ISO WD 22032*	Mar-02	GC/MS	**0.005 - 25 µg/kg**	Sludge, Sediment	--
Cadmium and its compounds	ISO 5961	EN ISO 5961	May-95	ET-AAS	**0,3 - 3 µg/l**	Water	yes (4)
		DIN 38406-16	Mar-90	Voltametry	**0,1 µg/l - 50 mg/l**	Water [D,G,S]	no (1)
		ISO/DIS 17294-2	Nov-02	ICP-MS	**? 0,5 µg/l**	Water [D,G,S,W]	yes (1)
		EN ISO 11885	Apr-98	ICP-AES	**? 0,01 mg/l**	Water [D,G,S,W]	yes (1)
		ISO DIS 15586 [5]	May 01	ET-AAS	**0,4 - 4 µg/l**	Water [D,G,S,W] ,Sediment	--
C10-13-chloroalkanes		**no Standard available**	--	--	--	--	no (3)
Chlorfenvinphos		DIN EN 12918	Nov-99	GC	0,01 - 1 µg/l	Water [D,G,S,W]	no (3), yes (1)

Priority Substance	**Danube TNMN**	**Available standard method (Ref.)**			**Scope of method**		**Method-Applicability**
	agreed method	**Standard**	**Year**	**Principle**	**Proposed Range of Application**[1]	**Matrix**	**Applicability in routine labs - (yes/no) or remarks**
		ISO 11370 2000	Jan-95	TLC, AMD-Technique	**? 50 ng/l**	Water	no (1)
Chlorpyrifos *(-ethyl, -methyl)*		DIN EN 12918	Nov-99	GC	**0,01 - 1 µg/l**	Water [D,G,S,W]	no (3), yes (1)
1,2-Dichloroethane		EN ISO 10301	Aug-97	GC or Headspace-GC	? 5 or ? 100 µg/l	Water [D,G,S,W]	yes (4)
		Draft ISO 15680 [5]	Sep-01	Purge/Trap + Therm. Desorp.	10 ng/l - 100 µg/l	Water [D,G,S,W]	--
Dichloromethane		EN ISO 10301	Aug-97	GC or Headspace-GC-ECD or other	**? 50 µg/l**	Water [D,G,S,W]	no (1), yes (3)
		Draft ISO 15680 [5]	Sep-01	Purge/Trap + Therm. Desorp.	10 ng/l - 100 µg/l	Water [D,G,S,W]	--
Di(2-ethylhexyl)phthalate (DEHP)		ISO DIS 18856	Mar-02	GC/MS	0,02 - 0,15 µg/l	Water [D,G,S,W]	no (2), yes (2)
Diuron		EN ISO 11369	Nov-97	HPLC/UV	**? ca. 0,1 µg/l**	Water [D,G]	no (2), yes (2)
Endosulfan		EN ISO 6468	Feb-97	GC/ECD	**? ca. 10 ng/l**	Water [D,G,S,W]	no (2), yes (1)
		US EPA 8081		GC/ECD	**? ca. 10 µg/L**	Water, Soil, Sludge	yes (1)
Fluoranthene		ISO 17993: 2002 or see PAH´s			? 0,01 µg/l [6]		no (1), yes (1)
		US EPA 8270		GC/MS	? 0,01 µg/l	Water, Soil, Sludge	yes (1)
Hexachlorobenzene		EN ISO 6468	Feb-97	GC/ECD	**? ca. 10 ng/l**	Water [D,G,S,W]	yes (3)
		US EPA 8081		GC/ECD	**? ca. 10 µg/L**	Water, Soil, Sludge	yes (1)
		US EPA 505	Jul-91	GC/ECD (MS for conf.)	**0,01-0,4 µg/L**	Water [D,G,S]	--
Hexachlorobutadiene		EN ISO 10301	Aug-97	GC or Headspace-GC-ECD or other	**? 0,01 µg/l**	Water [D,G,S,W]	no (2), yes (2)
Hexachlorocyclohexane		EN ISO 6468	Feb-97	GC/ECD	? ca. 10 ng/l	Water [D,G,S,W]	yes (4)
gamma-HCH (Lindane)	ISO 6468:1996	*EN ISO 6468*	Feb-97	GC/ECD	? ca. 10 ng/l	Water [D,G,S,W]	--
Isoproturon		EN ISO 11369	Nov-97	HPLC/UV	? ca. 0,1 µg/l	Water [D,G]	no (2), yes (2)
Lead and its compounds	ET AAS (EN ISO 11885)	DIN 38406-6	Jul-98	ET-AAS	**5 - 50 µg/l**	Water	yes (3)
		ISO 8288		flame AAS	**n.a.**		yes (1)
		US EPA 7421		ET-AAS	5-100 µg/L	Water, Soil, Sludge	yes (1)
		DIN 38406-16	Mar-90	Voltametry	0,1 µg/l - 50 mg/l	Water [D,G,S]	no (1)
		ISO/DIS 17294-2	Nov-02	ICP-MS	? 0,1 µg/l	Water [D,G,S,W]	yes (2)
		EN ISO 11885	Apr-98	ICP-AES	**? 0,07 mg/l**	Water [D,G,S,W]	yes (2)

Priority Substance	**Danube TNMN**	**Available standard method (Ref.)**			**Scope of method**		**Method-Applicability**
	agreed method	**Standard**	**Year**	**Principle**	**Proposed Range of Application[1]**	**Matrix**	**Applicability in routine labs - (yes/no) or remarks**
		ISO DIS 15586[5]	May 01	ET-AAS	**10 - 100 µg/l**	Water [D,G,S,W] ,Sediment	--
Mercury and its compounds	ISO 1483	EN 1483	Aug-97	Cold Vapour-AAS	**0,1 - 10 µg/l**	Water [D,G,S,W]	no (1), yes (3)
		EN 12338	Oct-98	CV-AAS with Amalgamation	0,01 - 1 µg/l	Water [D,G,S,W]	yes (2)
		EN 13506	Nov-01	Atomic fluor. spectrometry	0,01 - 10 µg/l	Water	--
Naphthalene		ISO 17993: 2002 or see PAH´s			? 0,01 µg/l[6]		yes (2)
		Draft ISO 15680[5]	Sep-01	Purge/Trap + Therm. Desorp.	0,01 - 100 µg/l	Water [D,G,S,W]	--
		US EPA 8270		GC/MS	? 0,01 µg/l	Water, Soil, Sludge	yes (1)
Nickel and its compounds	ET AAS (EN ISO 11885)	DIN 38406-11	Sep-91	ET-AAS	**5 - 100 µg/l**	Water	yes (3)
		ISO 8288		flame AAS	**n.a.**		yes (1)
		US EPA 7521		ET-AAS	**5-50 µg/L**	Water, Soil, Sludge	yes (1)
		DIN 38406-16	Mar-90	Voltametry	0,1 - 10 µg/l	Water [D,G,S]	no (1)
		ISO/DIS 17294-2	Nov-02	ICP-MS	**? 1 µg/l**	Water [D,G,S,W]	yes (2)
		EN ISO 11885	Apr-98	ICP-AES	**?**	Water [D,G,S,W]	yes (2)
		ISO DIS 15586[5]	May 01	ET-AAS	**7 - 70 µg/l**	Water [D,G,S,W] ,Sediment	--
Nonylphenols		ISO CD 18857-1	Jul-01	GC/MS	0,005 - 0,2 µg/l (0.1-50 [W])	Water [D,G,S,W]	no (1), yes (2)
		Sweedish EPA Raport 3829-1990		GC/ECD	**n.a.**		yes (1)
Octylphenols		ISO CD 18857-1	Jul-01	GC/MS	0,005 - 0,2 µg/l (0.1-50 [W])	Water [D,G,S,W]	no (3), yes (1)
Pentachlorobenzene		EN ISO 6468	Feb-97	GC/ECD	? ca. 10 ng/l	Water [D,G,S,W]	yes (3)
		US EPA 8081		GC/ECD	**? ca. 10 µg/L**	Water, Soil, Sludge	yes (1)
Pentachlorophenol		EN 12673	May-99	GC/ECD/MS after Deriv.	0,1 - 1000 µg/l	Water [D,G,S,W]	yes (4)
		ISO 8165-2	Jul-99	GC/ECD after Deriv.	? 0,1 µg/l	Water	no (1), yes (1)
Polyaromatic Hydrocarbons (PAH´s)		ISO 17993: 2002		HPLC/Fluo	? 0,01 µg/l[6]	Water [D,G,S]	yes (1)
		US EPA 8270		GC/MS	? 0,01 µg/l	Water, Soil, Sludge	yes (3)

Priority Substance	**Danube TNMN**	**Available standard method (Ref.)**			**Scope of method**		**Method-Applicability**
	agreed method	**Standard**	**Year**	**Principle**	**Proposed Range of Application**^{1}	**Matrix**	**Applicability in routine labs - (yes/no) or remarks**
		DIN 38414-23	Feb-02	HPLC/Fluo	? 0,05 mg/kg	Sludge, Sediment	no (1), yes (1)
		XP X33-012	Mar-00	HPLC/UV or GC/MS	n.a.	Sludge	--
Benzo(a)pyrene		*ISO 17993: 2002 or see PAH´s*		HPLC/Fluo	? 0,01 µg/l ^{6}	Water [D,G,S]	--
Benzo(b)fluoroanthene		*ISO 17993: 2002 or see PAH´s*		HPLC/Fluo	? 0,01 µg/l ^{6}	Water [D,G,S]	--
Benzo(g,h,i)perylene		*ISO 17993: 2002 or see PAH´s*		HPLC/Fluo	? 0,01 µg/l ^{6}	Water [D,G,S]	--
Benzo(k)fluoroanthene		*ISO 17993: 2002 or see PAH´s*		HPLC/Fluo	**? 0,01 µg/l ^{6}**	Water [D,G,S]	--
Indeno(1,2,3-cd)-pyrene		*ISO 17993: 2002 or see PAH´s*		HPLC/Fluo	? 0,01 µg/l ^{6}	Water [D,G,S]	--
Simazine		EN ISO 11369	Nov-97	HPLC/UV	? ca. 0,1 µg/l	Water [D,G]	no (1), yes (1)
		EN ISO 10695: 2000	Nov-00	GC/MS or GC/NPD	? 50 ng/l	Water [D,G,S,W]	no (1), yes (1)
		ISO 11370 2000	Jan-95	TLC, AMD-Technique	? 50 ng/l	Water	no (1)
		US EPA 505	Jul-91	GC/ECD (MS for conf.)	**12-50 µg/L**	Water [D,G,S]	--
Tributyltin compounds		ISO/DIS 17353		GC/MS - FPD - AES	**10 - 1000 ng/l**	Water (D,G,S,W]	no (1), yes (3)
		WD DIN 38414-XX	??		**n.a.**	Sludge, Sediment	no (1), yes (1)
		NF T 90-250	Jul-01	GC	20 - 2000 µg Sn/kg dry matter	Sediment	--
		ISO/AWI 23161	Apr-02	GC/MS	**???**	Soil	--
Trichlorobenzenes		EN ISO 6468	Feb-97	GC/ECD	? ca. 10 ng/l	Water [D,G,S,W]	no (1), yes (3)
		US EPA 8081		GC/ECD	**? ca. 10 µg/L**	Water, Soil, Sludge	yes (1)
		Draft ISO 15680 ^{5}	Sep-01	Purge/Trap + Therm. Desorp.	10 ng/l - 100 µg/l	Water [D,G,S,W]	--
Trichloromethane	ISO 10301:1997	EN ISO 10301	Aug-97	GC or Headspace-GC-ECD or other	? 0,05 or ? 0,3 µg/l	Water [D,G,S,W]	yes (4)
		Draft ISO 15680 ^{5}	Sep-01	Purge/Trap + Therm. Desorp.	10 ng/l - 100 µg/l	Water [D,G,S,W]	--
Trifluralin		EN ISO 10695: 2000	Nov-00	GC/MS or GC/ECD or GC/NPD	**? 50 ng/l**	Water [D,G,S,W]	no (2), yes (2)
		ISO 11370 2000	Jan-95	TLC, AMD-Technique	**? 50 ng/l**	Water	no (1)
COD	ISO 6060:1989						

Priority Substance	**Danube TNMN**	**Available standard method (Ref.)**			**Scope of method**		**Method-Applicability**
	agreed method	**Standard**	**Year**	**Principle**	**Proposed Range of Application**[1]	**Matrix**	**Applicability in routine labs - (yes/no) or remarks**
Ammoniacal nitrogen	ISO 7150-1:1984						
total N	EN ISO 11905-1:1998						
	ISO 11261:1995						
Total P	ISO 1189:1996						
Arsenic	ISO 11969:1996						
Copper	ET-AAS (EN ISO 11885)						
Zinc	ET-AAS (EN ISO 11885)						
Chromium	ISO 9174:1990						

EN = European Standard
ISO = International Standard
DIN = German Standard
DIN V = German Pre-standard
WD = Working Draft

Format code:
black = conc. ≤ AA-QS
red (normal) = conc. ≤ AA-QS for In & Tr
but > AA-QS for Co & Te
red bold = conc. > both AA-QS

[1] The proposed application range derives from chapter "Scope of the method"
[2] The application range for surface water corresponds to the lowest concentrations for which tests of precision and bias have been carried out, according to the definition in ISO/TR 13530, 1997-09
[3] Concentrations of the analyte(s) in the intercomparison samples used for the determination of repeatability and reproducibility; S_R = relative reproducibility standard deviation
[4] Performance data according to ISO 5725
[5] Standard is part of CEN working programm (2001-11)
[6] ≥ 0,01 µg/l for surface water, ≥ 0,005 µg/l for drinking water
[7] Two kinds of quality standards are proposed, referring to (1) annual average concentration **AA-QS** and (2) short term concentration peaks, maximum admissible concentration **MAC-QS**

Format code:
Priority Substance normal format = WFD priority substance
Priority Substance italic format = 76/464/EEC priority substance or quality standard proposed
Priority substance in black = at least one method with application range ≤ AA-QS or 76/464/EEC quality objective
Priority Substance red (normal) = available methods with application range ≤ AA-QS for In & Tr but > AA-QS for Co & Te
Priority Substance red & bold = no standard method available at all or no available method with application range £ AA-QS for In & Tr nor for Co & Te