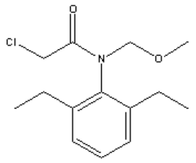
ANNEX I: List of ISO Standards for soil analysis

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

ANNEX II: Substance Guidance Sheets

Compound

Alachlor



CAS Number	**Log K_{OW}**	**Water Solubility [mg/L]**
15972-60-8	~ 2.97	~ 240

AA-EQS [µg/L]		**MAC-EQS [µg/L]**	
Inland Surface Waters	**Other Surface Waters**	**Inland Surface Waters**	**Other Surface Waters**
0.3	0.3	0.7	0.7

Available Standard Method

EN ISO 10695:2000
Determination of selected organic nitrogen and phosphorus compounds - Gas chromatography methods [*Note: Alachlor is not explicitly mentioned in this standard but the method may also be applied to the analysis of alachlor provided the method has been properly validated for this compound*].

Matrix Drinking waters, ground waters, surface waters and waste waters containing up to 50 mg/L of suspended solids
Sampling *ISO 5667-2:1991*

Pretreatment

Storage

Method Description

Liquid/liquid extraction with dichloromethane or liquid/solid extraction (SPE) on reversed-phase (RP)-C18 material or other adsorbent. Elution of the cartridges with e.g. methanol or acetone.
After concentration, the sample extracts are analysed by gas chromatography, using a nitrogen-phosphorus or mass spectrometric detector.

Limit of Quantification (LOQ): 0.04 µg/L

Method Validation: no data available

Other Analytical Methods

SPE-GC-MS
Separation by gas chromatography, identification and quantification of the analyte by gas chromatography coupled to mass spectrometric detection (GC-MS) using electron impact (EI) mode.
GC-MS fragment ions: m/z 160, 188, 161 and 146 [1-3]
SPE extraction of 500 mL water; LOQ ~ 12 ng/L [1]
SPE extraction of 1 L water; LOQ ~ 3 ng/L [2]
SPE extraction of 200 mL water; LOQ ~ 30 ng/L [3]

GC-NPD
EPA method 507 [4]

LC-ESI-MS/MS
C18 SPE of 50 mL water; MRM 270 > 161.5; LOQ ~ 0.1 µg/L [5]

On-line SPE-LC-MS-MS
On-line SPE of 10 mL samples; MRM 270 > 238; LOQ ~ 47 ng/L [6]

References

[1] J. Quintana, I. Martí, F. Ventura, Monitoring of Pesticides in Drinking and Related Waters in NE Spain with a Multiresidue SPE-GC–MS Method Including an Estimation of the Uncertainty of the Analytical Results. *Journal of Chromatography A* 938, 2001, 3-13.

[2] T. D. Bucheli, F. C. Grüebler, S. R. Müller, R. P. Schwarzenbach, Simultaneous Determination of Neutral and Acidic Pesticides in Natural Waters at the Low Nanogram per Liter Level. *Analytical Chemistry* 69, 1997, 1569-1576.

[3] D. de Almeida Azevedo, S. Lacorte, T. Vinhas, P. Viana, D. Barceló, Monitoring of Priority Pesticides and Other Organic Pollutants in River Water From Portugal by Gas Chromatography–Mass Spectrometry and Liquid Chromatography–Atmospheric Pressure Chemical Ionization Mass Spectrometry. *Journal of Chromatography A* 879, 2000, 13-26.

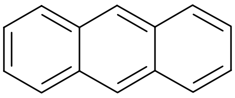
[4] D. Barceló, Environmental Protection Agency and Other Methods for the Determination of Priority Pesticides and Their Transformation Products in Water. *Journal of Chromatography A*, 643, 1993, 117-143.

[5] R. A. Yokley, L. C. Mayer, S.-B. Huang, J. D. Vargo, Analytical Method for the Determination of Metolachlor, Acetochlor, Alachlor, Dimethenamid, and Their Corresponding Ethanesulfonic and Oxanillic Acid Degradates in Water Using SPE and LC/ESI-MS/MS. *Analytical Chemistry* 74, 2002, 3754-3759.

[6] M. Kuster, M. J. Lopez de Alda, C. Barata, D. Raldua, D. Barceló, Analysis of 17 polar to semi-polar pesticides in the Ebro river delta during the main growing season of rice by automated on-line solid-phase extraction-liquid chromatography-tandem mass spectrometry. *Talanta* 75, 2008, 390-401.

Compound

Anthracene



CAS Number	Log K_{OW}	Water Solubility [mg/L]
120-12-7	4.55	0.0434

AA-EQS [µg/L]		MAC-EQS [µg/L]	
Inland Surface Waters	**Other Surface Waters**	**Inland Surface Waters**	**Other Surface Waters**
0.1	0.1	0.4	0.4

Available Standard Method

EN ISO 17993:2003

Determination of 15 polycyclic aromatic hydrocarbons (PAH) in water by HPLC with fluorescence detection after liquid-liquid extraction

Matrix Drinking, ground, waste and surface water

Sampling

Pretreatment

Storage

Method Description

EN ISO 17993:2003 specifies a method using high performance liquid chromatography (HPLC) with fluorescence detection for the determination of 15 selected polycyclic aromatic hydrocarbons (PAH).

Limit of Quantification (LOQ): 0.01 µg/L

Method Validation

l Number of laboratories
n_{AP} percental rate of outliers
$\overline{\overline{X}}$ Total mean after elimination of outliers
s_R standard deviation between the laboratories
CV_R reproducibility variation coefficient

Interlaboratory study 1996 in Germany

Matrix	*l*	n_{AP} *in %*	$\overline{\overline{X}}$ *in µg/L*	s_R *in µg/L*	CV_R *in %*
Drinking water	33	0	26.84	4.474	16.7

Other Analytical Methods

USA EPA 8270c, 1996 [1]

Semivolatile organic compounds by GC/MS

This method claims detection limits of 10 µg/L which is obviously too high. Other analytical methods based on this standard using modern GC/MS equipment however may attain the required low LOQs.

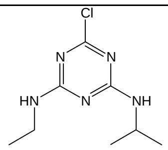
Comments

References

[1] http://www.accustandard.com/asi/pdfs/epa_methods/8270c.pdf

Compound

Atrazine



CAS Number	**Log K_{OW}**	**Water Solubility [mg/L]**
1912-24-9	~ 2.5	~ 33

AA-EQS [µg/L]		**MAC-EQS [µg/L]**	
Inland Surface Waters	**Other Surface Waters**	**Inland Surface Waters**	**Other Surface Waters**
0.6	0.6	2.0	2.0

Available Standard Method

EN ISO 10695:2000

Determination of selected organic nitrogen and phosphorus compounds - Gas chromatography methods

Matrix Drinking waters, ground waters, surface waters and waste waters containing up to 50 mg/L of suspended solids

Sampling *ISO 5667-1 and 5667-2*

Pretreatment

Storage

Method Description

Liquid/liquid extraction with dichloromethane or liquid/solid extraction (SPE) on reversed-phase (RP)-C18 material or other adsorbent. Elution of the cartridges with e.g. methanol or acetone.

After concentration, the sample extracts are analysed by gas chromatography, using a nitrogen-phosphorus or mass spectrometric detector.

Limit of Quantification (LOQ):

Liquid/liquid extraction method: 0.5 µg/L

Liquid/solid extraction method: 0.015 µg/L

Method Validation

l Number of laboratories
n_{AP} percental rate of outliers
$\bar{\bar{X}}$ Total mean after elimination of outliers
s_R standard deviation between the laboratories
CV_R reproducibility variation coefficient

Interlaboratory study 1993 for liquid/solid extraction

Matrix	***l***	***n_{AP} in %***	***$\bar{\bar{X}}$ in µg/L***	***s_R in µg/L***	***CV_R in %***
Drinking water	13	0	0.133	0.0104	35.6

Other Analytical Methods

Gas Chromatography - Mass Spectrometry

GC-MS determination of the ions 200 and 215; LOQ ~ 1 ng/L (after SPE) [1-3] (EPA method 525)

GC-NPD

EPA method 507 [4]

GC-ECD

EPA method 505; microextraction with hexane and GC-ECD analysis [4]]

Liquid Chromatography - Mass Spectrometry

Identification and quantification of atrazine (and other pesticides) by liquid chromatography coupled to (tandem) mass spectrometric detection (LC-MS-MS) using positive electrospray ionization (ESI)
LC-MS fragment ions: m/z 216 and 174 [5]
LC-MS-MS transitions: 216 > 174 and 132 [6]
LOQ ~ 1 ng/L (depending on the SPE enrichment factor)

Comments

References

[1] Z. Cai, V. M. S. Ramanujam, D. E. Giblin, M. L. Gross, and R. F. Spalding, Determination of Atrazine in Water at Low- and Sub-Parts-Per-Trillion Levels by Using Solid-Phase Extraction and Gas Chromatography/High-Resolution Mass Spectrometry. *Analytical Chemistry* 65, 1993, 21-26.

[2] T. D. Bucheli, F. C. Grüebler, S. R. Müller, R. P. Schwarzenbach, Simultaneous Determination of Neutral and Acidic Pesticides in Natural Waters at the Low Nanogram per Liter Leve., *Analytical Chemistry* 69, 1997, 1569-1576.

[3] C. Planas, A. Puig, J. Rivera, J. Caixach, Analysis of pesticides and metabolites in Spanish surface waters by isotope dilution gas chromatography/mass spectrometry with previous automated solid-phase extraction; Estimation of the uncertainty of the analytical results. Journal of. Chromatography A 1131, 2006, 242–252

[4] D. Barceló, Environmental Protection Agency and Other Methods for the Determination of Priority Pesticides and Their Transformation Products in Water. *Journal of Chromatography A* 643, 1993, 117-143.

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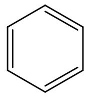
[6] R. J. C. A. Steen, A. C. Hogenboom, P. E. G. Leonards, R. A. L. Peerboom, W. P. Cofino, U. A. Th. Brinkman, Ultra-Trace-Level Determination of Polar Pesticides and Their Transformation Products in Surface and Estuarine Water Samples Using Column Liquid Chromatography–Electrospray Tandem Mass Spectrometry. *Journal of Chromatography A* 857, 1999, 157-166.

Compound

Benzene



CAS Number	Log K_{OW}	Water Solubility [mg/L]
71-43-2	2.13	1750

AA-EQS [µg/L]		MAC-EQS [µg/L]	
Inland Surface Waters	**Other Surface Waters**	**Inland Surface Waters**	**Other Surface Waters**
10	8	50	50

Available Standard Method

ISO 11423-1:1997

Determination of benzene and some derivatives – Head-space gas chromatographic method

Matrix Water

Sampling

Pretreatment

Storage

Method Description

A defined volume of unfiltered water sample is heated in a gas-tight septum-covered vial. After establishment of equilibrium between the gaseous and the liquid phases, an aliquot of the gaseous phase is transferred to a gas chromatograph.

Limit of Quantification (LOQ): ~ 2 µg/L

Method Validation

l Number of laboratories
n_{AP} percental rate of outliers
$\bar{\bar{X}}$ Total mean after elimination of outliers
s_R standard deviation between the laboratories
CV_R reproducibility variation coefficient

Interlaboratory study 1991 (Head Space GC – ISO 11423-1)

Matrix	l	n_{AP} in %	$\bar{\bar{X}}$ in µg/L	s_R in µg/L	CV_R in %
Surface water	8	14.3	5.6	0.88	15.7
Interlaboratory study 1991 (GC-FID – ISO 11423-2)					
Surface water	9	6.5	4.55	1.34	29.4

Other Analytical Methods

Determination of benzene and some derivatives - Method using extraction and gas chromatography (ISO 11423-2) The unfiltered water sample is extracted with a non-polar solvent (e.g. pentane) and the extract is analysed by GC-MS.
LOQ ~ 5 µg/L

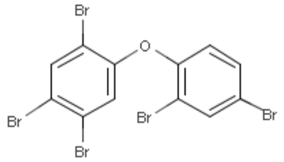
ISO 15680:2003
Gas-chromatographic determination of a number of monocyclic aromatic hydrocarbons, naphthalene and several chlorinated compounds using purge-and-trap and thermal desorption. (Selected ion: 78)
LOQ ~ 2 ng/L for benzene

Comments

References

Compound

Pentabromodiphenylether



CAS Number	Log K_{OW}	Water Solubility [µg/L]
32534-81-9	6.57	13.3

AA-EQS [µg/L]		MAC-EQS [µg/L]	
Inland Surface Waters	**Other Surface Waters**	**Inland Surface Waters**	**Other Surface Waters**
0.0005	0.0002	*not applicable*	*not applicable*

Available Standard Method

No standardised method for the determination of PBDE in water available

ISO 22032:2006
Determination of selected polybrominated diphenylethers (PBDE) in sediment and sewage sludge - Method using extraction and gas chromatography/mass spectrometry

Matrix Sediment
Sampling *ISO 5667-13*

Pretreatment homogenizing, freezing and freeze-drying, grind and sieve it

Storage at 4 °C in the darkness in wide necked bottles

Method Description

ISO 22032:2006 specifies a method for the determination of selected PBDEs representative for penta-, octa-, and decaBDE technical formulations in sediment using gas chromatography/mass spectrometry in the electron impact or electron capture ionisation mode. Extraction of PBDEs from the dried sample by an organic solvent is followed by clean-up of the extract by e.g. multi-layer silica gel column chromatography. For quantification an internal standard calibration is applied.

Limit of Quantification (LOQ): When applying GC-EI-MS, the method is applicable to samples containing 0.05 µg/kg to 25 µg/kg of tetra- to decabromo congeners. Approximately ten times lower concentrations can be quantified when using GC-ENCI-MS.

Method Validation

l Number of laboratories
n_{AP} percental rate of outliers
$\bar{\bar{X}}$ Total mean after elimination of outliers
s_R standard deviation between the laboratories
CV_R reproducibility variation coefficient

Interlaboratory Study 2004/2005

Matrix	***Substance***	***l***	***n_{AP} in %***	***$\bar{\bar{X}}$ in µg/kg***	***s_R in µg/kg***	***CV_R in %***
Sediment	BDE 47	16	0	362	50.5	14.0
	BDE 100	16	0	93.3	28.96	31.0
	BDE 99	16	0	518	99.6	19.2
	BDE 154	16	0	39.2	9.11	23.2
	BDE 153	16	0	47.7	9.28	19.5

Other Analytical Methods

Numerous studies of PBDEs in environmental samples are based on the determination by gas chromatography/mass spectrometry in the electron impact or negative ion chemical ionisation mode [1].

U.S. EPA Method 527 employs solid-phase extraction with analysis by gas chromatography/ mass spectrometry as described in PEPICH et al. 2005 [2], but MDL is fairly high (0.39 µg/l).

EPA Method 1614, 2007 [3] applies HRGC/HRMS for the analysis of PBDE in water, soil, sediment and tissue. MDL for BDE 99 is 0.00004 µg/l.

Comments

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

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

References

[1] A. Covaci, S. Voorspoels, J. de Boer, Determination of brominated flame retardants, with emphasis on polybrominated diphenyl ethers (PBDEs) in environmental and human samples—a review. *Environment International* 29, 2003, 735-756.

[2] B. V. Pepich, B. Prakash, M. M. Domino, T. A. Dattilio, Development of U.S. EPA method 527 for the Analysis of Selected Pesticides and Flame Retardants in the UCMR Survey. *Environmental Science & Technology* 39, 2005, 4996-5004.

[3] http://www.accustandard.com/asi/pdfs/epa_methods/1614.pdf.

[4] F. Luckey, B. Fowler, S. Litten, Establishing Baseline Levels of Polybrominated Diphenyl Ethers in Lake Ontario Surface Waters. The Second International Workshop on Brominated Flame Retardants, Stockholm University, Sweden, May 14-16, 2001, 337-339.

[5] D. R. Oros, D. Hoover, F. Rodigari, D. Crane, J. Sericano, Levels and Distribution of Polybrominated Diphenyl Ethers in Water, Surface Sediments, and Bivalves from the San Francisco Estuary. *Environmental Science & Technoogy* 39, 2005, 33-41.

[6] M. Polo, G. Gómez-Noya, J.B. Quintana, M. Llompart, C. García-Jares, R. Cela, Development of a solid-phase microextraction gas chromatography/tandem mass spectrometry method for polybrominated diphenyl ethers and polybrominated biphenyls in water samples. *Analytical Chemistry* 76, 2004, 1054-1062.

[7] R. J. Law, C. R. Allchin, J. de Boer, A. Covaci, D. Herzke, P. Lepom, S. Morris, J. Tronczynski, C. A. de Wit, Levels and trends of brominated flame retardants in the European environment. *Chemosphere* 64(2), 2006, 187-208.

Compound

Cadmium and its compounds

CAS Number	Log K_D [L/kg]	Water Solubility [mg/L]
7440-43-9	***suspended matter/water:*** 4.7 (Cd) [1] ***sediment/water**:* 3.6 (Cd) [1]	depending on compound

Water hardness [mg $CaCO_3$/L]	**AA-EQS [µg/L]** *(depending on water hardness classes)*		**MAC-EQS [µg/L]** *(depending on water hardness classes)*	
	Inland Surface Waters	**Other Surface Waters**	**Inland Surface Waters**	**Other Surface Waters**
Class 1: < 40	≤ 0.08	0.2	≤ 0.45	≤ 0.45
Class 2: 40 to < 50	0.08		0.45	0.45
Class 3: 50 to < 100	0.09		0.6	0.6
Class 4: 100 to < 200	0.15		0.9	0.9
Class 5: ≥ 200	0.25		1.5	1.5

Available Standard Method

EN ISO 17294-2:2004

Application of inductively coupled plasma mass spectrometry (ICP-MS) - Part 2: Determination of 62 elements

Matrix Drinking waters, ground waters, surface waters and waste waters

Sampling *ISO 5667-1, 5667-2 and 5667-3*

Pretreatment For dissolved elements, filter aqueous sample through a 0.45-µm pore membrane filter. Adjust the pH of the filtrate to < 2 with HNO_3.

Storage

Method Description

EN ISO 17294-2:2004 specifies a method for the determination of the cadmium in water (for example drinking water, surface water, groundwater, wastewater and eluates). Taking into account the specific and additionally occurring interferences, these elements can also be determined in digests of water, sludges and sediments.

The detection limits of most elements are affected by blank contamination and depend predominantly on the laboratory air-handling facilities available.

The lower limit of application is higher in cases where the determination is likely to suffer from interferences or in case of memory effects.

Limit of Quantification (LOQ):

Drinking water and relatively unpolluted water: 0.1 µg/L - 1.0 µg/L

Method Validation

l Number of laboratories
n_{AP} percental rate of outliers
$\bar{\bar{X}}$ Total mean after elimination of outliers
s_R standard deviation between the laboratories
CV_R reproducibility variation coefficient

Interlaboratory study 1997 in Germany

Matrix	l	n_{AP} ***in %***	$\bar{\bar{X}}$ ***in µg/L***	s_R ***in µg/L***	CV_R ***in %***
Surface water	37	5.2	5.75	0.491	8.5

Other Analytical Methods

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

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

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

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

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

Comments

References

Compound *C_{10-13}-Chloroalkanes*	$C_xH_{(2x-y+2)}Cl_y$ where x = 10-13 AND y = 1-13

CAS Number	**Log K_{OW}**	**Water Solubility [mg/L]**
85535-84-8	4.39-8.69 (depending on chlorine content)	0.15-0.47 (59% chlorine content)

AA-EQS [µg/L]		**MAC-EQS [µg/L]**	
Inland Surface Waters	**Other Surface Waters**	**Inland Surface Waters**	**Other Surface Waters**
0.4	0.4	1.4	1.4

Available Standard Method	**Method Description**
ISO CD 12010 **Error! Reference source not found.** **Matrix** **Sampling** **Pretreatment** **Storage**	Determination of the sum of SCCP in technical mixtures with chlorine contents 49 % to 67 % independent of the chlorine content and independent of the C-number distribution pattern of the congeners. No recognition of the chlorine content is necessary. Extraction of the whole water sample by liquid-liquid-extraction by an organic solvent, alternatively by solid phase extraction. After concentration and clean up, capillary gas chromatography of the approximately 6300 congeners at a relatively short column within a short retention range. Detection of selected mass fragments by mass spectrometry in the selected ion monitoring mode using negative ion chemical ionisation (NCI). The selection of the mass fragments is specific for the variety of technical mixtures as well as for the chlorine content and C-number distribution patterns in environmental samples. Alternative selections of mass fragment combinations for quantification are given in this standard too. The chromatogram is to be integrated over the full retention range of the SCCP. The quantification of the sum of SCCP is performed after calibrating by a multiple linear regression model with solutions of different technical mixtures and internal standardisation. The method works with at minimum three different defined standard mixtures, which resemble the C-number distribution and the chlorine content of different technical mixtures. This reflects the fact that the variety in respect of chlorine content and C-number distribution of technical SCCP-mixtures as well as of SCCP in environmental samples cannot be described by a single defined standard. The selection of the mass fragments for quantification and the special calibration allow a quantification of the sum of SCCP independently of chlorine content and C-number distribution within an expanded measurement uncertainty of 35% to 45%.

Method Validation
no data available

Other Analytical Methods
GC-ECNI-HRMS in the SIM mode at an ion source temperature of 120°C [1]. The molecular compositions of commercial SCCPs and of SCCP-containing extracts were determined by monitoring the two most intensive ions in the [M-Cl]- cluster, one for quantification and the other for confirmation for the following formula groups:

C10 (Cl5 to Cl10), C11 (Cl5 to Cl10), C12 (Cl6 to Cl10), and C13 (Cl7 to Cl9), and assuming that integrated signals are proportional to molar concentrations weighted by the number of chlorine atoms in the formula group. Quantification was achieved by selecting the biggest peak corresponding to [M-Cl]- ion in the most abundant formula group present in the sample and correcting for variations in the formula group abundances between standard and sample. The analytical detection limit was 60 pg of injected SCCP at a signal-to-noise ratio of 4:1, while LOQ was 23 ng/g.

Short-column (62 cm) GC-ECNI- LRMS at an ion source temperature of 100°C using methane as reagent gas [2]. Detection limits in the full- scan mode ranged from 10 to100 pg depending on carbon chain length of the n-alkane and on the degree of chlorination. The method was applied to the analysis of SCCP in fish samples.

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

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

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

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

Comments

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

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

References

[1] G. T. Tomy, G. A. Stern, D. C. G. Muir, A. T. Fisk, C. D. Cymbalisty, J. B. Westmore, Quantifying C10-C13 polychloroalkanes in environmental samples by high-resolution gas chromatography/electron capture negative ion high-resolution mass spectrometry. *Analytical Chemistry* 69, 1997, 2762-2771.

[2] M. Coelhan, Determination of short-chain polychlorinated paraffins in Fish Samples by short-column GC/ECNI-MS. *Analytical Chemistry* 71, 1999, 4498-4505.

[3] S. Moore, L. Vromet, B. Rondeau, Comparison of metastable atom bombardment and electron capture negative ionization for the analysis of polychloroalkanes. *Chemosphere* 54, 2004, 453-459.

[4] Z. Zencak, M. Reth, M. Oehme, Determination of Total Polychlorinated n-Alkane Concentration in Biota by Electron Ionization-MS/MS. *Analytical Chemistry* 76, 2004, 1957-1962.

[5] M. Reth, Z. Zencak, M. Oehme, New quantification procedure for the analysis of chlorinated paraffins using electron capture negative ionization mass spectrometry. *Journal of Chromatography A* 1081, 2005, 225–231.

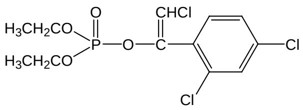
[6] F. Pellizzato, M. Ricci, A. Held, H. Emons. Analysis of short-chain chlorinated paraffins: a discussion paper. *International Journal of Environmental Analytical Chemistry* 9, 2007, 924-930.

[7] F. Pellizzato, M. Ricci, A. Held, H. Emons. Determination of short-chain chlorinated paraffins by carbon skeleton gas chromatography. Organohalogen Componds 70, 2008, 776-778.

[8] M. Coelhan, M. Saraci, H. Parlar, A comparative study of polychlorinated alkanes as standards for the determination of C10-C13 polychlorinated paraffins in fish samples. *Chemosphere* 40, 2000, 685-689.

Compound

Chlorfenvinphos



CAS Number	**Log K_{OW}**	**Water Solubility [mg/L]**
470-90-6	~ 3.81	~ 145 [1]

AA-EQS [µg/L]		**MAC-EQS [µg/L]**	
Inland Surface Waters	**Other Surface Waters**	**Inland Surface Waters**	**Other Surface Waters**
0.1	0.1	0.3	0.3

Available Standard Method

EN ISO 10695:2000

Determination of selected organic nitrogen and phosphorus compounds - Gas chromatography methods

Note: Chlorfenvinphos is not explicitly mentioned in this standard but the method may also be applied to the analysis of chlorfenvinphos provided the method has been properly validated for this compound.

Matrix Drinking waters, ground waters, surface waters and waste waters containing up to 50 mg/L of suspended solids

Sampling

Pretreatment

Storage

Method Description

Liquid/liquid extraction with dichloromethane or liquid/solid extraction (SPE) on reversed-phase (RP)-C18 material or other adsorbent. Elution of the cartridges with e.g. methanol or acetone.

After concentration, the sample extracts are analysed by gas chromatography, using a nitrogen-phosphorus or mass spectrometric detector.

Limit of Quantification (LOQ): 0.01 µg/L

Method Validation

no data available

Other Analytical Methods

Solid-phase microextraction (SPME)

SPME in 4 mL glass vials with a 60 µm PDMS-DVB coated fibre at 60ºC [2].

Gas Chromatography - Mass Spectrometry

GC-MS determination of the ions 267, 323, 295 [2, 4]

LOQ ~ 25 ng/L [2]

LOQ ~ 1 ng/L (after SPE of 500 mL water) [4]

GC tandem MS-MS

Parent ion m/z 267; product ions m/z 159 and 203 [2]

LOQ ~ 25 ng/L [2]

Solid-phase extraction (SPE) – HPLC/UV

LOQ ~ 25 ng/L [5]

GC - Flame Photometric Detection (FPD)

EPA method 1657; LOQ ~ 2 ng/L (solvent extraction) [1, 6]

Comments

Existence of E and Z double bond isomers; the Z-isomer has a water solubility of 121 mg/L and the E-isomer of 7.3 mg/L (at 20ºC); the mixture 145 mg/L at 23ºC; log K_{OW} ~ 3.85 (Z-isomer) and 4.22 (E-isomer).

References

[1] US Department of Health and Human Services, Agency for Toxic Substances and Disease Registry (ATSDR), Toxicological Profile Information Sheet, URL: http://www.atsdr.cdc.gov/toxprofiles/tp83.html.

[2] C. Gonçalves, M. F. Alpendurada, Solid-phase micro-extraction–gas chromatography–(tandem) mass spectrometry as a tool for pesticide residue analysis in water samples at high sensitivity and selectivity with confirmation capabilities. *Journal of Chromatography A* 1026, 2004, 239-250.

[3] C. Goncalves, M. F. Alpendurada, Assessment of pesticide contamination in soil samples from an intensive horticulture area, using ultrasonic extraction and gas chromatography–mass spectrometry. Talanta 65, 2005, 1179-1189.

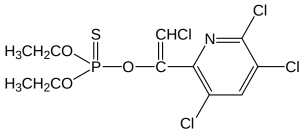
[4] C. Planas, A. Puig, J. Rivera, J. Caixach, Analysis of pesticides and metabolites in Spanish surface waters by isotope dilution gas chromatography/mass spectrometry with previous automated solid-phase extraction; Estimation of the uncertainty of the analytical results. *Journal of Chromatography A* 1131, 2006, 242–252.

[5]] C. Schlett, Multi-residue analysis of pesticides by HPLC after solid-phase extraction. *Fresenius' Journal of Analytical Chemistry.* 339, 1991, 344-347.

[[6] F.J. Lopez, J. Beltran, M. Forcada, F. Hernandez, Comparison of simplified methods for pesticide residue analysis; Use of large-volume injection in capillary gas chromatography. *Journal of Chromatography A* 823, 1998, 25-33.

Compound

Chlorpyrifos



CAS Number	**Log K_{OW}**	**Water Solubility [mg/L]**
2921-88-2	~ 4.96	~ 0.762

AA-EQS [µg/L]		**MAC-EQS [µg/L]**	
Inland Surface Waters	**Other Surface Waters**	**Inland Surface Waters**	**Other Surface Waters**
0.03	0.03	0.1	0.1

Available Standard Method

EN ISO 10695:2000

Determination of selected organic nitrogen and phosphorus compounds - Gas chromatography methods

Note: Chlorpyriphos is not explicitly mentioned in this standard but the method may also be applied to the analysis of chlorpyriphos provided the method has been properly validated for this compound.

Matrix Drinking waters, ground waters, surface waters and waste waters containing up to 50 mg/L of suspended solids

Sampling

Pretreatment

Storage

Method Description

Liquid/liquid extraction with dichloromethane or liquid/solid extraction (SPE) on reversed-phase (RP)-C18 material or other adsorbent. Elution of the cartridges with e.g. methanol or acetone.
After concentration, the sample extracts are analysed by gas chromatography, using a nitrogen-phosphorus or mass spectrometric detector.

Limit of Quantification (LOQ): 0.01 µg/L

Method Validation

no data available

Other Analytical Methods

Solid-phase microextraction (SPME)
SPME in 4 mL glass vials with a 60 µm PDMS-DVB coated fibre at 60ºC [2]

Solid-phase extraction (SPE)
SPE with C18 cartridges; elution with ethylacetate [3]

Gas Chromatography - Mass Spectrometry
GC-MS determination of the ions 199, 197, 314, 316 [1-5]
LOQ ~ 1-2 ng/L [2, 5]

GC tandem MS-MS
Parent ion m/z 314; product ions m/z 286 and 258 [2]
LOQ ~ 1 ng/L [2]

GC-NPD:
LOQ ~ 20 ng/L [3]

GC - Flame Photometric Detection (FPD) [7]

Comments

Chlorpyrifos is a non-polar insecticide. If released to water, chlorpyrifos partitions significantly from the water column to sediments.

References

[1] M. Kirchner, E. Matisová, S. Hrouzková, J. de Zeeuw, Possibilities and limitations of quadrupole mass spectrometric detector in fast gas chromatography. *Journal of Chromatography A* 1090, 2005, 126-132.

[2] C. Gonçalves, M.F. Alpendurada, Solid-phase micro-extraction–gas chromatography–(tandem) mass spectrometry as a tool for pesticide residue analysis in water samples at high sensitivity and selectivity with confirmation capabilities. *Journal of Chromatography A* 1026, 2004, 239-250.

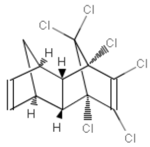
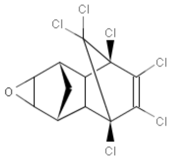
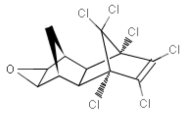
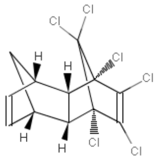
[3] S. Lacorte, C. Molina, D. Barceló, Screening of organophosphorus pesticides in environmental matrices by various gas chromatographic techniques. *Analytica Chimica Acta* 281, 1993, 71-84.

[4] K. Kawata, T. Asada, K. Oikawa, Determination of pesticides in compost by pressurized liquid extraction and gas chromatography–mass spectrometry. *Journal of Chromatography A* 1090, 2005, 10-15.

5] C. Planas, A. Puig, J. Rivera, J. Caixach, Analysis of pesticides and metabolites in Spanish surface waters by isotope dilution gas chromatography/mass spectrometry with previous automated solid-phase extraction; Estimation of the uncertainty of the analytical results. Journal of Chromatography A, 1131, 2006, 242–252

[6] US Department of Health and Human Services, Agency for Toxic Substances and Disease Registry (ATSDR), Toxicological Profile Information Sheet, URL: http://www.atsdr.cdc.gov/toxprofiles/tp84.html

[7] F. J. Lopez, J. Beltran, M. Forcada, F. Hernandez, Comparison of simplified methods for pesticide residue analysis; Use of large-volume injection in capillary gas chromatography. *Journal of Chromatogaphy. A* 823, 1998, 25-33.

Compound			
			
Aldrin	*Dieldrin*	*Endrin*	*Isodrin*

	CAS Number	**Log K_{OW}**	**Water Solubility [mg/L]**
Aldrin	309-00-2	~ 6.50	~ 0.011
Dieldrin	60-57-1	~ 6.2	~ 0.110
Endrin	72-20-8	~ 5.6	~ 0.20
Isodrin	465-73-6	~ 6.75	~ 0.014

AA-EQS [µg/L]		**MAC-EQS [µg/L]**	
Inland Surface Waters	**Other Surface Waters**	**Inland Surface Waters**	**Other Surface Waters**
Σ = 0.01	Σ = 0.005	*not applicable*	*not applicable*

Available Standard Method

EN ISO 6468:1996

Determination of certain organochlorine insecticides, polychlorinated biphenyls and chlorobenzenes – Gas chromatographic method after liquid-liquid extraction

Matrix Drinking, ground, surface and waste waters

Sampling

Pretreatment

Storage

Method Description

Liquid-liquid extraction of organochlorine insecticides, chlorobenzenes and PCBs by an extraction solvent. After concentration and clean-up the sample extracts are analysed by gas chromatography, using an electron-capture detector (GC-ECD).

The method is applicable to samples containing up to 50 mg/L of suspended solids.

Limit of Quantification (LOQ): ~ 0.001 – 0.01 µg/L

Method Validation

l Number of laboratories
n_{AP} percental rate of outliers
$\bar{\bar{X}}$ Total mean after elimination of outliers
s_R standard deviation between the laboratories
CV_R reproducibility variation coefficient

Interlaboratory study (Extraction of surface water with Hexane)

Substance	***l***	***n_{AP} in %***	***$\bar{\bar{X}}$ in ng/L***	***s_R in µg/L***	***CV_R in %***
Dieldrin	14	0	33.3	17.2	51.7
Endrin	14	9.8	50.0	11.1	22.3

Other Analytical Methods

Solid-phase extraction gas chromatography - mass spectrometry
SPE with Oasis HLB cartridges; elution with dichloromethane.
GC-MS determination of the ions 66 for aldrin, 79 for dieldrin, 281 for endrin, and 193 for isodrine [1,2].

LOQ ~ 20 ng/L for aldrin,
10 ng/L for dieldrin,
15 ng/L for endrin, and
12 ng/L for isodrin (SPE extraction of 200 mL water) [1]

SPME GC-MS
SPME in 4 mL glass vials with a 60 µm PDMS-DVB coated fibre at 60ºC;
LOQ ~ 12 ng/L for aldrin, 9 ng/L for dieldrin, 60 ng/L for endrin, and 10 ng/L for isodrin [2]

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

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

Comments

References

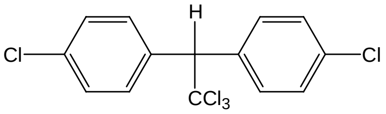
[1] S. Lacorte, I. Guiffard, D. Fraisse, D. Barceló, Broad Spectrum Analysis of 109 Priority Compounds Listed in the 76/464/CEE Council Directive Using Solid-Phase Extraction and GC/EI/MS. *Analytical Chemistry* 72, 2000, 1430-1440.

[2] C. Gonçalves, M.F. Alpendurada, Solid-phase micro-extraction–gas chromatography–(tandem) mass spectrometry as a tool for pesticide residue analysis in water samples at high sensitivity and selectivity with confirmation capabilities. *Journal of Chromatography A* 1026, 2004, 239-250.

[3] E. Pitarch, C. Medina, T. Portolés, F.J. López, F. Hernández, Determination of priority organic micro-pollutants in water by gas chromatography coupled to triple quadrupole mass spectrometry. Analytica Chimica Acta 583, 2007, 246–258.

Compound

DDT total
para-para-DDT



CAS Number		**Log K_{OW}**	**Water Solubility [mg/L]**
DDT total	*not applicable*	*p,p'*-DDT ~ 6.91	*p,p'*-DDT ~ 0.025
para-para-DDT	50-29-3	*o,p'*-DDT ~ 6.79	*o,p'*-DDT ~ 0.085
		p,p'-DDE ~ 6.51	*p,p'*-DDE ~ 0.12
		p,p'-DDD ~ 6.02	*p,p*'-DDD ~ 0.090

AA-EQS [µg/L]				**MAC-EQS [µg/L]**	
Inland Surface Waters		**Other Surface Waters**		**Inland Surface Waters**	**Other Surface Waters**
DDT total	0.025	DDT total	0.025	*not applicable*	*not applicable*
para-para-DDT	0.01	para-para-DDT	0.01		

Available Standard Method
EN ISO 6468:1996
Determination of certain organochlorine insecticides, polychlorinated biphenyls and chlorobenzenes – Gas chromatographic method after liquid-liquid extraction

Matrix Drinking, ground, surface and waste waters
Sampling

Pretreatment

Storage

Method Description

Liquid-liquid extraction of organochlorine insecticides, chlorobenzenes and PCBs by an extraction solvent. After concentration and clean-up the sample extracts are analysed by gas chromatography, using an electron-capture detector (GC-ECD).

The method is applicable to samples containing up to 50 mg/L of suspended solids.

Limit of Quantification (LOQ): ~ 0.001 – 0.01 µg/L

Method Validation

l Number of laboratories
n_{AP} percental rate of outliers
$\bar{\bar{X}}$ Total mean after elimination of outliers
s_R standard deviation between the laboratories
CV_R reproducibility variation coefficient

Interlaboratory study (Extraction of p,p′-DDT with Hexane)

Matrix	*l*	n_{AP} *in %*	$\bar{\bar{X}}$ *in ng/L*	s_R *in µg/L*	CV_R *in %*
Drinking water	11	10.3	35.7	22.9	64.1

Other Analytical Methods

Solid-phase extraction - gas chromatography - mass spectrometry
SPE with Oasis HLB cartridges; elution with dichloromethane.
GC-MS determination of the ions 235 for DDT and DDD, and 246 for DDE.
The second qualitative ions are 165 for DDT and DDD, and 176 for DDE.

LOQ ~ 4 ng/L for *p,p'*-DDT,
11 ng/L for *o,p'*-DDT,
4 ng/L for *p,p'*-DDE, and
12 ng/L for *p,p*'-DDD (SPE extraction of 200 mL water) [1,2]

SPME - GC-MS
SPME in 4 mL glass vials with a 60 µm PDMS-DVB coated fibre at 60°C; LOQ ~ 12 ng/L for DDT, 2 ng/L for DDD and 1 ng/L for DDE [3]

GC-ECD

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

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

Comments

Technical grade DDT consists of 65-80 % of *p,p'*-DDT, 15-21 % of *o,p'*-DDT, up to 4 % of *p,p'*-DDD. *p,p'*-DDE is a metabolite of DDT.
DDT is very persistent in the environment, with a reported half-life between 2-25 years; it has a low solubility in water.

References

[1] S. Lacorte, I. Guiffard, D. Fraisse, D. Barceló, Broad Spectrum Analysis of 109 Priority Compounds Listed in the 76/464/CEE Council Directive Using Solid-Phase Extraction and GC/EI/MS. *Analytical Chemistry*, 2000, 1430-1440.

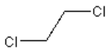
[2] D. de Almeida Azevedo, S. Lacorte, T. Vinhas, P. Viana, D. Barceló, Monitoring of Priority Pesticides and Other Organic Pollutants in River Water From Portugal by Gas Chromatography Mass Spectrometry and Liquid Chromatography–Atmospheric Pressure Chemical Ionization Mass Spectrometry. *Journal of Chromatography A* 879, 2000, 13-26.

[3] C. Gonçalves, M.F. Alpendurada, Solid-phase micro-extraction–gas chromatography–(tandem) mass spectrometry as a tool for pesticide residue analysis in water samples at high sensitivity and selectivity with confirmation capabilities. *Journal of Chromatography A* 1026, 2004, 239-250.

[4] R. Bettinetti, V. Croce, S. Galassi, P. Volta, Pp'DDT and pp'DDE accumulation in a food chain of Lake Maggiore (Northern Italy): testing steady-state condition, *Enviromental. Scence and Pollution Research International* 13, 2006, 59-66.

Compound

1,2-Dichloroethane



CAS Number	**Log K_{OW}**	**Water Solubility [g/L]**
107-06-2	1.45	8.5-9.0

AA-EQS [µg/L]		**MAC-EQS [µg/L]**	
Inland Surface Waters	**Other Surface Waters**	**Inland Surface Waters**	**Other Surface Waters**
10	10	*not applicable*	*not applicable*

Available Standard Method
EN ISO 15680: 2003
Gas-chromatographic determination of a number of monocyclic aromatic hydrocarbons, naphthalene and several chlorinated compounds using purge-and-trap and thermal desorption

Matrix drinking water, ground water, surface water, seawater and (diluted) waste water
Sampling *ISO 5667-1, 5667-2 and ISO 5667-3*
Pretreatment

Storage hermetically sealed at 4 °C, avoid direct sunlight, analysis within 5 days

Method Description

EN ISO 15680:2003 specifies a general method for the determination of volatile organic compounds (VOCs) in water by purge-and-trap isolation and gas chromatography (GC).

Detection is preferably carried out by mass spectrometry in the electron impact mode (EI), but other detectors may be applied as well.

Limit of Quantification (LOQ): 0.01 µg/L

Method Validation

no data available

Other Analytical Methods

EN ISO 10301:1997 specifies two methods for the determination of highly volatile halogenated hydrocarbons in water using gas chromatography with e.g. electron capture detector after: a) the extraction by an organic solvent or using, b) a head-space method (LOQ: 100 µg/L).

The EPA Method 1624 is designed to determine the volatile organic pollutants in water amenable to purge and trap gaschromatography-mass spectrometry.

Hubrechts et al. 2003 give a review of gas chromatography-based methods for analysis of volatile organic compounds in estuarine waters with special emphasis on monitoring [1].

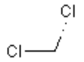
Purge and trap GC-MS
SIM-GC-MS detection of the ions 62, 98, 64; LOQ ~ 2 ng/L [2]
(Modification of EPA method 524.2:VOCs in Water Using GC-MS, http://www.accustandard.com/asi/pdfs/epa_methods/524_2.pdf,)

Comments

References

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

[2] E. Martínez, S. Lacorte, I. Llobet, P. Viana, D. Barceló, Multicomponent analysis of volatile organic compounds in water by automated purge and trap coupled to gas chromatography–mass spectrometry. *Journal of Chromatography A* 959, 2002, 181-190.

Compound *Dichloromethane*	

CAS Number 75-09-2	**Log K_{OW}** ~ 1.3	**Water Solubility [g/L]** ~ 20

AA-EQS [µg/L]		**MAC-EQS [µg/L]**	
Inland Surface Waters 20	**Other Surface Waters** 20	**Inland Surface Waters** *not applicable*	**Other Surface Waters** *not applicable*

Available Standard Method
EN ISO 15680:2003
Gas-chromatographic determination of a number of monocyclic aromatic hydrocarbons, naphthalene and several chlorinated compounds using purge-and-trap and thermal desorption

Matrix drinking water, ground water, surface water, seawater and (diluted) waste water
Sampling *ISO 5667-1, 5667-2 and ISO 5667-3*
Pretreatment

Storage at 4 °C air tight and no direct sunlight, analysis within 5 days

Method Description

EN ISO 15680:2003 specifies a general method for the determination of volatile organic compounds (VOCs) in water by purge-and-trap isolation and gas chromatography (GC).

Detection is preferably carried out by mass spectrometry in the electron impact mode (EI), but other detectors may be applied as well.

Limit of Quantification (LOQ): 0.01 µg/L

Method Validation

l Number of laboratories
n_{AP} percental rate of outliers
$\overline{\overline{X}}$ Total mean after elimination of outliers
s_R standard deviation between the laboratories
CV_R reproducibility variation coefficient
n.a. = not available

Interlaboratory study

Matrix	*l*	*n_{AP} in %*	*$\overline{\overline{X}}$ in µg/L*	*s_R in µg/L*	*CV_R in %*
Drinking water (0.2 µg/L)	11	n.a.	n.a.	n.a.	55
Surface water (0.2 µg/L)	10	n.a.	n.a.	n.a.	68

Other Analytical Methods

EN ISO 10301:1997 specifies two methods for the determination of highly volatile halogenated hydrocarbons in water using gas chromatography with e.g. electron capture detector after: a) the extraction by an organic solvent or using, b) a head-space method (LOQ: 100 µg/L).

The EPA Method 1624 is designed to determine the volatile organic pollutants in water amenable to purge and trap gaschromatography-mass spectrometry.

HUYBRECHTS et al. 2003 give a review of gas chromatography-based methods for analysis of volatile organic compounds in estuarine waters with special emphasis on monitoring [1].

Purge and trap GC-MS
SIM-GC-MS detection of the ions 84, 86, 49; LOQ ~ 62 ng/L [2]
(Modification of EPA method 524.2 “VOCs in Water Using GCMS”)

Comments

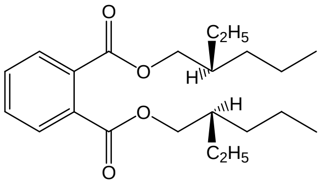
References

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

[2] E. Martínez, S. Lacorte, I. Llobet, P. Viana, D. Barceló, Multicomponent analysis of volatile organic compounds in water by automated purge and trap coupled to gas chromatography–mass spectrometry. *Journal Chromatography A* 959, 2002, 181-190.

Compound

Di(2-ethylhexyl)phthalate (DEHP)



CAS Number	**Log K_{OW}**	**Water Solubility [µg/L]**
117-81-7	7.5	3

AA-EQS [µg/L]		**MAC-EQS [µg/L]**	
Inland Surface Waters	**Other Surface Waters**	**Inland Surface Waters**	**Other Surface Waters**
1.3	1.3	*not applicable*	*not applicable*

Available Standard Method

EN ISO 18856: 2005

Determination of selected phthalates using gas chromatography/mass spectrometry

Matrix ground water, surface water, wastewater and drinking water

Sampling *ISO 5667-1, 5667-2 and 5667-3*

Pretreatment

Storage at 4 °C in the darkness, analysis within 4 days

Method Description

EN ISO 18856:2005 specifies a method for the determination of phthalates in water after solid phase extraction and gas chromatography/mass spectrometry.

Limit of Quantification (LOQ):

0.02 µg/L - 0.150 µg/L depending on the blank

Method Validation

l Number of laboratories
n_{AP} percental rate of outliers
$\overline{\overline{X}}$ Total mean after elimination of outliers
s_R standard deviation between the laboratories
CV_R reproducibility variation coefficient

Interlaboratory study 2003

Matrix	***l***	***n_{AP} in %***	***$\overline{\overline{X}}$ in ng/L***	***s_R in ng/L***	***CV_R in %***
Surface water	7	0	373	257	69

Other Analytical Methods

SPME-GC-MS

GC-MS determination of the ion 149; LOQ ~ 15 to 30 ng/L [1,2]

Comments

The analysis is difficult due to the omnipresence of phthalates. Specific care shall be taken to minimise blanks. The use of plastic material shall be avoided unconditionally.

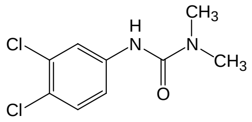
References

[1] A. Peñalver, E. Pocurull, F. Borrull, R.M. Marcé, Comparison of different fibers for the solid-phase microextraction of phthalate esters from water. *Journal of Chromatography A* 922, 2001, 377-384.

[2] J. B. Baugros, B. Giroud, G. Dessalces, M. F. Grenier-Loustalot, C. Cren-Olivé. Multiresidue analytical methods for the ultra-trace quantification of 33 priority substances present in the list of REACH in real water samples. Analytica Chimica Acta 607, 2008, 191-203

Compound

Diuron



CAS Number	**Log K_{OW}**	**Water Solubility [mg/L]**
330-54-1	~ 2.7	~ 42

AA-EQS [µg/L]		**MAC-EQS [µg/L]**	
Inland Surface Waters	**Other Surface Waters**	**Inland Surface Waters**	**Other Surface Waters**
0.2	0.2	1.8	1.8

Available Standard Method

EN ISO 11369:1997

Determination of selected plant treatment agents in water by high performance liquid chromatography with UV detection after solid-liquid extraction.

Matrix Drinking and ground water

Sampling

Pretreatment

Storage

Method Description

The plant treatment substances in the water sample are extracted by solid-liquid extraction (SPE) on reversed-phase (RP)-C18 material, eluted with a solvent, and then separated, identified and quantified by high performance liquid chromatography (HPLC) using UV detection.

Limit of Quantification (LOQ): 0.1 µg/L

Method Validation

l Number of laboratories
n_{AP} percental rate of outliers
$\overline{\overline{X}}$ Total mean after elimination of outliers
s_R standard deviation between the laboratories
CV_R reproducibility variation coefficient

Interlaboratory trial

Matrix	*l*	n_{AP} *in %*	$\overline{\overline{X}}$ *in µg/L*	s_R *in µg/L*	CV_R *in %*
Drinking water	33	0	0.1026	0.0299	29.1
Ground water	32	5.1	0.2815	0.0570	20.2

Other Analytical Methods

Liquid Chromatography - Mass Spectrometry
Identification and quantification of diuron (and other pesticides) by liquid chromatography coupled to (tandem) mass spectrometric detection (LC-MS-MS) using positive electrospray ionization (ESI)
LC-MS fragment ions: m/z 233 [1,2]
LC-MS-MS transitions: 233 > 72 and 46 [3,4,5]

LOQ ~ 1 ng/L (depending on the SPE enrichment factor)

Liquid Chromatography – Diode Array Detector
Sea water analysis: Off-line SPE – LC-DAD; LOQ ~ 0.01 µg/L [6]

Gas Chromatography - Mass Spectrometry (after derivatisation)
Phenylurea herbicides require a derivatisation step to prevent the degradation of these thermolabile compounds in the GC injector; LOQ ~ 1 ng/L [7]
SPE-derivatisation-GC-MS; LOQ ~ 50 ng/L [8]

Comments

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

References

[1] C. Crescenzi, A. Di Corcia, R. Samperi, N. L. Dietz, E. Guerriero, Development of a Multiresidue Method for Analyzing Pesticide Traces in Water Based on Solid-Phase Extraction and Electrospray Liquid Chromatography Mass Spectrometry. Environmental Science & Technology 31, 1997, 479-488.

[2] R. Loos, G. Hanke, S. J. Eisenreich: Multi-Component Analysis of Polar Water Pollutants Using Sequential Solid-Phase Extraction Followed by LC-ESI-MS. Journal of Environmental Monitoring 5, 2003, 384-394.

[3] M. H. Lamoree, C. P. Swart, A. van der Horst, B. van Hattum, Determination of Diuron and the Antifouling Paint Biocide Irgarol 1051 in Dutch Marinas and Coastal Waters. Journal of Chromatography A 970, 2002, 183-190.

[4] R. J. C. A. Steen, A. C. Hogenboom, P. E. G. Leonards, R. A. L. Peerboom, W. P. Cofino, U. A. Th. Brinkman, Ultra-Trace-Level Determination of Polar Pesticides and Their Transformation Products in Surface and Estuarine Water Samples Using Column Liquid Chromatography–Electrospray Tandem Mass Spectrometry. Journal of Chromatography A 857, 1999, 157-166.

[5] M. Kuster, M. J. Lopez de Alda, C. Barata, D. Raldua, D. Barceló, Analysis of 17 polar to semi-polar pesticides in the Ebro river delta during the main growing season of rice by automated on-line solid-phase extraction-liquid chromatography-tandem mass spectrometry. Talanta 75, 2008, 390-401.

[6] G. Gatidou, A. Kotrikla, N. S. Thomaidis, T. D. Lekkas, Determination of the Antifouling Booster Biocides Irgarol 1051 and Diuron and their Metabolites in Seawater by High Performance Liquid Chromatography–Diode Array Detector. Analytica Chimica Acta 528, 2005, 89-99.

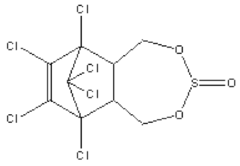
[7] A. C. Gerecke, C. Tixier, T. Bartels, R. P. Schwarzenbach, S. R. Müller, Determination of Phenylurea Herbicides in Natural Waters at Concentrations Below 1 ng l^{-1} Using Solid-Phase Extraction, Derivatisation, and Solid-Phase Microextraction–Gas Chromatography–Mass Spectrometry. Journal of Chromatography A 930, 2001, 9-19.

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

Compound

Endosulfan

(alfa and beta isomer)



CAS Number	Log K_{OW}	Water Solubility [mg/L]
115-29-7	3.83	0.325

AA-EQS [µg/L]		MAC-EQS [µg/L]	
Inland Surface Waters	**Other Surface Waters**	**Inland Surface Waters**	**Other Surface Waters**
0.005	0.0005	0.01	0.004

Available Standard Method

EN ISO 6468:1996

Determination of certain organochlorine insecticides, polychlorinated biphenyls and chlorobenzenes - Gas chromatographic method after liquid-liquid extraction

Matrix Drinking, ground, waste and surface water

Sampling

Pretreatment

Storage

Method Description

*EN ISO 6468:1996 d*escribes a method for determination of certain organochlorine insecticides, polychlorinated biphenyls (PCBs) and chlorobenzenes (except the mono- and dichlorobenzenes) in drinking water, ground water, surface waters and waste waters. The method is applicable to samples containing up to 50 mg/L of suspended solids.

Limit of Quantification (LOQ): 0.001 up to 0.01 µg/L

Method Validation

l Number of laboratories
n_{AP} percental rate of outliers
$\overline{\overline{X}}$ Total mean after elimination of outliers
s_R standard deviation between the laboratories
CV_R reproducibility variation coefficient

Interlaboratory study (Extraction of β-Endosulfan with Hexane)

Matrix	*l*	n_{AP} *in %*	$\overline{\overline{X}}$ *in ng/L*	s_R *in µg/L*	CV_R *in %*
Surface water	14	6.6	21.2	14.4	67.9

Other Analytical Methods

SPE extraction of 500 ml water with 200 mg SDB, elution with ethyl acetate; GC-MS determination
LOQ for α-endosulfan ~ 11 ng/L [1]

SPE-GC-NCI-MS
C18-SPE, 100 mL, LOQ for α- or β-endosulfan ~ 25 ng/L [2]

The LOQ of these alternative SPE-GC-MS methods may be low enough if good equipment and well trained personnel are available. The uncertainty however is rather high (depends on required U whether this method will be feasible).

Comments

The technical grade of endosulfan is a mixture of two stereoisomers, α- and β-endosulfan (in a ratio of 7:3). In the environment in particular in soil the metabolite endosulfan-sulfate is also present.

By the SPE extraction of higher water volumes lower LOQs could be achieved.
New research results show that sufficient LOQs in the low ng/L or even pg/L range can be achieved with negative chemical ionization (NCI) GC-MS, using SPE of 1 or 10 L water [3].

References

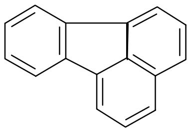
[1] J. Quintana, I. Martí, F. Ventura, Monitoring of Pesticides in Drinking and Related Waters in NE Spain with a Multiresidue SPE-GC–MS Method Including an Estimation of the Uncertainty of the Analytical Results. *Journal of Chromatography A* 938, 2001, 3-13.

[2] E. Pitarch, C. Medina, T. Portolés, F.J. López, F. Hernández, Determination of priority organic micro-pollutants in water by gas chromatography coupled to triple quadrupole mass spectrometry. Analytica Chimica Acta 583, 2007, 246–258.

[3] M. Oehme, N. Theobald, A.-C. Baaß, J. Hüttig, M. Reth, S. Weigelt-Krenz, Z. Zencak, M. Haarich, Identification of organic compounds in the North and Baltic Sea, Federal Environment Agency, Research Report 20025224, 2008, ISSN 1862-4804, http://www.umweltdaten.de/publikationen/fpdf-l/3509.pdf

Compound

Fluoranthene



CAS Number	Log K_{OW}	Water Solubility [mg/L]
206-44-0	5.16	0.265

AA-EQS [µg/L]		MAC-EQS [µg/L]	
Inland Surface Waters	**Other Surface Waters**	**Inland Surface Waters**	**Other Surface Waters**
0.1	0.1	1	1

Available Standard Method

EN ISO 17993:2003

Determination of 15 polycyclic aromatic hydrocarbons (PAH) in water by HPLC with fluorescence detection after liquid-liquid extraction

Matrix Drinking, ground, waste and surface water

Sampling

Pretreatment

Storage

Method Description

EN ISO 17993:2003 specifies a method using high performance liquid chromatography (HPLC) with fluorescence detection for the determination of 15 selected polycyclic aromatic hydrocarbons (PAH).

Limit of Quantification (LOQ):

Drinking and ground water: > 0.005 µg/L

Surface water: > 0.01 µg/L

Method Validation

l Number of laboratories

n_{AP} percental rate of outliers

$\overline{\overline{X}}$ Total mean after elimination of outliers

s_R standard deviation between the laboratories

CV_R reproducibility variation coefficient

Interlaboratory study 1996 in Germany

Matrix	*l*	*n_{AP} in %*	*$\overline{\overline{X}}$ in µg/L*	*s_R in µg/L*	*CV_R in %*
Spiked drinking water	30	10	46.48	4.225	9.1

Other Analytical Methods

USA EPA 8270c, 1996 [1]: Semivolatile organic compounds by GC/MS.This method claims detection limits of 10 µg/L which is obviously too high. Other analytical methods based on this standard using modern GC/MS equipment however may attain the required low LOQs.

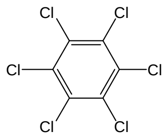
Comments

References

[1] http://www.accustandard.com/asi/pdfs/epa_methods/8270c.pdf

Compound

Hexachlorobenzene



CAS Number	**Log K_{OW}**	**Water Solubility [mg/L]**
118-74-1	5.73	0.006

AA-EQS [µg/L]		**MAC-EQS [µg/L]**	
Inland Surface Waters	**Other Surface Waters**	**Inland Surface Waters**	**Other Surface Waters**
0.01	0.01	0.05	0.05

Available Standard Method

EN ISO 6468:1996

Determination of certain organochlorine insecticides, polychlorinated biphenyls and chlorobenzenes – Gas chromatographic method after liquid-liquid extraction

Matrix Drinking, ground, surface and waste waters

Sampling

Pretreatment

Storage

Method Description

Liquid-liquid extraction of organochlorine insecticides, chlorobenzenes and PCBs by an extraction solvent. After concentration and clean-up the sample extracts are analysed by gas chromatography, using an electron-capture detector (GC-ECD).

The method is applicable to samples containing up to 50 mg/L of suspended solids.

Limit of Quantification (LOQ): ~ 0.001 – 0.01 µg/L

Method Validation

l Number of laboratories
n_{AP} percental rate of outliers
$\overline{\overline{X}}$ Total mean after elimination of outliers
s_R standard deviation between the laboratories
CV_R reproducibility variation coefficient

Interlaboratory study (Extraction with Hexane)

Matrix	l	n_{AP} in %	$\overline{\overline{X}}$ in ng/L	s_R in µg/L	CV_R in %
Surface water	15	0	48.8	16.6	34.1

Other Analytical Methods

Gas chromatography - mass spectrometry
GC-MS determination of the ion 284.

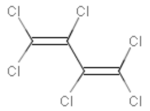
GC-ECD
EPA methods 505 (GC-ECD) and 625 (GC-MS): Liquid-liquid extraction of 1 L water with dichloromethane.
LOQ ~ 3 ng/L

Comments

An overview of HCB levels in the aquatic environment is given by Barber et al. (2005) [1]

References

[1] J. L. Barber, A. J. Sweetman, D. van Wijk, K. C. Jones, Hexachlorobenzene in the global environment: Emissions, levels, distribution, trends and processes. *Science of The Total Environment* 349, 2005, 1-44.

Compound *Hexachlorobutadiene*	

CAS Number	**Log K_{OW}**	**Water Solubility [mg/L]**
87-68-3	4.9	2.55 at 20 °C

AA-EQS [µg/L]		**MAC-EQS [µg/L]**	
Inland Surface Waters	**Other Surface Waters**	**Inland Surface Waters**	**Other Surface Waters**
0.1	0.1	0.6	0.6

Available Standard Method *EN ISO 10301:1997* Determination of highly volatile halogenated hydrocarbons - Gas-chromatographic methods	**Method Description** *EN ISO 10301:1997* specifies two methods for the determination of highly volatile halogenated hydrocarbons in water using gas chromatography with e.g. electron capture detector after: a) the extraction by an organic solvent or using, b) a head-space method. The static headspace method may not offer sufficient sensitivity dependent on the instrumentation available.
Matrix **Sampling** *ISO 5667-1, 5667-2 and ISO 5667-3* **Pretreatment** **Storage**	**Limit of Quantification (LOQ):** 100 µg/L

Method Validation

no data available

Other Analytical Methods

EPA method 8260B [1]. Volatile Organic Compounds by GC/MS. This method is suitable for a variety of matrices.

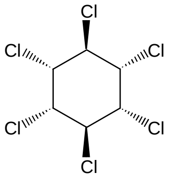
Comments

References

[1] http://www.accustandard.com/asi/pdfs/epa_methods/8260b.pdf

Compound

Hexachlorocyclohexane
(HCH)
α-, β-, γ- and δ- isomers



(γ-HCH; lindane)

CAS Number	**Log K_{OW}**	**Water Solubility [mg/L]**
608-73-1	α-HCH ~ 3.8 β-HCH ~ 3.78 γ-HCH ~ 3.72 δ-HCH ~ 4.14	α-HCH ~ 10 β-HCH ~ 5 γ-HCH ~ 7.3 δ-HCH ~ 10

AA-EQS [µg/L]		**MAC-EQS [µg/L]**	
Inland Surface Waters	**Other Surface Waters**	**Inland Surface Waters**	**Other Surface Waters**
0.02	0.002	0.04	0.02

Available Standard Method

EN ISO 6468:1996
Determination of certain organochlorine insecticides, polychlorinated biphenyls and chlorobenzenes – Gas chromatographic method after liquid-liquid extraction

Matrix Drinking, ground, surface and waste waters

Sampling

Pretreatment

Storage

Method Description

Liquid-liquid extraction of organochlorine insecticides, chlorobenzenes and PCBs by an extraction solvent. After concentration and clean-up the sample extracts are analysed by gas chromatography, using an electron-capture detector (GC-ECD).

The method is applicable to samples containing up to 50 mg/L of suspended solids.

Limit of Quantification (LOQ): ~ 0.001 – 0.01 µg/L

Method Validation

l Number of laboratories
n_{AP} percental rate of outliers
$\bar{\bar{X}}$ Total mean
s_R standard deviation between the laboratories
CV_R reproducibility variation coefficient

Interlaboratory study (Extraction of γ-HCH with Hexane)

Matrix	*l*	*n_{AP} in %*	*$\bar{\bar{X}}$ in ng/L*	*s_R in µg/L*	*CV_R in %*
Surface water	15	14.3	38.6	14.3	38.4

Other Analytical Methods

Solid-phase extraction gas chromatography - mass spectrometry
GC-MS determination of the ions 181, 217, and 219 for the HCHs [1-4]

LOQ ~ 10 ng/L for α-HCH,
5 ng/L for β-HCH,
5 ng/L for γ-HCH and
10 ng/L for δ- HCH (SPE extraction of 200 mL water) [1,2]

LOQ for γ-HCH (lindane) ~ 9 ng/L (SPE extraction of 500 mL water) [3].
LOQ for γ-HCH (lindane) ~ 2 ng/L (SPE extraction of 500 mL water) [4].

SPE-GC- triple quadrupole-MS-MS
C18-SPE, 100 mL, SRM 219 > 183; LOQ ~ 25 ng/L (for lindane) [5]

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

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

Comments

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

References

[1] S. Lacorte, I. Guiffard, D. Fraisse, D. Barceló, Broad Spectrum Analysis of 109 Priority Compounds Listed in the 76/464/CEE Council Directive Using Solid-Phase Extraction and GC/EI/MS. *Analytical Chemistry* 72, 2000, 1430-1440.

[2] D. de Almeida Azevedo, S. Lacorte, T. Vinhas, P. Viana, D. Barceló, Monitoring of Priority Pesticides and Other Organic Pollutants in River Water From Portugal by Gas Chromatography–Mass Spectrometry and Liquid Chromatography–Atmospheric Pressure Chemical Ionization Mass Spectrometry. *Journal of Chromatography A* 879, 2000, 13-26.

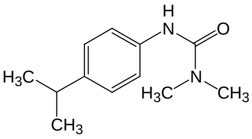
[3] J. Quintana, I. Martí, F. Ventura, Monitoring of Pesticides in Drinking and Related Waters in NE Spain with a Multiresidue SPE-GC–MS Method Including an Estimation of the Uncertainty of the Analytical Results. *Journal of Chromatography A* 938, 2001, 3-13.

[4] C. Planas, A. Puig, J. Rivera, J. Caixach, Analysis of pesticides and metabolites in Spanish surface waters by isotope dilution gas chromatography/mass spectrometry with previous automated solid-phase extraction; Estimation of the uncertainty of the analytical results. Journal of Chromatography A, 1131 (2006) 242– 252.

[5] E. Pitarch, C. Medina, T. Portolés, F.J. López, F. Hernández, Determination of priority organic micro-pollutants in water by gas chromatography coupled to triple quadrupole mass spectrometry. Analytica Chimica Acta 583, 2007, 246–258

Compound

Isoproturon



CAS Number	**Log K_{OW}**	**Water Solubility [mg/L]**
34123-59-6	~ 2.5	~ 70

AA-EQS [µg/L]		**MAC-EQS [µg/L]**	
Inland Surface Waters	**Other Surface Waters**	**Inland Surface Waters**	**Other Surface Waters**
0.3	0.3	1.0	1.0

Available Standard Method

EN ISO 11369:1997

Water quality - Determination of selected plant treatment agents in water by high performance liquid chromatography with UV detection after solid-liquid extraction.

Matrix Drinking and ground water

Sampling

Pretreatment

Storage

Method Description

The plant treatment substances in the water sample are extracted by solid-liquid extraction (SPE) on reversed-phase (RP)-C18 material, eluted with a solvent, and then separated, identified and quantified by high performance liquid chromatography (HPLC) using UV detection.

Limit of Quantification (LOQ): 0.1 µg/L

Method Validation

l Number of laboratories
n_{AP} percental rate of outliers
$\bar{\bar{X}}$ Total mean after elimination of outliers
s_R standard deviation between the laboratories
CV_R reproducibility variation coefficient

Interlaboratory study

Matrix	***l***	***n_{AP} in %***	***$\bar{\bar{X}}$ in µg/L***	***s_R in µg/L***	***CV_R in %***
Drinking water	32	0	0.1727	0.0394	22.8
Ground water	32	6	0.1110	0.0249	22.5

Other Analytical Methods

Liquid Chromatography - Mass Spectrometry

Identification and quantification of isoproturon (and other pesticides) by liquid chromatography coupled to (tandem) mass spectrometric detection (LC-MS-MS) using positive electrospray ionization (ESI).
LC-MS fragment ions: m/z 207 [1,2]
LC-MS-MS transitions: 207 > 72 [3,4]

LOQ ~ 1 ng/L (depending on the SPE enrichment factor)

Gas Chromatography - Mass Spectrometry (after derivatisation)

Phenylurea herbicides require a derivatisation step to prevent the degradation of these thermolabile compounds in the GC injector; LOQ ~ 1 ng/L [5].

SPE-derivatisation-GC-MS: LOQ ~ 40 ng/L [6]

Comments

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

References

[1] C. Crescenzi, A. Di Corcia, R. Samperi, N. L. Dietz, E. Guerriero, Development of a Multiresidue Method for Analyzing Pesticide Traces in Water Based on Solid-Phase Extraction and Electrospray Liquid Chromatography Mass Spectrometry. *Environmental Science & Technology* 31, 1997, 479-488.

[2] R. Loos, G. Hanke, S. J. Eisenreich: Multi-Component Analysis of Polar Water Pollutants Using Sequential Solid-Phase Extraction Followed by LC-ESI-MS. *Journal of Environmental Monitoring* 5, 2003, 384-394.

[3] R. Bossi, K. V. Vejrup, B. B. Mogensen, W. A. H. Asman, Analysis of Polar Pesticides in Rainwater in Denmark by Liquid Chromatography–Tandem Mass Spectrometry. *Journal of Chromatography A* 957, 2002, 27-36.

[4] M. Kuster, M. J. Lopez de Alda, C. Barata, D. Raldua, D. Barceló, Analysis of 17 polar to semi-polar pesticides in the Ebro river delta during the main growing season of rice by automated on-line solid-phase extraction-liquid chromatography-tandem mass spectrometry. *Talanta* 75, 2008, 390-401.

[5] A. C. Gerecke, C. Tixier, T. Bartels, R. P. Schwarzenbach, S. R. Müller, Determination of Phenylurea Herbicides in Natural Waters at Concentrations Below 1 ng l^{-1} Using Solid-Phase Extraction, Derivatisation, and Solid-Phase Microextraction–Gas Chromatography–Mass Spectrometry. *Journal of Chromatography A* 930, 2001, 9-19.

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

Compound

Lead and its compounds

CAS Number	**Log K_D [L/kg]**	**Water Solubility [mg/L]**
7439-92-1	***suspended matter/water:*** 5.6 (Pb) [1] ***sediment/water***: 5.1 (Pb) [1]	depending on compound

AA-EQS [µg/L]		**MAC-EQS [µg/L]**	
Inland Surface Waters	**Other Surface Waters**	**Inland Surface Waters**	**Other Surface Waters**
7.2	7.2	*not applicable*	*not applicable*

Available Standard Method

EN ISO 17294-2:2004

Application of inductively coupled plasma mass spectrometry (ICP-MS) - Part 2: Determination of 62 elements

Matrix Drinking waters, ground waters, surface waters and waste waters

Sampling *ISO 5667-1, 5667-2 and 5667-3*

Pretreatment For dissolved elements, filter aqueous sample through a 0.45-µm pore membrane filter. Adjust the pH of the filtrate to < 2 with HNO_3.

Storage

Method Description

EN ISO 17294-2:2004 specifies a method for the determination of the lead in water (for example drinking water, surface water, groundwater, wastewater and eluates). Taking into account the specific and additionally occurring interferences, these elements can also be determined in digests of water, sludges and sediments. The working range depends on the matrix and the interferences encountered.

Limit of Quantification (LOQ):

Drinking water and relatively unpolluted water:
0.1 up to 1 µg/L

Method Validation

l Number of laboratories
n_{AP} percental rate of outliers
$\bar{\bar{x}}$ Total mean after elimination of outliers
s_R standard deviation between the laboratories
CV_R reproducibility variation coefficient

Interlaboratory study 1997 in Germany

Matrix	***l***	***n_{AP} in %***	***$\bar{\bar{x}}$ in µg/L***	***s_R in µg/L***	***CV_R in %***
Surface water	39	2.5	13.6	1.13	8.3

Other Analytical Methods

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

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

DIN 38406-6:1998-07 determination using atomic absorption spectrometry

DIN 38406-16 (1990-03) specifies a voltammetric determination.

EPA 200.8 (1994) determination of trace elements in waters by inductively coupled plasma - mass spectrometry (LOQ: 0.6 µg/L)

Standard Methods Online (http://standardmethods.org/) 3125: Metals in Water by ICP/MS (LOQ: 0.005 µg/L)

Comments
References

Compound

Mercury and its compounds

CAS Number	**Log K_D [L/kg]**	**Water Solubility [mg/L]**
7439-97-6	***suspended matter/water:*** 5.3 (Hg) [1] ***sediment/water:*** 4.9 (Hg) [1]	Depending on compound

AA-EQS [µg/L]		**MAC-EQS [µg/L]**	
Inland Surface Waters	**Other Surface Waters**	**Inland Surface Waters**	**Other Surface Waters**
0.05	0.05	0.07	0.07

Available Standard Method

EN ISO 17852:2008

Determination of mercury by atomic fluorescence spectrometry

Matrix Drinking waters, ground waters and surface waters

Sampling *ISO 5667-1, 5667-2 and 5667-3*

Pretreatment stabilise with Potassium dichromate and acidification to pH< 2 with high purity Nitric Acid

Storage

Method Description

EN ISO 17852:2008 specifies a method for the determination of mercury in water using atomic fluorescence spectrometry.

Limit of Quantification (LOQ): appr. 0.001 µg/L (largely depends on the operational parameters)

Method Validation

l Number of laboratories

n_{AP} percental rate of outliers

$\overline{\overline{X}}$ Total mean after elimination of outliers

s_R standard deviation between the laboratories

CV_R reproducibility variation coefficient

Interlaboratory study 1999 in Great Britain

Matrix	l	n_{AP} ***in %***	$\overline{\overline{X}}$ ***in µg/L***	s_R ***in µg/L***	CV_R ***in %***
Surface water	18	9.4	44.2	11.57	25.8

Other Analytical Methods

EN 12338:1998 specifies the determination after enrichment by amalgamation

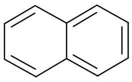
ISO 16590:2000 specifies methods involving enrichment by amalgamation

Comments

References

Compound

Naphthalene



CAS Number	**Log K_{OW}**	**Water Solubility [mg/L]**
91-20-3	3.3	31

AA-EQS [µg/L]		**MAC-EQS [µg/L]**	
Inland Surface Waters	**Other Surface Waters**	**Inland Surface Waters**	**Other Surface Waters**
2.4	1.2	*not applicable*	*not applicable*

Available Standard Method

EN ISO 17993:2003
Determination of 15 polycyclic aromatic hydrocarbons (PAH) in water by HPLC with fluorescence detection after liquid-liquid extraction

EN ISO 15680: 2003
Gas-chromatographic determination of a number of monocyclic aromatic hydrocarbons, naphthalene and several chlorinated compounds using purge-and-trap and thermal desorption

Matrix Drinking, ground, waste and surface water

Sampling

Pretreatment

Storage

Method Description

EN ISO 17993:2003 specifies a method using high performance liquid chromatography (HPLC) with fluorescence detection for the determination of 15 selected polycyclic aromatic hydrocarbons (PAH).

EN ISO 15680:2003 specifies a general method for the determination of volatile organic compounds (VOCs) in water by purge-and-trap isolation and gas chromatography (GC). Annexes A, B and C provide examples of analytes that can be determined. Detection is carried out by mass spectrometry in the electron impact mode (EI).

Limit of Quantification (LOQ):
HPLC - Drinking and ground water: > 0.005 µg/L
HPLC - Surface water: > 0.01 µg/L
Purge-and-Trap/Thermal Desorption GC-MS:
> 0.01 µg/L

Method Validation

l Number of laboratories
n_{AP} percental rate of outliers
$\bar{\bar{X}}$ Total mean after elimination of outliers
s_R standard deviation between the laboratories
CV_R reproducibility variation coefficient
n.a. = not available

Interlaboratory study (ISO 17993)

Matrix	***l***	***n_{AP} in %***	***$\bar{\bar{X}}$ in µg/L***	***s_R in µg/L***	***CV_R in %***
Spiked drinking water	33	3	52.85	15.5	29.3

Interlaboratory study (ISO 15680)

Matrix	***l***	***n_{AP} in %***	***$\bar{\bar{X}}$ in µg/L***	***s_R in µg/L***	***CV_R in %***
Surface water (0.2 µg/L)	17	n.a.	n.a.	n.a.	32

Other Analytical Methods

USA EPA 8270c,1996, [1] claims detection limit of 10 µg/L, which is obviously too high. Other analytical methods based on this standard using modern GC/MS equipment however may attain the required low LOQs.

Comments

References

[1] http://www.accustandard.com/asi/pdfs/epa_methods/8270c.pdf

Compound
Nickel and its compounds

CAS Number	Log K_D [L/kg]	Water Solubility [mg/L]
7440-02-0	***suspended matter/water:*** 4.6 (Ni) [1] ***sediment/water***: 4.0 (Ni) [1]	depending on compound

AA-EQS [µg/L]		MAC-EQS [µg/L]	
Inland Surface Waters	**Other Surface Waters**	**Inland Surface Waters**	**Other Surface Waters**
20	20	*not applicable*	*not applicable*

Available Standard Method
EN ISO 17294-2:2004
Application of inductively coupled plasma mass spectrometry (ICP-MS) - Part 2: Determination of 62 elements

Matrix Drinking waters, ground waters, surface waters and waste waters
Sampling *ISO 5667-1, 5667-2 and 5667-3*

For dissolved elements, filter aqueous sample through a 0.45 µm pore membrane filter. Adjust the pH of the filtrate to < 2 with HNO_3.

Storage

Method Description

EN ISO 17294-2:2004 specifies a method for the determination of the nickel in water (for example drinking water, surface water, groundwater, wastewater and eluates). Taking into account the specific and additionally occurring interferences, these elements can also be determined in digests of water, sludges and sediments. The working range depends on the matrix and the interferences encountered.

Limit of Quantification (LOQ):
Drinking water and relatively unpolluted water: 0.1 - 1.0 µg/l

Method Validation

l Number of laboratories
n_{AP} percental rate of outliers
$\bar{\bar{X}}$ Total mean after elimination of outliers
s_R standard deviation between the laboratories
CV_R reproducibility variation coefficient

Interlaboratory study 1997 in Germany

Matrix	*l*	n_{AP} *in %*	$\bar{\bar{X}}$ *in µg/L*	s_R *in µg/L*	CV_R *in %*
Surface water	35	11	5.44	0.786	14.5

Other Analytical Methods

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

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

EPA 200.8 1994 [1]: Determination of trace elements in waters by inductively coupled plasma - mass spectrometry (LOQ: 0.5 µg/L)

Standard Methods Online (http://standardmethods.org/) 3125: Metals in Water by ICP/MS (LOQ: 0.02 µg/L)

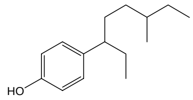
Comments

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

Compound

Nonylphenol

(One Isomer)



CAS Number	Log K_{OW}	Water Solubility [mg/L]
25154-52-3	~ 4.48	~ 6

AA-EQS [µg/L]		MAC-EQS [µg/L]	
Inland Surface Waters	**Other Surface Waters**	**Inland Surface Waters**	**Other Surface Waters**
0.3	0.3	2.0	2.0

Available Standard Method

EN ISO 18857-1:2006

Determination of selected alkylphenols - Part 1: Method for non-filtered samples using liquid extraction and gas chromatography with mass selective detection

Matrix Drinking, ground and surface water

Sampling

Pretreatment

Storage

Method Description

Method for the determination of 4-nonylphenols (mixture of isomers) in non-filtered samples of drinking water, ground water and surface water.

Extraction of nonylphenol from the acidified water sample with toluene. Cleaning of the extract, if necessary with silica. Gas chromatographic separation and identification of the alkylphenol by mass spectrometry without derivatisation (mass fragments m/z 135 and 107). Quantification with an internal standard (^{13}C p-n-NP; m/z 113).

Limit of Quantification (LOQ): 0.02 to 0.2 µg/L

Method Validation

l Number of laboratories
n_{AP} percental rate of outliers
$\bar{\bar{x}}$ Total mean after elimination of outliers
s_R standard deviation between the laboratories
CV_R reproducibility variation coefficient

Interlaboratory study 2002

Matrix	*l*	*n_{AP} in %*	*$\bar{\bar{x}}$ in µg/L*	*s_R in µg/L*	*CV_R in %*
Surface water	11	26.7	0.0828	0.016	18.8

Other Analytical Methods

Solid-phase extraction
Extraction of alkylphenols from water with solid-phase extraction (SPE) using C18 or polymeric adsorbents. Elution with methanol, acetone, ethylacetate, or dichloromethane [2-6].

Liquid Chromatography - Mass Spectrometry
Identification and quantification of the analytes by liquid chromatography coupled to (tandem) mass spectrometric detection (LC-MS-MS) using negative electrospray ionization (ESI).
LC-MS fragment ion: m/z 219 [2]
LC-MS-MS transitions: 219 > 133 and 219 > 147 [3,4]; LOQ ~ 5 ng/L
Internal standard: 4n-NP; transition 219 > 106

GC-MS after derivatisation
Several derivatisation techniques for alkylphenols prior to GC-MS determination have been reported.
E.g., the phenol group can be converted to a pentafluorobenzoylate ester (LOQ ~ 0.05 ng/L) [5], or silylated using bis(trimethylsilyl)trifluoroacetamide (BSTFA) (LOQ ~ 1 ng/L) [6], or methyl-N-(trimethylsilyl)trifluoroacetamide (MSTFA) [7].

Comments

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

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

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

References

[1] European Commission, European Chemicals Bureau, European Union Risk Assessment Report, 4-Nonylphenol (Branched) and Nonylphenol. EUR 20387 EN, 2002, URL: http://ecb.jrc.it/existing-chemicals/.

[2] M. Petrović, D. Barceló, Determination of Anionic and Nonionic Surfactants, Their Degradation Products, and Endocrine-Disrupting Compounds in Sewage Sludge by Liquid Chromatography/Mass Spectrometry. *Analytical Chemistry* 72, 2000, 4560-4567.

[3] J. E. Loyo-Rosales, I. Schmitz-Afonso, C.P. Rice, A. Torrents, Analysis of Octyl- and Nonylphenol and Their Ethoxylates in Water and Sediments by Liquid Chromatography/Tandem Mass Spectrometry. *Analytical Chemistry* 75, 2003, 4811-4817.

[4] A. Jahnke, J. Gandrass, W, Ruck, Simultaneous Determination of Alkylphenol Ethoxylates and their Biotransformation Products by Liquid Chromatography/Electrospray Ionisation Tandem Mass Spectrometry. *Journal of Chromatography A* 1035, 2004, 115-122.

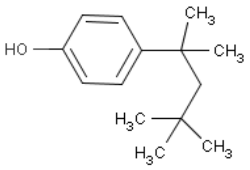
[5] H. M. Kuch, K. Ballschmiter, Determination of Endocrine-Disrupting Phenolic Compounds and Estrogens in Surface and Drinking Water by HRGC-(NCI)-MS in the Picogram per Liter Range. *Environmental Science & Technology* 35, 2001, 3201-3206.

[6] R. Liu, J. L. Zhou, A. Wilding, Simultaneous determination of endocrine disrupting phenolic compounds and steroids in water by solid-phase extraction – gas chromatography–mass spectrometry. *Journal of Chromatography A* 1022, 2004, 179-189.

[7] R. Haller, N. Hansen, Nonylphenols, Experimental Work Including Ruggedness Test, 2006, Eurofins, URL: http://www.ecn.nl/docs/society/horizontal/Report_ruggedness_NP.pdf

[8] K. Guenther, E. Kleist, B. Thiele, Estrogen-active nonylphenols from an isomer-specific viewpoint: a systematic numbering system and future trends. *Anal. Bioanal. Chem.* 384, 2006, 542-546.

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

Compound	
Octylphenol *(4-tert-Octylphenol)*	

CAS Number	**Log K_{OW}**	**Water Solubility [µg/L]**
140-66-9	5.28	5

AA-EQS [µg/L]		**MAC-EQS [µg/L]**	
Inland Surface Waters	**Other Surface Waters**	**Inland Surface Waters**	**Other Surface Waters**
0.1	0.01	*not applicable*	*not applicable*

Available Standard Method

EN ISO 18857-1:2006

Determination of selected alkylphenols - Part 1: Method for non-filtered samples using liquid extraction and gas chromatography with mass selective detection

Matrix Drinking, ground and surface water

Sampling

Pretreatment

Storage

Method Description

Method for the determination of octylphenol in non-filtered samples of drinking water, ground water and surface water.

Extraction of octylphenol from the acidified water sample with toluene. Cleaning of the extract, if necessary with silica. Gas chromatographic separation and identification of the alkylphenol by mass spectrometry without derivatisation (mass fragments m/z 135 and 107). Quantification with an internal standard (^{13}C p-n-NP; m/z 113).

Limit of Quantification (LOQ): 0.005 – 0.2 µg/L

Method Validation

l Number of laboratories
n_{AP} percental rate of outliers
$\overline{\overline{X}}$ Total mean after elimination of outliers
s_R standard deviation between the laboratories
CV_R reproducibility variation coefficient

Interlaboratory study 2002

Matrix	***l***	***n_{AP} in %***	***$\overline{\overline{X}}$ in µg/L***	***s_R in µg/L***	***CV_R in %***
Surface water	13	13.3	0.0668	0.01789	26.8

Other Analytical Methods

Solid-phase extraction
Extraction of alkylphenols from water with solid-phase extraction (SPE) using C18 or polymeric adsorbents. Elution with methanol, acetone, ethylacetate, or dichloromethane [2-6].

Liquid Chromatography - Mass Spectrometry
Identification and quantification of the analytes by liquid chromatography coupled to (tandem) mass spectrometric detection (LC-MS-MS) using negative electrospray ionization (ESI).
LC-MS fragment ion: m/z 205 [2]
LC-MS-MS transitions: 205 > 133 [3-4]
Internal standard: 4n-NP; transition 219 > 106

GC-MS after derivatisation
Several derivatisation techniques for alkylphenols prior to GC-MS determination have been reported.
E.g., the phenol group can be converted to a pentafluorobenzoylate ester (LOQ ~ 0.05 ng/L) [5], or silylated (LOQ ~ 2.6 ng/L) [6].

Comments

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

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

References

[1] M. Ahel, W. Giger, Aqueous solubility of alkylphenols and alkylphenol polyethoxylates. *Chemosphere* 26, 1993, 1461-1470.

[2] M. Petrović, D. Barceló, Determination of Anionic and Nonionic Surfactants, Their Degradation Products, and Endocrine-Disrupting Compounds in Sewage Sludge by Liquid Chromatography/Mass Spectrometry. *Anaytical Chemistry* 72, 2000, 4560-4567.

[3] J. E. Loyo-Rosales, I. Schmitz-Afonso, C.P. Rice, A. Torrents, Analysis of Octyl- and Nonylphenol and Their Ethoxylates in Water and Sediments by Liquid Chromatography/-Tandem Mass Spectrometry. *Anaytical Chemistry* 75, 2003, 4811-4817.

[4] A. Jahnke, J. Gandrass, W, Ruck, Simultaneous Determination of Alkylphenol Ethoxylates and their Biotransformation Products by Liquid Chromatography/Electrospray Ionisation Tandem Mass Spectrometry. *Journal of Chromatography A* 1035, 2004, 115-122.

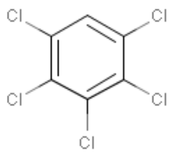
[5] H. M. Kuch, K. Ballschmiter, Determination of Endocrine-Disrupting Phenolic Compounds and Estrogens in Surface and Drinking Water by HRGC-(NCI)-MS in the Picogram per Liter Range. *Environmental Science & Technoogy* 35, 2001, 3201-3206.

[6] R. Liu, J. L. Zhou, A. Wilding, Simultaneous determination of endocrine disrupting phenolic compounds and steroids in water by solid-phase extraction – gas chromatography–mass spectrometry. *Journal of Chromatography A* 1022, 2004, 179-189.

[7] OSPAR Commission, 2006 update, OSPAR background document on octylphenol, URL: http://www.ospar.org/documents/dbase/publications/p00273_BD%20on%20octylphenol%20_2006%20version.pdf

Compound

Pentachlorobenzene



CAS Number	Log K_{OW}	Water Solubility [mg/L]
60-93-5	5.17	0.831

AA-EQS [µg/L]		MAC-EQS [µg/L]	
Inland Surface Waters	**Other Surface Waters**	**Inland Surface Waters**	**Other Surface Waters**
0.007	0.0007	*not applicable*	*not applicable*

Available Standard Method

EN ISO 6468:1996

Determination of certain organochlorine insecticides, polychlorinated biphenyls and chlorobenzenes – Gas chromatographic method after liquid-liquid extraction

Matrix Drinking, ground, surface and waste waters

Sampling

Pretreatment

Storage

Method Description

Liquid-liquid extraction of organochlorine insecticides, chlorobenzenes and PCBs by an extraction solvent. After concentration and clean-up the sample extracts are analysed by gas chromatography, using an electron-capture detector (GC-ECD).

The method is applicable to samples containing up to 50 mg/L of suspended solids.

Limit of Quantification (LOQ): ~ 0.001 – 0.01 µg/L

Method Validation

no data available

Other Analytical Methods

Gas chromatography - mass spectrometry
GC-MS determination of the ions 250, 215, 180

GC-ECD
EPA methods 505 (GC-ECD) [1] and 625 (GC-MS) [2]: Liquid-liquid extraction of 1 L water with dichloromethane.
LOQ ~ 3 ng/L

GC- triple-quad MS-MS [3]
SPE extraction of 100 mL water (elution with ethyl acetate / DCM) followed by GC- triple-quad MS-MS. Precursor ions 248 and 250, product 142; LOQ = 25 ng/L.

With NCI and the extraction of bigger water volumes, a lower LOQ might be achieved.

Comments

If released to water, pentachlorobenzene will adsorb strongly to sediments and bioconcentrate in fish. It will be subject to evaporation with a half-life of 6.5 hours estimated for evaporation from a river 1 m deep, flowing at 1 m/sec and a wind velocity of 3 m/sec. The volatilization half-life from a model pond, which considers the effects of adsorption, can be estimated to be about 60 days. It will not be expected to significantly biodegrade or hydrolyze.

References

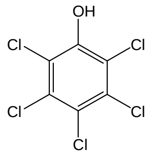
[1] http://www.accustandard.com/asi/pdfs/epa_methods/505.pdf

[2] http://www.accustandard.com/asi/pdfs/epa_methods/625.pdf

[3] E. Pitarch, C. Medina, T. Portolés, F.J. López, F. Hernández, Determination of priority organic micro-pollutants in water by gas chromatography coupled to triple quadrupole mass spectrometry. *Analytica Chimica Acta* 583, 2007, 246-258.

Compound

Pentachlorophenol



CAS Number	Log K_{OW}	Water Solubility [mg/L]
87-86-5	~ 5.0	~ 14

AA-EQS [µg/L]		MAC-EQS [µg/L]	
Inland Surface Waters	**Other Surface Waters**	**Inland Surface Waters**	**Other Surface Waters**
0.4	0.4	1	1

Available Standard Method

EN 12673:1998

Gas chromatographic determination of some selected chlorophenols in water

Matrix Drinking, ground, rain, waste, sea and surface water

Sampling

Pretreatment

Storage

Method Description

This European Standard describes the gas chromatographic determination of 19 chlorophenols in water.

The methods consists of acetylaction of the chlorophenols with acetic anhydride followed by liquid/liquid extraction with hexane and determination by gas chromatography (GC) and electrone capture detection (ECD) or mass selective detection (MSD).

Limit of Quantification (LOQ): 0.1 µg/L (Extraction volume:50 mL)

Method Validation

l Number of laboratories

n_{AP} percental rate of outliers

$\overline{\overline{X}}$ Total mean after elimination of outliers

s_R standard deviation between the laboratories

CV_R reproducibility variation coefficient

Interlaboratory study November 1996

Matrix	*l*	n_{AP} *in %*	$\overline{\overline{X}}$ *in µg/L*	s_R *in µg/L*	CV_R *in %*
Drinking water	12	22.2	0.11	0.028	24
Surface water	13	7.1	0.20	0.042	21

Other Analytical Methods

Gas Chromatography - Mass Spectrometry

Characteristic ions for MS detection (of acetate): 266, 264, 268, 270 (DIN EN 12673).

Silyl derivatisation GC-MS

Derivatisation with Bis(trimethylsilyl)trifluoroacetamide (BSTFA); MS quantification ions 323, 321, 93. Dynamic concentration range: 1-1500 µg/L (without enrichment)

Solid-phase extraction

SPE with styrene-divinylbenzene (SDB) cartridges at pH 2.6; elution with 4 mL methanol; recovery ~ 90 % [2].

SPME-GC-MS

SPME from 2 mL sample volume; scan MS acquisition; claiming a LOQ of ~ 5 ng/L [3]

Derivatisation SPME-GC-MS

Derivatisation with acetic anhydride in 22 mL headspace vials followed by SPME and GC-MS determination (scan mode); LOQ ~ 3 ng/L [4].

SPE-LC-MS

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

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

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

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

Comments

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

References

[1] D. Li, J. Park, J.-R. Oh, Silyl Derivatisation of Alkylphenols, Chlorophenols, and Bisphenol A for Simultaneous GC/MS Determination, *Anaytical Chemistry* 73, 2001, 3089-3095.

[2] I. Rodríguez, M. C. Mejuto, M. H. Bollaín, R. Cela, Evaluation of two solid-phase extraction procedures for the preconcentration of chlorophenols in drinking water, *Journal of Chromatography A* 786, 1997, 285-292.

[3] A. Ribeiro, M. H. Neves, M. F. Almeida, A. Alves and L. Santos, Direct determination of chlorophenols in landfill leachates by solid-phase micro-extraction–gas chromatography–mass spectrometry, *Journal of Chromatography A* 975, 2002, 267-274.

[4] M. Llompart, M. Lourido, P. Landín, C. García-Jares, R. Cela, Optimization of a derivatisation–solid-phase microextraction method for the analysis of thirty phenolic pollutants in water samples, *Journal of Chromatography A* 963, 2002, 137-148.

[5] D. Puig, I. Silgoner, M. Grasserbauer, D. Barceló, Part-Per-Trillion Level Determination of Priority Methyl-, Nitro-, and Chlorophenols in River Water Samples by Automated On-Line Liquid/Solid Extraction Followed by Liquid Chromatography/Mass Spectrometry Using Atmospheric Pressure Chemical Ionization and Ion Spray Interfaces, *Anaytical Chemistry*. 69, 1997, 2756-2761.

[6] R. Wissiack, E. Rosenberg, Universal Screening Method for the Determination of US Enviromental Protection Agency Phenols at the Lower ng l Level in Water Samples by On-Line Solid-Phase Extraction-High-Performance Liquid Chromatography-Atmospheric Pressure Chemical Ionization Mass Spectrometry Within a Single Run, *Journal of Chromatography A* 963, 2002, 149-157.

[7] O. Jauregui, E. Moyano, M.T. Galceran, Liquid Chromatography-Atmospheric Pressure Ionization Mass Spectrometry for the Determination of Chloro- and Nitrophenolic Compounds in Tap Water and Sea Water, *Journal of Chromatography A* 787, 1997, 79-89.

Compound	
Benzo[a]pyrene	$C_{20}H_{12}$
Benzo[b]fluoroanthene	$C_{20}H_{12}$
Benzo[g,h,i]perylene	$C_{22}H_{12}$
Benzo[k]fluoroanthene	$C_{20}H_{12}$
Indeno[1,2,3-cd]pyrene	$C_{22}H_{12}$

	CAS Number	**Log K_{OW}**	**Water Solubility [mg/L]**
Benzo[a]pyrene	50-32-8	6.13	0.00162
Benzo[b]fluoroanthene	205-99-2	5.78	0.0015
Benzo[k]fluoroanthene	207-08-9	6.11	0.0008
Benzo[g,h,i]perylene	191-24-2	6.63	0.00026
Indeno[1,2,3-cd]pyrene	193-39-5	6.70	0.00019

	AA-EQS [µg/L]		**MAC-EQS [µg/L]**	
	Inland Surface Waters	**Other Surface Waters**	**Inland Surface Waters**	**Other Surface Waters**
Benzo[a]pyrene	0.05	0.05	0.1	0.1
Benzo[b]fluoroanthene *Benzo[k]fluoroanthene*	Σ = 0.03	Σ = 0.03	*not applicable*	*not applicable*
Benzo[g,h,i]perylene *Indeno[1,2,3-cd]pyrene*	Σ = 0.002	Σ = 0.002	*not applicable*	*not applicable*

Available Standard Method
EN ISO 17993: 2003
Determination of 15 polycyclic aromatic hydrocarbons (PAH) in water by HPLC with fluorescence detection after liquid-liquid extraction

Matrix Drinking, ground, waste and surface water
Sampling

Pretreatment

Storage

Method Description

EN ISO 17993:2003 specifies a method using high performance liquid chromatography (HPLC) with fluorescence detection for the determination of 15 selected polycyclic aromatic.

Limit of Quantification (LOQ):
Drinking and ground water: > 0.005 µg/L
Surface water: > 0.01 µg/L

Method Validation

l Number of laboratories
n_{AP} percental rate of outliers
$\overline{\overline{X}}$ Total mean after elimination of outliers
s_R standard deviation between the laboratories
CV_R reproducibility variation coefficient

National interlaboratory study for spiked drinking water 1996 (German)

Substance	***l***	***n_{AP} in %***	***$\overline{\overline{X}}$ in pg/L***	***s_R in pg/L***	***CV_R in %***
Benzo[a]pyrene	33	3.1	20.43	4.17	20.4
Benzo[b]fluoroanthene	33	3.1	27.41	4.719	17.2
Benzo[k]fluoroanthene	32	3.2	10.87	2.382	21.9

Benzo[g,h,i]perylene	32	6.2	25.21	5.941	23.6
Indeno[1,2,3-cd]pyrene	29	12	26.31	4.417	17.9

Other Analytical Methods

EPA 8270c [1] claims detection limit of 10 µg/L which is obviously too high. Other analytical methods based on this standard using modern GC/MS equipment however may attain the required low LOQs.

Comments

The methods do not attain low enough LOQs and uncertainties for compliance checking with the AA-EQS for the sum of *Benzo[b]fluoroanthene and Benzo[k]fluoroanthene as well as the sum of Benzo[g,h,i]perylene and Indeno[1,2,3-cd]pyrene.* In addition, not enough validation data are available regarding the analysis of surface water samples in particular samples containing substantial amounts of SPM.

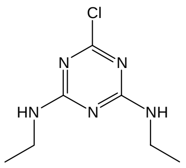
A new ISO standard for the determination of PAH in water using gas chromatography with mass spectrometry detection in under development (ISO/CD 28540)

References

[1] http://www.accustandard.com/asi/pdfs/epa_methods/8270c.pdf

Compound

Simazine



CAS Number	Log K_{OW}	Water Solubility [mg/L]
1912-24-9	~ 2.2	~ 6.2

AA-EQS [µg/L]		MAC-EQS [µg/L]	
Inland Surface Waters	**Other Surface Waters**	**Inland Surface Waters**	**Other Surface Waters**
1	1	4	4

Available Standard Method
EN ISO 10695:2000
Determination of selected organic nitrogen and phosphorus compounds - Gas chromatography methods

Matrix Drinking waters, ground waters, surface waters and waste waters containing up to 50 mg/L of suspended solids

Sampling

Pretreatment

Storage

Method Description

Liquid/liquid extraction with dichloromethane or liquid/solid extraction (SPE) on reversed-phase (RP)-C18 material or other adsorbent. Elution of the cartridges with e.g. methanol or acetone.
After concentration, the sample extracts are analysed by gas chromatography, using a nitrogen-phosphorus or mass spectrometric detector.

Limit of Quantification (LOQ):
Liquid/liquid extraction method: 0.5 µg/L
Liquid/solid extraction method: 0.012 µg/L

Method Validation

l Number of laboratories
n_{AP} percental rate of outliers
$\bar{\bar{X}}$ Total mean after elimination of outliers
s_R standard deviation between the laboratories
CV_R reproducibility variation coefficient

Interlaboratory study 1993 for liquid/solid extraction

Matrix	l	n_{AP} in %	$\bar{\bar{X}}$ in µg/L	s_R in µg/L	CV_R in %
Drinking water	12	16.4	0.058	0.0044	27.3

Other Analytical Methods

Gas Chromatography - Mass Spectrometry
GC-MS determination of the ions 201and 186; LOQ ~ 1 ng/L (after SPE) [1, 2]
(EPA method 525)
GC-NPD
EPA method 507 [3]
GC-ECD
EPA method 505; microextraction with hexane and GC-ECD analysis [32]

Liquid Chromatography - Mass Spectrometry
Identification and quantification of simazine (and other pesticides) by liquid chromatography coupled to (tandem) mass spectrometric detection (LC-MS-MS) using positive electrospray ionization (ESI).
LC-MS fragment ions: m/z 202 and 124 [4]
LC-MS-MS transition: 202 > 132 [5, 6]

LOQ ~ 1 ng/L (depending on the SPE enrichment factor)

Comments

References

[1] T. D. Bucheli, F. C. Grüebler, S. R. Müller, R. P. Schwarzenbach, Simultaneous Determination of Neutral and Acidic Pesticides in Natural Waters at the Low Nanogram per Liter Level. *Anaytical Chemistry* 69, 1997, 1569-1576.

[2] C. Planas, A. Puig, J. Rivera, J. Caixach, Analysis of pesticides and metabolites in Spanish surface waters by isotope dilution gas chromatography/mass spectrometry with previous automated solid-phase extraction; Estimation of the uncertainty of the analytical results. Journal of Chromatography A, 1131, 2006, 242–252.

[32] D. Barceló, Environmental Protection Agency and Other Methods for the Determination of Priority Pesticides and Their Transformation Products in Water. *Journal of Chromatography A*, 643, 1993, 117-143.

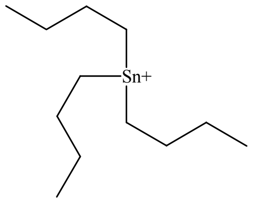
[4] C. Crescenzi, A. Di Corcia, R. Samperi, N. L. Dietz, E. Guerriero, Development of a Multiresidue Method for Analyzing Pesticide Traces in Water Based on Solid-Phase Extraction and Electrospray Liquid Chromatography Mass Spectrometry. *Environmental Science & Technoogy* 31, 1997, 479-488.

[5] R. Bossi, K. V. Vejrup, B. B. Mogensen, W. A. H. Asman, Analysis of Polar Pesticides in Rainwater in Denmark by Liquid Chromatography–Tandem Mass Spectrometry. *Journal of Chromatography A* 957, 2002, 27-36.

[6] M. Kuster, M. J. Lopez de Alda, C. Barata, D. Raldua, D. Barceló, Analysis of 17 polar to semi-polar pesticides in the Ebro river delta during the main growing season of rice by automated on-line solid-phase extraction-liquid chromatography-tandem mass spectrometry. Talanta 75, 2008, 390-401.

Compound

Tributyltin compounds



CAS Number	Log K_{OW}	Water Solubility [mg/L]
688-73-3		~ 2 mg/L

AA-EQS [µg/L]		MAC-EQS [µg/L]	
Inland Surface Waters	**Other Surface Waters**	**Inland Surface Waters**	**Other Surface Waters**
0.0002	0.0002	0.0015	0.0015

Available Standard Method

EN ISO 17353:2005

Determination of selected organotin compounds - Gas chromatographic method

Matrix Drinking, surface and waste waters containing not more than 2g/L of suspended material.

Sampling

Pretreatment

Storage

Method Description

Method for the identification and quantification of organotin compounds and/or cations in water.

Compounds:

Monobutyltin cation (MBT) $BuSn^{3+}$

Dibutyltin cation (DBT) Bu_2Sn^{2+}

Tributyltin cation (TBT) Bu_3Sn^+

Tetrabutyltin (TTBT) Bu_4Sn

Organotin compounds in water are ethylated with sodium tetraethyl-borate ($NaBEt_4$) and extracted with hexane. The extract can be cleaned with silica. After concentration, the tetra-substituted OTC are separated by capillary gas chromatography and detected with a suitable system (MS, FPD, AED). The concentration is determined by calibration over the total procedure using an internal standard mixture.

Limit of Quantification (LOQ): 0.010 – 1 µg/L

Method Validation

l Number of laboratories
n_{AP} percental rate of outliers
$\bar{\bar{X}}$ Total mean
s_R standard deviation between the laboratories
CV_R reproducibility variation coefficient

Interlaboratory study 1998 in Germany

Matrix	*l*	n_{AP} *in %*	$\bar{\bar{X}}$ *in ng/L*	s_R *in µg/L*	CV_R *in %*
Spiked surface water	11	8.3	388.2	92.16	23.7

Other Analytical Methods

LLE-EI-GC-MS

100 mL seawater, pH 5.4, derivatisation with $NaBEt_4$, hexane extraction; LOQ ~ 0.8 ng/L [1].

GC-NCI-MS

LOQ 0.1 ng/L [2].

Liquid phase microextraction (LPME) – GC-MS-MS

4mL water sample; 4-fluorophenyl derivatisation; LOQ 0.36 ng/L [3].

LLE-GC-FDP

1 L sea water, pH 5.5, ethylation in aqueous phase with $NaBEt_4$, iso-octane/n-pentane extraction;
LOQ 0.01 ng/L [4].

LLE-LC-MS

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

GC-ICP-MS

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

Comments

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

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

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

References

[1] G. Centineo, P. Rodríguez-González, E. Blanco González, J. I. García Alonso, A. Sanz-Medel, N. Font Cardona, J. Luis Aranda Mares, S. Ballester Nebot. Isotope dilution GC-MS routine method for the determination of butyltin compounds in water. *Anal. Bioanal. Chem.* 384, 2006, 908-914.

[2] K. Mizuishi, M. Takeuchi, T. Hobo. Trace analysis of tributyltin and triphenyltin compounds in sea water by gas chromatography–negative ion chemical ionization mass spectrometry. *Journal of Chromatography A* 800, 1998, 267-273.

[3] H. Shioji, S. Tsunoi, H. Harino, M. Tanaka. Liquid-phase microextraction of tributyltin and triphenyltin coupled with gas chromatography–tandem mass spectrometry. *Journal of Chromatography A*, 1048, 2004, 81-88.

[4] P. Michel, B. Averty. Distribution and Fate of Tributyltin in Surface and Deep Waters of the Northwestern Mediterranean. *Environmental Science & Technoogy* 33, 1999, 2524-2528.

[5] K. Békri, R. Saint-Louis, É. Pelletier. Determination of tributyltin and 4-hydroxybutyldibutyltin chlorides in seawater by liquid chromatography with atmospheric pressure chemical ionization-mass spectrometry. *Analytica Chimica Acta* 578, 2006, 203-212.

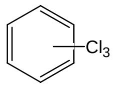
[6] M. Monperrus., E. Tessier., D. Amouroux, O.F.X. Donard. Simultaneous speciation of mercury and butyltin compounds in natural waters and snows by propylation and species specific isotope dilution mass spectrometry analysis. *Anal Bioanal Chem*, 381, 2005, 854-862.

[7] M. Monperrus, O. Zuloaga, E. Krupp, D. Amouroux, R. Wahlen, B. Fairman, O.F.X. Donard. Rapid, accurate and precise determination of tributyltin in sediments and biological samples by species specific isotope dilution-microwave extraction-gas chromatography-ICP mass spectrometry. *J. Anal. Atomic Spetrosc.* 18(3), 2003, 247-253.

Compound

Trichlorobenzenes

(all isomers)



CAS Number	Log K_{OW}	Water Solubility [mg/L]
12002-48-1	4.02 – 4.49	6-19

AA-EQS [µg/L]		MAC-EQS [µg/L]	
Inland Surface Waters	**Other Surface Waters**	**Inland Surface Waters**	**Other Surface Waters**
0.4	0.4	*not applicable*	*not applicable*

Available Standard Method

EN 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

Matrix drinking water, ground water, surface water, seawater and (diluted) waste water

Sampling *ISO 5667-1, 5667-2 and ISO 5667-3*

Pretreatment

Storage at 4 °C air tight and no direct sunlight, analysis within 5 days

Method Description

EN ISO 15680:2003 specifies a general method for the determination of volatile organic compounds (VOCs) in water by purge-and-trap isolation and gas chromatography (GC).

Detection is preferably carried out by mass spectrometry in the electron impact mode (EI), but other detectors may be applied as well

Selected ions: 180, 182, 145

Limit of Quantification (LOQ): 0.01 µg/L

Method Validation

l Number of laboratories
n_{AP} percental rate of outliers
$\bar{\bar{x}}$ Total mean after elimination of outliers
s_R standard deviation between the laboratories
CV_R reproducibility variation coefficient
n.a. = not available

Interlaboratory study

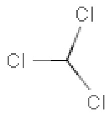
Matrix	l	n_{AP} *in %*	$\bar{\bar{x}}$ *in ng/L*	s_R *in ng/L*	CV_R *in %*
Drinking water (0.2 µg/L)	5	n.a.	n.a.	n.a.	27
Surface water (0.2 µg/L)	4	n.a.	n.a.	n.a.	35

Other Analytical Methods

ISO 6468:1996: Water quality - Determination of certain organochlorine insecticides, polychlorinated biphenyls and chlorobenzenes - Gas chromatographic method after liquid-liquid extraction. LOQ ~ 0.01µg/l.

Comments

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

Compound *Trichloromethane*	

CAS Number	**Log K_{OW}**	**Water Solubility [mg/L]**
67-66-3	1.97	8.7

AA-EQS [µg/L]		**MAC-EQS [µg/L]**	
Inland Surface Waters	**Other Surface Waters**	**Inland Surface Waters**	**Other Surface Waters**
2.5	2.5	*not applicable*	*not applicable*

Available Standard Method

EN ISO 15680: 2003

Gas-chromatographic determination of a number of monocyclic aromatic hydrocarbons, naphthalene and several chlorinated compounds using purge-and-trap and thermal desorption

Matrix drinking water, ground water, surface water, seawater and (diluted) waste water

Sampling *ISO 5667-1, 5667-2 and ISO 5667-3*

Pretreatment

Storage at 4 °C air tight and no direct sunlight, analysis within 5 days

Method Description

EN ISO 15680:2003 specifies a general method for the determination of volatile organic compounds (VOCs) in water by purge-and-trap isolation and gas chromatography (GC).

Detection is preferably carried out by mass spectrometry in the electron impact mode (EI), but other detectors may be applied as well.

Limit of Quantification (LOQ): 0.01 µg/L

Method Validation

l Number of laboratories
n_{AP} percental rate of outliers
$\overline{\overline{X}}$ Total mean after elimination of outliers
s_R standard deviation between the laboratories
CV_R reproducibility variation coefficient
n.a. = not available

Interlaboratory study

Matrix	l	n_{AP} *in %*	$\overline{\overline{X}}$ *in ng/L*	s_R *in ng/L*	CV_R *in %*
Drinking water (0.2 µg/L)	15	n.a.	n.a.	n.a.	29
Surface water (0.2 µg/L)	13	n.a.	n.a.	n.a.	30

Other Analytical Methods

EN ISO 10301:1997 specifies two methods for the determination of highly volatile halogenated hydrocarbons in water using gas chromatography with e.g. electron capture detector after: a) the extraction by an organic solvent or using, b) a head-space method (LOQ: 100 µg/L).

The EPA Method 1624 is designed to determine the volatile organic pollutants in water amenable to purge and trap gas chromatography-mass spectrometry.

Huybrechts et al. 2003 give a review of gas chromatography-based methods for analysis of volatile organic compounds in estuarine waters with special emphasis on monitoring. [1]

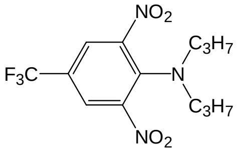
Comments

References

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

Compound

Trifluralin



CAS Number	**Log K_{OW}**	**Water Solubility [mg/L]**
1582-09-8	~ 5.3	~ 0.3

AA-EQS [µg/L]		**MAC-EQS [µg/L]**	
Inland Surface Waters	**Other Surface Waters**	**Inland Surface Waters**	**Other Surface Waters**
0.03	0.03	*not applicable*	*not applicable*

Available Standard Method

EN ISO 10695:2000

Determination of selected organic nitrogen and phosphorus compounds - Gas chromatography methods

Matrix Drinking waters, ground waters, surface waters and waste waters containing up to 50 mg/L of suspended solids

Sampling

Pretreatment

Storage

Method Description

Liquid/liquid extraction with dichloromethane or liquid/solid extraction (SPE) on reversed-phase (RP)-C18 material or other adsorbent. Elution of the cartridges with e.g. methanol or acetone.

After concentration, the sample extracts are analysed by gas chromatography, using a nitrogen-phosphorus or mass spectrometric detector.

Limit of Quantification (LOQ): ~ 0.05 µg/L

Method Validation

l Number of laboratories
n_{AP} percental rate of outliers
$\bar{\bar{X}}$ Total mean after elimination of outliers
s_R standard deviation between the laboratories
CV_R reproducibility variation coefficient

Interlaboratory study 1993 for liquid/solid extraction

Matrix	***l***	***n_{AP} in %***	***$\bar{\bar{x}}$ in µg/L***	***s_R in µg/L***	***CV_R in %***
Raw water	14	8.6	0.296	0.0264	46.3

Other Analytical Methods

Gas Chromatography - Mass Spectrometry
GC-MS determination of the ions 306, 264, 336 [1-5]
LOQ ~ 13 ng/L (SPE extraction of 500 mL water) [1]
LOQ ~ 5 ng/L (SPE extraction of 200 mL water) [4]
LOQ ~ 1 ng/L (SPE extraction of 500 mL water) [5]

EPA method 508.1 (GC-ECD) [6]
SPE-GC- triple quadrupole-MS-MS
C18-SPE, 100 mL, 306 > 264; LOQ ~ 25 ng/L [7]

SPE-GC-NCI-MS
C18-SPE, 100 mL, LOQ ~ 25 ng/L [7]

Comments

If released to water, trifluralin is expected to biodegrade under both aerobic and anaerobic conditions and to undergo direct photolytic degradation. It is expected to bioconcentrate in fish and aquatic organisms and adsorb strongly to sediment and suspended organic matter. It may also volatilize from water to the atmosphere. If released to the atmosphere, trifluralin is expected to undergo a rapid gas-phase photolysis.

References

[1] J. Quintana, I. Martí, F. Ventura, Monitoring of Pesticides in Drinking and Related Waters in NE Spain with a Multiresidue SPE-GC–MS Method Including an Estimation of the Uncertainty of the Analytical Results. *Journal of Chromatography* A 938, 2001, 3-13.

[2] M. Kochman, A. Gordin, P. Goldshlag, S. J. Lehotay, A. Amirav, Fast, High-Sensitivity, Multipesticide Analysis of Complex Mixtures With Supersonic Gas Chromatography–Mass Spectrometry. *Journal of Chromatography A* 974, 2002, 185-212.

[3] S. Lacorte, I. Guiffard, D. Fraisse, D. Barceló, Broad Spectrum Analysis of 109 Priority Compounds Listed in the 76/464/CEE Council Directive Using Solid-Phase Extraction and GC/EI/MS. *Anaytical Chemistry* 72, 2000, 1430-1440.

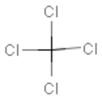
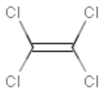
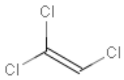
[4] D. de Almeida Azevedo, S. Lacorte, T. Vinhas, P. Viana, D. Barceló, Monitoring of Priority Pesticides and Other Organic Pollutants in River Water From Portugal by Gas Chromatography–Mass Spectrometry and Liquid Chromatography–Atmospheric Pressure Chemical Ionization Mass Spectrometry. *Journal of Chromatography A* 879, 2000, 13-26.

[5] C. Planas, A. Puig, J. Rivera, J. Caixach, Analysis of pesticides and metabolites in Spanish surface waters by isotope dilution gas chromatography/mass spectrometry with previous automated solid-phase extraction; Estimation of the uncertainty of the analytical results. *Journal of Chromatography* A, 1131, 2006, 242–252.

[6] http://www.accustandard.com/asi/pdfs/epa_methods/508_1.pdf

[7] E. Pitarch, C. Medina, T. Portolés, F.J. López, F. Hernández, Determination of priority organic micro-pollutants in water by gas chromatography coupled to triple quadrupole mass spectrometry. Analytica Chimica Acta 583, 2007, 246–258.

Compound

Carbontetrachloride	*Tetrachloroethylene*	*Trichloroethylene*
		

CAS Number		**Log K_{OW}**	**Water Solubility [mg/L]**
Carbontetrachloride	56-23-5	2.83	1160
Tetrachloroethylene	127-18-4	3.4	100
Trichloroethylene	79-01-6	2.42	1100

	AA-EQS [µg/L]		**MAC-EQS [µg/L]**	
	Inland Surface Waters	**Other Surface Waters**	**Inland Surface Waters**	**Other Surface Waters**
Carbontetrachloride	12	12	*not applicable*	*not applicable*
Tetrachloroethylene	10	10		
Trichloroethylene	10	10		

Available Standard Method
EN ISO 10301:1997
Determination of highly volatile halogenated hydrocarbons - Gas-chromatographic methods

Matrix Drinking, ground, surface and waste waters
Sampling

Pretreatment

Storage

Method Description

EN ISO 10301:1997 specifies two methods for the determination of highly volatile halogenated hydrocarbons in water using gas chromatography with e.g. electron capture detector after: a) the extraction by an organic solvent or using, b) a head-space method.

Limit of Quantification (LOQ [µg/L]):

	Solvent	**Headspace**
Carbon tetrachloride	0.01-0.1	0.1
Tetrachloroethylene	0.1	0.2
Trichloroethylene	0.05-0.1	0.2

Method Validation

l Number of laboratories
n_{AP} percental rate of outliers
$\bar{\bar{X}}$ Total mean after elimination of outliers
s_R standard deviation between the laboratories
CV_R reproducibility variation coefficient

Interlaboratory study

Wastewater	***l***	***n_{AP} in %***	***$\bar{\bar{X}}$ in ng/L***	***s_R in µg/L***	***CV_R in %***
Solvent Extraction:					
Carbon Tetrachloride	18	0	76.2	7.2	9.4
Tetrachloroethylene	18	0	81.3	6.4	7.8
Trichloroethylene	18	6	74.7	7.3	9.7
Headspace:					
Carbon Tetrachloride	10	0	0.29	0.05	17.6
Tetrachloroethylene	17	0	27.63	0.62	2.3
Trichloroethylene	23	5	41.07	1.226	3.0

Other Analytical Methods
EPA method 502.2 - Purge and Trap concentration with photoionisation and electrolytical conductivity detection [1]. GC/MS confirmation can also be used.

EPA method 524.2 – Purge and Trap concentration with GC/MS analysis [2].

Comments

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

References

[1] http://www.accustandard.com/asi/pdfs/epa_methods/502_2.pdf
[1] http://www.accustandard.com/asi/pdfs/epa_methods/524_2.pdf

ANNEX III: Existing certified reference materials[1]

Table 1: Reference materials producers

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

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[1] EAQC-WISE project, funded under the 6th RDT Framework Programme, European Commission

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

Priority substance	Matrix	CRM-Identifier	Producer	Certified value	Reference
Alachlor	**P**	SRM-3070	NIST	24.0 mg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
Anthracene	**P**	DPAC-1	NRC-CNRC, Canada	13 µg/g	http://inms-ienm.nrc-cnrc.gc.ca/calserv/crm_e.html
	P	SIRM 10-2-30s	Q-chem Ltd., Slovakia	48.7 µg/g	http://www.comar.bam.de/
	P	SRM-1647d	NIST	20.77 µg/mL	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	P	SRM-2260a	NIST	3.231 µg/mL	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
Atrazine	**P**	SRM-3070	NIST	39.2 mg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
Benzene	**P**	7141-95M/1	GUP TSIKV	0.99 g/L	http://www.comar.bam.de/
	P	7141-95M/2	GUP TSIKV	0.495 g/L	http://www.comar.bam.de/
	P	7141-95M/3	GUP TSIKV	0.097 g/L	http://www.comar.bam.de/
	P	7141-95M	GUP TSIKV	99.87 %	http://www.comar.bam.de/
	P	C03	SMU	99.9 %	http://www.comar.bam.de/
	P	GBW 06104	Tian Jin Institute of Metrological Technology	99.95 %	http://www.comar.bam.de/
Cadmium and its compounds	**P**	6690-93/1	GUP TSIKV	1 g/L	http://www.comar.bam.de/
	P	7325-96	GUP TSIKV	0.0101 %	http://www.comar.bam.de/
	P	DMR-85c	CENAM, Mexico	1001.0 mg/L	http://www.comar.bam.de/
	P	DMR-8i	CENAM, Mexico	1 mg/L	http://www.comar.bam.de/
	P	GBW-08602	National Institute of Metrology, China	0.100 µg/kg	http://www.comar.bam.de/
	P	GBW-08607	National Institute of Metrology, China	0.100 µg/g	http://www.comar.bam.de/
	P	GBW-08608	National Institute of Metrology, China	10.0 µg/kg	http://www.comar.bam.de/
	P	JK-0012 Cd 1000	CERI, Japan	0.1 %	http://www.comar.bam.de/
1,2-Dichloroethane	**P**	7332-96	GUP TSIKV, Russia	99.76 %	http://www.comar.bam.de/
	P	SRM-3012	NIST	0.010039 g/g	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
Endosulfan	**P**	SRM-3069	NIST	4.66 mg/kg (I) 5.29 mg/kg (II)	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	P	SRM-2275	NIST	2.880 mg/kg (I) 2.943 mg/kg (II)	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
Hexachlorobenzene	**P**	SRM-1492	NIST	308 µg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	P	SRM-2261	NIST	1.968 µg/mL	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	P	SRM-3069	NIST	4.39 mg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
Hexachlorocyclohexane gamma-isomer	**P**	SLRM-10-2-08	Slovak Institute of Metrology, Slovakia	0.1 %	http://www.comar.bam.de/
	P	SRM-1492	NIST	310 µg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	P	SRM-2261	NIST	1.972 µg/mL	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	P	SRM-3069	NIST	4.22 mg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	P	SRM-8466	NIST	99.9 weight %	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
Lead and its compounds	**P**	7012-93/1	GUP TSIKV	1.01 g/L	http://www.comar.bam.de/
	P	DMR-63c	CENAM, Mexico	1002.1 mg/L	http://www.comar.bam.de/
	P	DMR-8i	CENAM, Mexico	10 mg/L	http://www.comar.bam.de/
Naphthalene	**P**	DPAC-1	NRC-CNRC, Canada	116 µg/g	http://inms-ienm.nrc-cnrc.gc.ca/calserv/crm_e.html
	P	SIRM 10-2-30s	Q-chem Ltd., Slovakia	49.8 µg/g	http://www.comar.bam.de/
	P	SRM-1586-1	NIST	126.5 µg /g	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	P	SRM-1586-2	NIST	126.6 µg /g	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	P	SRM-1647d	NIST	20.13 µg /mL	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	P	SRM-2270	NIST	77.0 mg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
Nickel and its compounds	**P**	DMR-8i	CENAM, Mexico	1 mg/L	http://www.comar.bam.de/
Pentachlorophenol	**P**	SRM-1584	NIST	15.4 µg/mL	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	P	SRM-3066	NIST	100.7 mg/L	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
PAHs benzo[a]pyrene	**P**	DPAC-1	NRC-CNRC, Canada	35 µg/g	http://inms-ienm.nrc-cnrc.gc.ca/calserv/crm_e.html
	P	GBW-08701	Beijing Municipal Environmental Monitoring Centre, China	5.75 µg/g	http://www.comar.bam.de/
	P	GBW-08702	Beijing Municipal Environmental Monitoring Centre, China	10.0 µg/g	http://www.comar.bam.de/
	P	SIRM 10-2-30s	Q-chem Ltd., Slovakia	49.4 µg/g	http://www.comar.bam.de/
	P	SRM-1586-1	NIST	49.2 µg /g	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	P	SRM-1586-2	NIST	44.1 µg /g	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	P	SRM-1647d	NIST	4.91 µg /mL	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	P	SRM-2260a	NIST	4.07 µg/mL	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	P	SRM-2270	NIST	37.3 mg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
fluoranthene	**P**	DPAC-1	NRC-CNRC, Canada	116 µg/g	http://inms-ienm.nrc-cnrc.gc.ca/calserv/crm_e.html
	P	DPAC-2	NRC-CNRC, Canada	117 µg/g	http://inms-ienm.nrc-cnrc.gc.ca/calserv/crm_e.html
	P	SRM-1647d	NIST	7.64 µg /mL	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	P	SRM-2260a	NIST	7.200 µg/mL	http://ts.nist.gov/MeasurementServices/ReferenceMaterials/232.cfm
	P	SRM-2269	NIST	62.6 mg/kg	http://ts.nist.gov/MeasurementServices/ReferenceMaterial

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

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

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

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

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

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

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

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

Table 4: Certified reference materials related to other pollutants

P - Pure compounds or solutions

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

Table 5: Certified reference materials related to other pollutants

Matrix: S – Sediment; W – Water; A – Aquatic plant or animal

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

ANNEX IV: Case Studies

Background information

Title/Name of case study:

PESTICIDES IN SURFACE WATER BODIES FROM AGRICULTURAL SOURCES (PESTICIDE PROGRAM).

Type of case study:

Monitoring to check the chemical and ecological status compliance (operational and investigative monitoring).

Reporting Institution:

Ministry of the Environment (Spain).

Web-Link: www.mma.es

Main sources for further information; literature:

"Analysis of pesticides and metabolites in Spanish surface waters by isotope dilution gas chromatography/mass spectrometry with previous automated solid-phase extraction. Estimation of the uncertainty of the analytical results".

Planas et al. Journal of Chromatography A, 1131 (2006) 242-252.

Objective of case study - background information:

Development of the methodology for monitoring the pollution caused by pesticides from agricultural sources.

Analysing pesticides is necessary to check the good chemical and ecological status compliance. The pesticides included in the monitoring program must be all the priority substances discharged and "other pesticides" discharged in significant quantities. It is not easy to select the "other pesticides" to analyse due to high number of possible compounds, changes in pesticides use, pesticide fate, etc.

To solve this, the surveillance of pesticide pollution from agricultural activities may combine 2 types of analytical methodologies. Type 1: Standardized techniques with high level of QA/QC to monitor EQS compliance (legally binding EQSs or calculated EQSs). Type 2: MS characterization to determine new pesticides not included in common lists in order to incorporate them in the selected compounds to monitor in the future.

This combined methodology is used to monitor pesticides in water bodies potentially at risk of failing to meet the pesticides EQS due to pressure from agricultural sources.

Contribution to…

Specific contribution linked to WFD monitoring programmes
Operational and investigative monitoring design.

Description
Monitoring points: water bodies potentially at risk of pesticides pollution from agricultural sources.
Matrix: Water
Frequency: 8 sampling/year
Methodology and substances
  Using Isotope dilution GC/MS with previous automated SPE
    10 pesticides from Priority Substances List ,
    04 pesticides from List II with national legally binding EQSs
    05 metabolite pesticides
    13 pesticides commonly used or detected in waters

  Using MS characterization of the all the pollutants present in the sample

Unknown pesticide presents in the sample

Experiences gained - Conclusions - Recommendations

Experience gained:

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

Conclusion:

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

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

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

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

Recommendations:

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

Outlook - Next steps – Accessibility of results/information

Background information

Title/Name of case study:

Conversion of pollutant concentrations measured in suspended particulate matter (SPM) into total concentrations in the whole water sample.

Type of case study:

Routine operation since 1990 in the water quality monitoring program of the international Rhine Commission (ICPR) for compliance checking of annual data of lipophilic pollutants with water quality targets.

Reporting Institution:

International Commission for the Protection of the Rhine (ICPR)

Web-Link:
http://www.iksr.de/fileadmin/user_upload/Dokumente/Berichte/IKSR_Bericht_Nr_143d.pdf

Objective of case study - background information –

In surface waters a number of the priority substances are adsorbed to SPM from 50 close to 100 percent. The water quality targets of the ICPR (analogous the EQS) for organic priority substances are expressed as total concentrations, that is the dissolved portion plus adsorbed portion of the substance in the whole water sample. For some organic priority substances the AA-EQS are very low, and the respective detection limits of the recommended analytical methods are insufficient. The objective is to support compliance checking with whole water EQS (or ICPR water quality targets) by conversion of SPM determinand concentration.

Contribution to support compliance checking with EQS

Specific contribution linked to WFD monitoring programmes
Surveillance monitoring design; specific monitoring of pollutants adsorbed to suspended particulate matter; compliance checking of SPM determinand concentration with whole water EQS.

Characterisation
For organic micropollutants like PCB, TBT, PAH or hexachlorobenzene, the ICPR had developed water quality targets for whole water. For reasons of the analytical method, surveillance of the quality targets was performed by sampling and analyzing these pollutants in suspended particles.
Sampling by centrifuge allows collecting the suspended material from several 1,000 litres of water within a few hours. Thus, a sufficient amount of SPM can be gained for chemical analysis, what corresponds to an enrichment from several 100 (or 1,000) litres of water. The amount of water centrifuged is recorded.

Course of procedure:
The concentration of contaminants is determined in µg/kg dw and converted to whole water by means of the SPM content (in mg/L):

$$C_{Ti} = (Si \times C_{si}) \times 10^{-6}$$

C_{Ti} = total contaminant content on the day of sampling in µg/L
Si = SPM content on the day of sampling in mg/L
C_{si} = contaminant content in SPM on the day of sampling in µg/kg.

This applies to substances that are adsorbed at SPM by more than 90 %.
For substances that are adsorbed by 50 % at SPM, the value is multiplied by the factor 2:

$$C_{Ti} = 2\,(Si \times C_{si}) \times 10^{-6}$$

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

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

Experiences gained - Conclusions - Recommendations

Experience gained:

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

Conclusion:

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

Recommendations:

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

Outlook - Next steps – Accessibility of results/information

Background information

Title/Name of case study:

Comments Concerning the National Swedish Contaminant Monitoring Programme in Marine Biota

Type of case study:

Monitoring activities within the Swedish contaminant programme in marine biota

Reporting Institution:

Environmental Protection Agency (Sweden)

Web-Link: www.naturvardsverket.se

Main sources for further information; literature:

Comments Concerning the National Swedish Contaminant Monitoring Programme in Marine Biota, 2006

Objective of case study - background information:

The data of concern in this report represent the bioavailable part of the investigated contaminants i.e. the part that has virtually passed through the biological membranes and may cause biological effects. The main objectives of the monitoring program in marine biota could be summarised as follows:

- to estimate the levels and the normal variation of various contaminants in marine biota from several representative sites, uninfluenced by local sources, along the Swedish coasts. The goal is to describe the general contaminant status and to serve as reference values for regional and local monitoring programmes

- to monitor long term time trends and to estimate the rate of found changes.

- to estimate the response in marine biota of measures taken to reduce the discharges of various contaminants

- to detect incidents of regional influence or widespread incidents of ‘Chernobyl’- character and to act as watchdog monitoring to detect renewed usage of banned contaminants.

- to indicate large scale spatial differences

- to explore the development and regional differences of the composition and pattern of e.g. PCB’s, HCH’s and DDT’s as well as the ratios between various contaminants.

Contribution to…

Specific contribution linked to WFD monitoring programmes

Surveillance monitoring design and operational monitoring design as soon as EQS are developed for biota.

Description

Substances monitored: Metals, for example Hg, Cd, Pb and Cu and organic substances, for example PCB, DDT, Lindane, brominated flameretardants and dioxins.

Sampling area: The sampling sites are located in areas regarded as locally uncontaminated and, as much as possible, uninfluenced by major river outlets or ferry routes and not too close to heavy populated areas.

Collected specimens: For many species adult specimens are less stationary than sub-adults. To increase comparability between years, young specimens are generally collected. Only healthy looking specimens with undamaged skin are selected. The collected specimens are placed individually in polyethene plastic bags, deep frozen as soon as possible and transported to the sample preparation laboratory.

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

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

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

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

Mussels are one of the most common used organisms for monitoring contaminants in biota. Adult mussels are sessile and hence it is easier to define the area the samples represent, compared to fish.
Blue mussel is among the ‘first choice species’ recommended within the JAMP (Joint Assessment and Monitoring Programme).

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

Outlook - Next steps – Accessibility of results/information

Background information

Title/Name of case study:
SCREENING OF INDUSTRIAL AND CONSUMER CHEMICALS IN FINLAND (VESKA 1)

Type of case study:

Screening to select sites and substances for surveillance monitoring of WFD

Reporting Institution:

Finnish Environment Institute SYKE

Web-Link: http://www.ymparisto.fi

Main sources for further information; literature:

Objectives of case study:

To study the occurrence and concentrations of the substances chosen by risk assessment in the aquatic environment close to emission sources

To produce information for the purpose of emission source identification.

To develop the analytics used to examine harmful substances and to build up cooperation network between laboratories.

To develop a risk assessment method that can be used to estimate the circulation of the studied compounds in nature and to minimize the expenses needed for their monitoring.

To set a criterion that could be used to preclude or add substances to a more detailed monitoring plan.

Contribution to…

Specific contribution linked to WFD monitoring programmes
Supply data for national surveillance monitoring programme 2006-2008

Description
The study was carried out in the vicinity of twelve industrialized cities in Finland, in water systems downstream municipal sewage treatment plants. Concentrations were measured in sludge and waste water samples (1-3 occasions) and surface water (1-3 occasions), sediment (once, surface 2-3 cm) and fish (4-10 specimen pooled, Northern pike, *Esox lucius*) muscle samples.

Organotin compounds (both butyl and phenyl –forms) were found in all matrices, often exceeding EQS or "benchmark" values. This will trigger more research, monitoring and management activities
MBT and DBT were found in sediments also below inland sewage treatment plants, indicating sources other than antifouling paints (stabilizer in plastics). TPhT indicated bioaccumulation: found less than TBT in sediments but more in fish

Alkylphenols, phthalates, organotin compounds, HCH, HCB and VOC-compounds were found in treated sewage water. Out of these, only DEHP and alkylphenols were found in excess of surface water EQS proposals.

In surface waters, only nonylphenol ethoxylates were found at the (national) EQS-level. Several substances were not detected (other alkylphenols, chlorobenzenes and volatile organic compounds). PAHs, PBDE, organotins and phthalates were, however, not measured in surface water phase.
In sediments, organotins, PAHs, HCHs and dibutylphthalate were most commonly found.

Experience gained:

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

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

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

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

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

Background information

Title/Name of case study:
PESTICIDE SCREENING IN FINNISH SURFACE WATERS (VESKA 2)

Type of case study:

Screening to select sites and substances for surveillance monitoring of WFD

Reporting Institution:

Finnish Environment Institute (SYKE)

Web-Link: http://www.ymparisto.fi/download.asp?contentid=49817&lan=EN

Main sources for further information; literature:

Objectives of case study:

To study the occurrence and concentrations of agricultural pesticides in Finnish surface waters.

To produce information for identification of emission source.

To develop a risk assessment method that can be used to minimize the expenses of later monitoring.

Contribution to…

Specific contribution linked to WFD monitoring programmes
Supply data for national surveillance monitoring programme 2006-2008

Description

Monitoring points: water bodies (streams and rivers) potentially at risk of pesticide pollution from agricultural sources
Matrix: surface water and the top of bottom sediment (0-1 cm)
Duration: 2004 - 2005
Frequency

- at one intensive site: weekly (May-Oct 2004) + monthly in winter (2004-2005)
- intermediate sites: monthly (Apr/May-Sep/Oct)
- areal screening sites: twice (Jun/Jul + Jul/Aug in 2005).

Analysed substance:

- 100 compunds from water samples using :multi-residue methods (GC-MS and LC-MS-MS) (including all pesticides in the EU Priority list and four of the six pesticides in the national list of pesticides)
- Tribenuronmethyl (a low-dose herbicide in the national list) from part of water samples using a specific analysing method
- The 14 pesticides analysed from sediment samples were selected basing on partitioning coefficients (from the EU and national lists of priority substances and other potential pesticides).

Number of samples: 190 water samples + 31 sediment samples

The study was carried out in two parts. The objective of the pilot year 2004 was to find the best timing for surface water sampling and to assist in the selection of the sampling sites for a survey for following year. In the second year (2005) the main objective was areal representativeness, but most of the sites were sampled only twice at the time of expected high concentrations.

In 2004 the focus was in upstream sites (catchment areas: 1-100 km^2) close to fields. Surface water was collected in an intensive site and in 6 other agricultural streams. Additional samples were collected once from 6 rivers (Sep/Oct). The pilot year indicated that agricultural land use percent was more important factor to explain pesticide detections than catchment area.

In 2005, sampling sites were selected from watershed register using agricultural land use percent as the main criterion: 35 agricultural sites and five reference sites from non-agricultural areas (catchment areas of the sampling points: .50 - 37 000 km^2). In addition, six rivers and two of the smaller streams sampled during the pilot year were sampled monthly (May-Oct) in 2005.

Pesticides in water samples (70 (in 2004) + 120 (in 2005) + quality assurance samples):
The number of different pesticides detected was 24 in 2004 and 46 in 2005. Detected concentrations were mainly low (traces). In 2005, one or more herbicides were detected in 90% of water samples. Phenoxy acid herbicides were most frequently found compounds. This may be explained by the volume of they use in Finland. Only following few exceedings of EQS values were observed during the screening, although the sampling was focused in the expected concentration peaks and in the areas of high pesticide loadings:

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

Pesticides in sediment samples (31 + a parallel sample):
In 2005, the top of bottom sediment (in all sites where possible) was sampled and 14 substances were analysed and 6 detected from sediment samples samples. Atrazine (forbidden in 1991) was detected in more than half of the sediment samples, prochloraz in every third sample, and the others in single samples. Currently there are no confirmed sediment EQS values for pesticides, but the earlier proposed values were exceeded in case of atrazine, prochloraz, endosulfan and its metabolite endosulfansulphate.

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

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

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

Outlook - Next steps – Accessibility of results/information
For year 2007 the statutory pesticide monitoring is planed to be performed in 8 rivers and in one stream (10-12 samples/site). Later (in 2008-) it will be reasonable to include some upstream sites to monitoring program.

Background information

Title/Name of case study:

FRENCH NATIONAL MONITORING NETWORK (RNO)

Réseau National d'Observation de la qualité du milieu marin

Type of case study:

A 30 years Chemical monitoring network (surveillance and operational monitoring)

Reporting Institution:

IFREMER (Institut français de recherche pour l'exploitation de la mer)
French Research Institute for Exploitation of the Sea

Web-Link: www.ifremer.fr and www.ifremer.fr/envlit/surveillance/rno.htm

Main sources for further information; literature:

Annual bulletin may be downloaded at : **www.ifremer.fr/envlit/surveillance/rnopublis.htm**

Objective of case study - background information:

1. Assessment of the levels and trends of the chemical contamination of the French coastal seas.

2. To meet OSPAR and Barcelona Conventions monitoring obligations

Contribution to…

Specific contribution linked to WFD monitoring programmes
Surveillance and Operational Monitoring

Description

Chemical contaminants monitored :

- metals : Ag, Cd, Cr, Cu, Hg, Ni, Pb, V, Zn
- organochlorinated compounds: DDT compounds, HCH isomers, PCB congeners
- PAH's : 16 US-EPA PAH's and some alkylated PAH's

Strategy of monitoring :

The RNO is largely based on bivalve molluscs (mussels and oysters) which are used as quantitative indicators of contamination. **Some 90 sampling points are sampled twice a year for metals and once a year for organic contaminants**. Analyses are carried out at a single laboratory, the Ifremer Center of Nantes. An aliquot of the samples is systematically archived for possible controls at a later date or the retrospective search of other contaminants (the bank contains more than 8000 samples, since 1981).

The contaminants are also measured in the sediments. The first centimetre of the surface sediments can integrate several years of contamination. A yearly sampling cruise is carried on 1/10 of the French maritime frontage, the whole French littoral being covered every 10 years. The contaminants measured are the same than in biota, in addition to descriptive and normalization parameters (grain size, organic carbon, carbonates, aluminium, iron, lithium and manganese). Some sediment cores are collected to reconstruct the history of the contamination over several decades.

Experience gained:

Direct monitoring in water is not used any longer because it is too expensive and not reliable. Indeed, the operational difficulties to collect valid samples (i.e. uncontaminated and representative) for analyses of substances present in water at trace levels are too great. First, collecting uncontaminated samples needs a care difficult to reach in routine monitoring. Secondly, the spatial and temporal representativeness of samples collected in Water Bodies affected by tides and currents, are too low. This is our first-hand experience of direct measurements of contaminants in water which was carried out between 1979 and 1984 and abandoned for the reasons above. This is coherent with the OSPAR Convention monitoring programme which is also based on biota and sediment.

Conclusion:

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

Recommendations:

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

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

Outlook - Next steps – Accessibility of results/information

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

Background information

Title/Name of case study:

What concentrations of hazardous substances do we find in the environment? Results from the Swedish Screening Programme 2003-2004 (Abstract)

Type of case study:

Screening

Reporting Institution:

Environmental Protection Agency (Sweden)

Web-Link: www.naturvardsverket.se

Main sources for further information; literature:

What concentrations of hazardous substances do we find in the environment? Results from the Swedish Screening Programme 2003-2004 Report 5524, February 2006.

Objective of case study - background information:

For the purpose of obtaining information regarding the concentrations of newly discovered persistent organic pollutants (POPs), as well as other potential problem substances used in society, the national environmental monitoring scheme was supplemented by a screening programme a few years ago. In this programme, one or more selected substances are measured on one or more occasions during a single year and in different media, such as sewage, fish or air.

Screening was initiated on a small scale in 1996-97 and has gradually increased in scope since then. The reason for including a substance in the screening programme may be that it is used on a large scale, that it has been prioritized in various international contexts, or that it has attracted national attention for other reasons.

Contribution to…

Specific contribution linked to WFD monitoring programmes

Data for substances those are not included in the regular monitoring programme.

Description

The screening studies have been modelled on the **DPSIR** strategy. This strategy analyses environmental problems based on **D**rivers such as those created by industry, **P**ressures on the environment such as polluting discharges that harm the **S**tate of the environment, which in turn results in an **I**mpact on human health and the environment, whereby we try to find **R**esponses or actions to deal with the problems.

A screening study consists of the following closely-connected parts:

Choice of substance
Preparatory theoretical study
Measurement study
Evaluation

Experience gained:

The primary purpose of the screening is not to support research on new POPs, but to comply with requirements on reporting of certain substances in various EU directives and international conventions. Many of these substances are of no relevance for Sweden, and the screening could help to show this so that resources do not have to be wasted on measurement of these substances.

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

Conclusion:
Further studies should be made of the following substance groups
Organophosphates
Bisphenol A
α- and β-endosulfan
Siloxanes
Chloro- and bromostyrenes

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

The following substance groups do not have to be followed regularly
Chlorinated paraffins
Limonene
Mirex
Isocyanates

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

Outlook - Next steps – Accessibility of results/information

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

Background information

Title/Name of case study:

MONITORING USING PASSIVE SAMPLING DEVICES TO IMPROVE TRACE METAL-RELATED RISK ASSESSMENTS

Type of case study:

Complementary monitoring by *in-situ* deployment of passive sampling to help reduce the uncertainty associated with infrequent grab sampling for compliance monitoring

Reporting Institution:

University of Portsmouth (UK), Bureau de Recherche Géologique et minière (Fr)

As part of the EU-funded FP6 project *Screening Methods for Water Data information in support of the implementation of the WFD (SWIFT-WFD)*

Web-Link: none

Main sources for further information; literature:

“Evaluation of the performance of the Chemcatcher and DGT passive sampling devices for monitoring heavy metals in water” Allan IJ, Knutsson J, Guigues N, Mills GA, Fouillac A-M and Greenwood R, (in preparation) *(2007)*

Objective of case study - background information:

Demonstration of the applicability of passive sampling to increase confidence in measures of water quality provided by infrequent spot (bottle) sampling campaigns.

Grab or bottle sampling followed by filtration at 0.45µm is to be used for compliance checks (AA-EQS & MAC-EQS).

Whilst monthly spot samples provide a precise estimate of concentrations of contaminants at the time of sampling, there is uncertainty concerning conditions prevailing in the periods between sampling events. This is of particular concern where concentrations are known to fluctuate or where there are significant or potential natural or anthropogenic pressures. One possible solution to this problem is to deploy passive samplers to provide time-weighted average (TWA) concentrations of concentrations of contaminants in the period between grab samples. This may confirm or contradict the data from the routine monitoring campaigns, and should help to reduce the possibility of making erroneous decisions in risk assessments required in the implementation of the WFD.

In this application the TWA concentrations of metals estimated using DGT and Chemcatcher samplers were compared with estimates based on spot sampling in the Meuse River (Eijsden, The Netherlands). In this trial 2 different grab sampling procedures were used at relatively high frequencies (one to three times per week) and metal analyses conducted in two different laboratories in a pilot-scale inter-organisational comparison that incorporated both the analytical determination and the sampling step.

Contribution to…

Specific contribution linked to WFD monitoring programmes
Surveillance and operational monitoring tasks

Description
Matrix: Water
Passive sampling: Use of the Diffusive Gradient in Thin Film (DGT) and Chemcatcher sampling devices following guidelines provided in the BSI Publicly Available Specification 61, and analysis of sampler extracts by ICP-MS in an university research laboratory.
Sampler exposure: Consecutive and/or overlapping 7, 14, 21 and 28 day periods
Grab sampling protocol 1: Routine weekly sampling, transport of the sample to the laboratory followed by filtration (0.45 µm) and ICP-MS analysis.
Grab sampling protocol 2: Sampling every two or three days, on-site filtration (0.45 µm) and analysis by

ICP-OES in an accredited laboratory.

Experience gained:

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

Conclusion:

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

Recommendations:

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

Outlook - Next steps – Accessibility of results/information

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

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

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