JRC Scientific and Technical Reports

Comparison of Monitoring Approaches for Selected Priority Pollutants in Surface Water

An Initiative in support to the Water Framework Directive Chemical Monitoring Activity

Georg Hanke, Jan Wollgast, Robert Loos, Javier Castro Jiménez, Gunther Umlauf, Giulio Mariani, Anne Müller, Tania Huber, Eugen H. Christoph, Giovanni Locoro, José Manuel Zaldívar and Giovanni Bidoglio

EUR 22922 EN - 2007

JRC EUROPEAN COMMISSION

Institute for Environment and Sustainability

Servizio Risorse Idriche e Tutela Ambientale
Provincia di Ferrara

The mission of the Institute for Environment and Sustainability is to provide scientific-technical support to the European Union's Policies for the protection and sustainable development of the European and global environment.

European Commission
Joint Research Centre
Institute for Environment and Sustainability

Contact information
Address: Georg Hanke
Institute for Environment and Sustainability T.P. 290
European Commission Joint Research Centre
I-21020 Ispra (VA)
E-mail: georg.hanke@jrc.it
Tel.: ++39-0332-785586
Fax: ++39-0331-786351

http://ies.jrc.ec.europa.eu
http://www.jrc.ec.europa.eu

JRC 40272

EUR 22922 EN
ISBN: 978-92-79-06945-1
ISSN 1018-5593
DOI: 10.2788/11053

Luxembourg: Office for Official Publications of the European Communities

Printed in Italy

Table of content

1 ABSTRACT 5

2 INTRODUCTION 5

2.1 EU LEGISLATION FOR CONTROL OF CHEMICAL POLLUTANTS 5
2.2 WFD ENVIRONMENTAL QUALITY STANDARDS DIRECTIVE PROPOSAL 5
2.3 CHEMICAL MONITORING ACTIVITY 5
2.4 CMA ON-SITE EXERCISE 6

3 SET-UP OF CMA ON-SITE 6

3.1 PRE-CAMPAIGNS 6
3.2 PRESENTATIONS 7
3.3 LOCATION SELECTION 7
3.4 DESCRIPTION OF EVENT 8
3.4.1 Selection of compounds 9
3.4.2 Standard solutions 10
3.4.3 River water extracts 10
3.4.4 Sampling event 11
3.5 PARTICIPANTS 11

4 HOMOGENEITY STUDIES 12

4.1 HOMOGENEITY STUDIES FOR STANDARDS 12
4.2 HOMOGENEITY STUDIES FOR EXTRACTS 13
4.3 HOMOGENEITY OF RIVER WATER 14
4.3.1 Water temperature 14
4.3.2 Suspended particulate matter 14
4.3.3 Homogeneity of PAH in river water 15
4.3.4 Homogeneity of PBDE in river water 16

5 APPROACHES FOR WATER MONITORING 17

5.1 METHODS EMPLOYED BY PARTICIPATING LABORATORIES 17
5.2 METHODS EMPLOYED BY JRC IES: 20

6 RESULTS 21

6.1 JRC RESULTS 21
6.1.1 JRC PAH results 21
6.1.2 JRC PBDE results 21
6.1.3 JRC whole water results 23
6.2 PAH AND PBDE RESULTS FROM PARTICIPATING LABORATORIES 26
6.2.1 PAH results from participating laboratories 26
6.2.2 PBDE results from participating laboratories 31

7 NONYLPHENOL / OCTYLPHENOL 35

7.1 EXPERIMENTAL NP/OP 35
7.2 RESULTS NP/OP 35
7.2.1 Octylphenol Standard 35
7.2.2 Standard S3 and extract E2 36
7.2.3 River Po water 38
7.3 CONCLUSIONS FOR NP/OP 39

8 CONCLUSIONS 42

9 OUTLOOK 42

10 ACKNOWLEDGEMENTS 43

11 REFERENCES 44

ANNEX I ANALYTICAL METHODS EMPLOYED BY PARTICIPATING LABORATORIES 46

ANNEX II ANALYTICAL METHODS EMPLOYED BY JRC 57

II.1 FILTRATION AND LIQUID/LIQUID EXTRACTION OF 20 L WATER 57

II.2 FILTRATION AND ADSORPTIVE EXTRACTION OF 45 L WATER 58
II.3 FILTRATION OF 11 L WATER ON GLASFIBER FILTER 59
II.4 FILTRATION AND ADSORPTIVE EXTRACTION OF 226 L WATER 59
II.5 CLEAN-UP OF SUSPENDED PARTICULATE MATTER 60
II.6 LIQUID/LIQUID EXTRACTION OF 2 L WATER 60
II.7 FILTRATION AND DISK-SPE OF 2 L WATER 60
II.8 INSTRUMENTAL GC/MS ANALYSES 61
II.8.1 HRGC-LRMS of PAH: *61*
II.8.2 HRGC-HRMS of PBDEs *61*
II.9 QUALITY ASSURANCE/QUALITY CONTROL 61
ANNEX III CMA ON-SITE INVITATION DOCUMENT 63
ANNEX IV CMA ON-SITE TECHNICAL ANNEX 64
ANNEX V CMA ON-SITE REPORTING SHEET TEMPLATES 68

1 Abstract

Laboratories from seven EU Member States under the coordination of the Joint Research Centre and in collaboration with the Provincia di Ferrara participated in a technical on-site project during which sampling and analytical methodologies for chemical monitoring according to proposed WFD provisions have been compared. Laboratories had been invited to take samples from a river according to their standard protocols and to analyse them for PAHs, PBDE and Nonyl-, Octylphenol. It was shown that it is possible to analyse contaminants at relevant levels. Results showed also that currently only experienced laboratories can achieve the required performance, indicating the need for improvement at European level.

2 Introduction

2.1 EU legislation for control of chemical pollutants

The Water Framework Directive (WFD) (2000/60/EC) shall provide regulation for the contamination of European water bodies through chemical pollutants. This is achieved via the Priority Substance List Decision (2455/2001/EC) and establishing of Environmental Quality Standards on European level through a Daughter Directive, currently in the process of adoption through the European Parliament and Council. For river basin specific pollutants the Water Framework Directive provisions include obligations for identification of relevant pollutants at smaller spatial scales and the derivation of appropriate limit values on national level. The Groundwater Directive (2006/118/EC) ensures the protection of groundwater against pollution and deterioration. Therefore, Member States should set-up water monitoring programs covering a wide range of possible contaminants in order to identify risks, priority issues and needs for action.

2.2 WFD Environmental Quality Standards Directive proposal

The proposal for a Directive COM(2006)398 regulating the pollution with chemical substances has been prepared by the European Commission. While still being under evaluation in the European Parliament and Council, technical discussions and preparations in the chemical monitoring activity are ongoing. The performance criteria are proposed in the draft Commission Decision.
JRC IES has been accompanying the preparation of the upcoming WFD Daughter Directive COM(2006)398 on Environmental Quality Standards EQS through chairing the workgroup on Analysis and Monitoring of Priority Substances AMPS (2003-2004), co-chairing the drafting of the CMA guidance document for surface waters within the Chemical Monitoring Activity CMA (2005-2006) and is currently co-chairing the Chemical Monitoring Activity in 2007-2009. The assessment of available methods for WFD compliance checking is among the prime objectives of the chemical monitoring activity. It is important that methodologies fulfil the requirements of the WFD chemical monitoring, e.g. by delivering concentration data of sufficient quality in order to assess compliance with the upcoming directive. Guidance on general WFD monitoring provision is available through the Guidance Document No. 7 “Monitoring under the Water Framework Directive” and for implementation of the ground water through the WFD CIS Guidance Document No. 15 “Guidance on Groundwater Monitoring”.

2.3 Chemical Monitoring Activity

Technical discussions with Member States delegates on chemical monitoring issues have been held in the Analysis and Monitoring of Priority Substances (AMPS) working group and the Chemical Monitoring Activity (CMA) in order to arrive at a common view on the necessary monitoring for the WFD. An interim version of a guidance document for chemical water monitoring has been prepared. This consultation process is important to harmonise the approaches and guarantee comparable results,

starting from the setting up of the monitoring networks, via the sampling and sample preparation to the chemical analysis. Chemical water analysis is done on routine basis in the Member States according to their national regulations and it is crucial that currently applied approaches will merge into a common strategy that will result in comparable assessments throughout Europe. The Guidance document can be found on the European Commission Information system Circa: Technical Guidance on Surface Water Chemical Monitoring - Interim Version 8.05.2007 (see chapter 11., References for the direct link). Also the method performance criteria have been proposed in the draft "Commission Decision adopting technical specifications for chemical monitoring and quality of analytical results in accordance with Directive 2000/60/EC of the European Parliament and of the Council". In that draft document an LoQ ≤ 30 % of EQS is required for WFD compliance checking.

2.4 CMA on-site exercise

As discussions in the different fora had revealed that EU Member States currently use different approaches for the monitoring of chemical substances in their river basins, it was proposed by JRC IES to organise a field campaign during which laboratories should meet and monitor selected priority pollutants together at a single spot.
Laboratories from 7 different Member States have therefore met in October 2006 in Ferrara, Italy at the Po River for the first CMA on-site event organised by JRC IES and the Provincia di Ferrara with the objective of testing several aspects of the guidance prepared in view of the implementation of the upcoming WFD Daughter Directive on Environmental Quality Standards.
Every laboratory employed its own approach and tools for this task. Target substances were PBDEs, PAHs, Nonyl- and Octylphenol, specifically selected as their analysis poses particular difficulties at the concentration levels relevant for compliance checking.
The teams sampled simultaneously water from a quay on the Po River. The homogeneity of the river water during the sampling period was tested by additional analyses and by monitoring of basic water quality parameters. Among the procedures applied were bottle sampling with subsequent solid phase extraction, liquid-liquid extraction, on-site filtration and centrifugation. Also large volume techniques have been employed.
In addition to the water samples taken from the River, ampoules with homogenised river water extracts and with standard solutions have been distributed to evaluate the sample preparation and several aspects of instrumental analysis on the analytical procedure.

3 Set-up of CMA on-site

3.1 Pre-campaigns

In order to plan the CMA on-site event two campaigns for site selection, preliminary water analysis and organisation where performed. The first campaign, on 29.6.07 was conducted at 3 different sites in the area of Ferrara. One spot at the Po di Volano, downstream of Ferrara, one on the Po river ca. 40 km downstream of Ferrara and one at Pontelagoscuro where investigated. After this screening, the sampling location at Pontelagoscuro was favorised due to the logistics.
A second preparatory campaign on 9.6.06 was aiming at confirmation for the sampling spot, organise the event, test sampling and analytical procedures and sampling a large volume sample in order to prepare the homogenised extract for distribution to the participants.

3.2 Presentations

In preparation of the practical parts a set of presentation was given, aiming at setting the scene for the practical monitoring next day:

- Georg Hanke, JRC IES:
  WFD Chemical Monitoring - State of play and organisational workshop aspects
- Susanne Boutrup, DMU, Denmark:
  Presentation on the sampling chapter of the WFD CMA Guidance Document
- Lars Håkanson, Uppsala University, Sweden:
  Variability in the aquatic environment - Implications for chemical monitoring
- Jan Wollgast, JRC IES:
  Partitioning of organic pollutants in the aquatic environment

3.3 Location selection

River Po at Pontelagoscuro

A large European river was to be selected for the exercise. The **Servizio Risorse Idriche e Tutela Ambientale, Provincia di Ferrara, Italy**, kindly offered to host the event. Recommendations for possible sites where given and the final site selection was made with agreement of the local environmental authorities. The contamination situation of the river had been tested in pre-campaigns in order to assess the possibility to work with concentrations relevant for WFD EQS issues.
A floating quay, with the restaurant “Il Pontile”, just upstream of the Pontelagoscuro bridge over the Po River, on the northern side, was selected, geographic coordinates: N 44.8894; E 11.6051 (WGS84). This quay allowed easy access, also for vehicles and was safe also for an elevated number of persons. The quay was accessible via a bridge and was moored ca. 15 m into the river Po. Water depth at the riverside of the quay was ca. 3 m. A safety boat was at disposal during the water sampling.

Floating quay at Pontelagoscuro

For some of the laboratory teams the logistics for sample collection far from their home laboratory was not routine. For sample preparation the JRC IES mobile laboratory was therefore at disposal of the participants. The equipment with fume hoods and stainless steel benches allowed the water filtration in a clean environment. As the laboratory is equipped with fume hoods, also the use of solvents in a clean and safe way is not problematic.

JRC IES mobile Laboratory

3.4 Description of event

The CMA on-site event was planned to bring the discussions that had been held in the AMPS and CMA groups into a practical context. A real monitoring example should show limitations and possibilities on selected examples in current approaches for water monitoring. This experience should help Member States to direct the development of their approaches and to support the finalisation of the CMA guidance document. Due to the restricted number of participants and the low number of repeated analysis, statistical treatment of the results was neither planned nor possible.

3.4.1 Selection of compounds

In accordance with the participating laboratories a selection of challenging parameters included in the upcoming EQS directive was made. The selection included substance groups that are being analysed routinely and others that are with the WFD for the first time under regulation. The analysis of these compounds in Europe at limits of determination derived from the annual average limit values in the proposed EQS Directive and the method performance criteria in the proposed Commission Decision are no common routine yet:

- **PAH**
- **PBDE**
- **Nonylphenol**
- **Octylphenol**

Proposed Environmental Quality Standard values for Inland waters for these substances are:

WFD Polycyclic aromatic hydrocarbons and proposed EQS

- Anthracene 100 ng/L
- Fluoranthene 100 ng/L
- Benzo(a)pyrene 50 ng/L
- Benzo(b)fluoranthene + Benzo(k)fluoranthene Σ 30 ng/L
- Benzo(g,h,i)perylene + Indeno(1,2,3-cd)pyrene Σ 2 ng/L

WFD Polybrominated biphenylethers, sum of

- BDE-28
- BDE-47
- BDE-99
- BDE-100
- BDE-153
- BDE-154

Proposed EQS Σ 0.5 ng/L

WFD Alkylphenols

- Nonylphenol (NP)
  Proposed EQS 0.3 µg/L
- Octylphenol (OP)
  Proposed EQS 0.1 µg/L

According to the proposed Commission decision on Analytical Quality Control, the applied methods should perform with a limit of determination at 30% of the annual average EQS value.

3.4.2 Standard solutions

A set of standard solution in flame sealed brown borosilicate glass ampoules was prepared. Certified standard solutions where therefore purchased, mixed and diluted to concentrations not known to the participants of the exercise. Analysis of these solutions by the participants should show variability of results by instrumental analysis, excluding thus variations deriving from sampling and sample-preparation procedures.

3.4.3 River water extracts

Variability in analytical results increases when samples contain natural matrix, such as salts, humic acids and other organic macromolecular material. Sample extracts from natural waters should therefore show the result variability when analysing identical samples containing environmental matrix.

For PAH and PBDE a 366 L water sample was collected on 9.6.06 from the Po river. The water was in-line filtered with a 2" glass fibre filtration cartridge and soxhlet extracted. The extract was diluted, homogenised and aliquots were filled into flame sealed borosilicate brown glass ampoules. The aliquot in each ampoule was the equivalent of 14.6 L of river Po water.

For Nonylphenol/Octylphenol a large volume sample taken from the Seveso river was extracted with solid phase extraction and extract aliquots were distributed in glass ampoules. Here the extract in each ampoule was equivalent to 1 L river water. Both standard and extract ampoules where shipped to the participants, as they contained, minimal, quantities of flammable solvent.

3.4.4 Sampling event

The joint sampling of river water was done on 11.October 2006. A detailed sampling plan was set-up in order to coordinate the various activities that needed to be performed simultaneously or in sequence. The river water was measured continuously for basic water quality parameters such as pH, conductivity and temperature. Sampling for the analysis of Suspended Particulate Matter (gravimetric) was done every 30 min and with higher frequency around 11:00. Samples for assessing the homogeneity of the river water where taken at hourly intervals and every 5 min ca. during the joint sampling. Participants sampled simultaneously at 11:00, the duration of the sampling itself was ca. 5 min.

Large volume sampling was carried out continuously from 10:00 to 15:00. Fig. 1 shows the scheme that was prepared for planning of the event and briefing of the participants. Red bars indicate the sampling events. The sampling by the participants had a duration of only ca. 5 min.

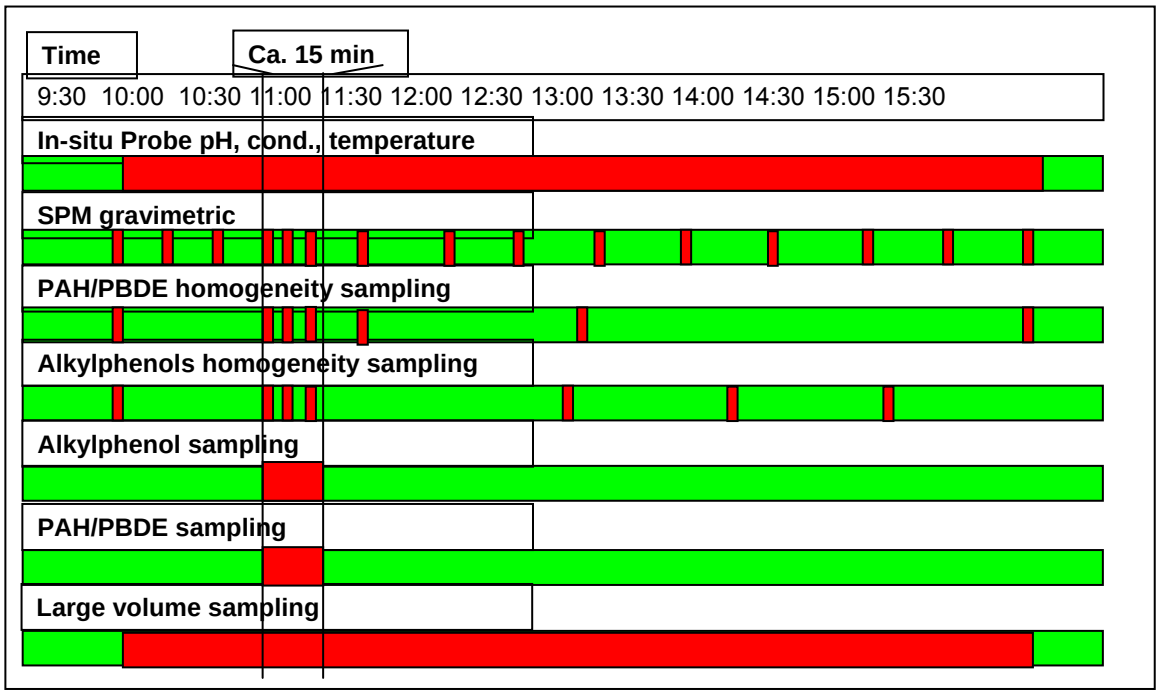


Figure 1: Sampling plan scheme for the CMA on-site exercise

3.5 Participants

Invited laboratories from 7 EU Member States (Austria, Bulgaria, Denmark, Germany, Italy, Netherlands, Spain) participated. The number of invited laboratories was considerably higher, but several laboratories could not participate due to timing or logistic problems. For the result presentation anonymous codes from CMA01 to CMA08 were attributed to the participants.

Participating laboratories:

- UBA, German Environment Agency, Germany
- CSIC, Consejo Superior de Investigaciones Cientificas, Spain
- Institute for Water Problems, Bulgaria
- Institute for Water Research, IRSA CNR, Italy
- Umweltbundesamt, Austrian Environment Agency, Austria

- BFG, German Federal Institute of Hydrology, Germany
- RIZA, Institute for Inland Water Management and Waste Water Treatment, Netherlands
- NERI, Danish National Environmental Research Institute, Denmark
- European Commission Joint Research Centre; Institute for Environment and Sustainability; Rural, Water and Ecosystem Resources Unit

4 Homogeneity studies

The homogeneity of the distributed standard solutions and sample extracts as well as the homogeneity of the water body during the common sampling procedure were of high importance for the exercise. Homogeneity tests on the ampoules and the river location have been performed before and during the field trial:

- Test of standard ampoules
- Test of river extract ampoules
- Continuous measurement of basic water quality parameters
- Frequent measurement of SPM concentration
- Frequent measurement of PAH, PBDE and NP/OP concentration

Ampoules with standards and river SPM extracts

4.1 Homogeneity studies for standards

Homogeneity of the prepared ampoules was tested by analysing 3 randomly selected ampoules prior to shipping. A set of ampoules was retained for further testing in case of necessity.

Table 1: PAH standard homogeneity test

PAH Standard	Standard S2-A	Standard S2-B	Standard S2-C			
[ng/ml]				**Average**	**St Dev**	**CV %**
Anthracene	63.8	62.8	68.2	64.95	2.876	4.43
Fluoranthene	56.8	56.0	62.4	58.42	3.508	6.00
Benzo(a)pyrene	48.6	47.5	48.3	48.14	0.583	1.21
Benzo(b+j+k)fluoranthene	84.1	88.0	94.9	89.01	5.491	6.17
Benzo(g,h,i)perylene	47.4	48.9	49.4	48.52	1.043	2.15
Indeno(1,2,3-cd)pyrene	42.5	44.3	44.1	43.61	1.011	2.32

Table 2: PBDE standard homogeneity test

PBDE Standard	Standard S1- A	Standard S1 - B	Standard S1 - C			
[ng/ml]				Average	St Dev	CV %
BDE-28	10.87	11.88	10.61	11.12	0.67	6.01
BDE-47	10.41	10.30	10.38	10.36	0.06	0.57
BDE-99	10.44	10.31	10.91	10.55	0.32	3.02
BDE-100	9.96	10.35	11.29	10.53	0.69	6.51
BDE-153	16.55	18.37	17.48	17.47	0.91	5.19
BDE-154	17.22	17.38	19.34	17.98	1.18	6.55
Total WFD PBDE	75.45	78.59	80.02	78.02	2.34	2.99

The homogeneity of the standard solutions after dilution, filling into ampoules and flame sealing was tested for PAH as well as for PBDE. Variation coefficients, below 7 % for all compounds, were consistent with the variability achievable with the instrumental analysis, proving the homogeneity of the distributed standards.

4.2 Homogeneity studies for extracts

Also the homogeneity of the prepared ampoules with the extract from a filter cartridge loaded with SPM from 366 L Po River water was tested by analysing a set of randomly selected ampoules prior to shipping.

Table 3: PAH extract homogeneity test

PAH extract	Extract E1 - A	Extract E1 - B	Extract E1 - C			
[ng/ml]				Average	St Dev	CV %
Anthracene	2.6	2.6	2.9	2.69	0.167	6.23
Fluoranthene	21.3	21.3	21.2	21.25	0.006	0.03
Benzo(a)pyrene	11.1	11.1	11.1	11.09	0.009	0.08
Benzo(b+j+k)fluoranthene	18.6	18.6	18.8	18.68	0.136	0.73
Benzo(g,h,i)perylene	12.1	12.1	12.3	12.14	0.100	0.82
Indeno(1,2,3-cd)pyrene	8.1	8.1	8.3	8.17	0.077	0.94

Table 4: PBDE extract homogeneity test

PBDE Extract	Extract E1 - A	Extract E1 - B	Extract E1 - C			
[ng/ml]				Average	St Dev	CV %
BDE-28	0.02	0.01	0.01	0.01	0.003	26.37
BDE-47	0.56	0.40	0.38	0.44	0.098	21.98
BDE-99	0.50	0.41	0.37	0.43	0.069	16.05
BDE-100	0.13	0.11	0.09	0.11	0.021	18.65
BDE-153	0.13	0.11	0.09	0.11	0.020	18.42
BDE-154	0.07	0.08	0.07	0.07	0.004	4.80
Total WFD PBDE	1.41	1.11	1.02	1.18	0.206	17.47

Matrix loaded samples did not show increased variability in the PAH measurements, while PBDE measurements showed an increased coefficient of variability of ca. 20%. Measurement of BDE-28 was more variable, but at very low concentrations. The measurements showed the homogeneity of the distributed sample extracts.

4.3 Homogeneity of river water

Sampling was performed at a large river, including thereby all sources of variation, also the sampling itself, into the comparison. The homogeneity of the river water body during the sampling event had therefore to be shown. A set of basic water quality parameters was measured on-line, the amount of total suspended matter at a high frequency and the target analytes where measured repeatedly.

4.3.1 Water temperature

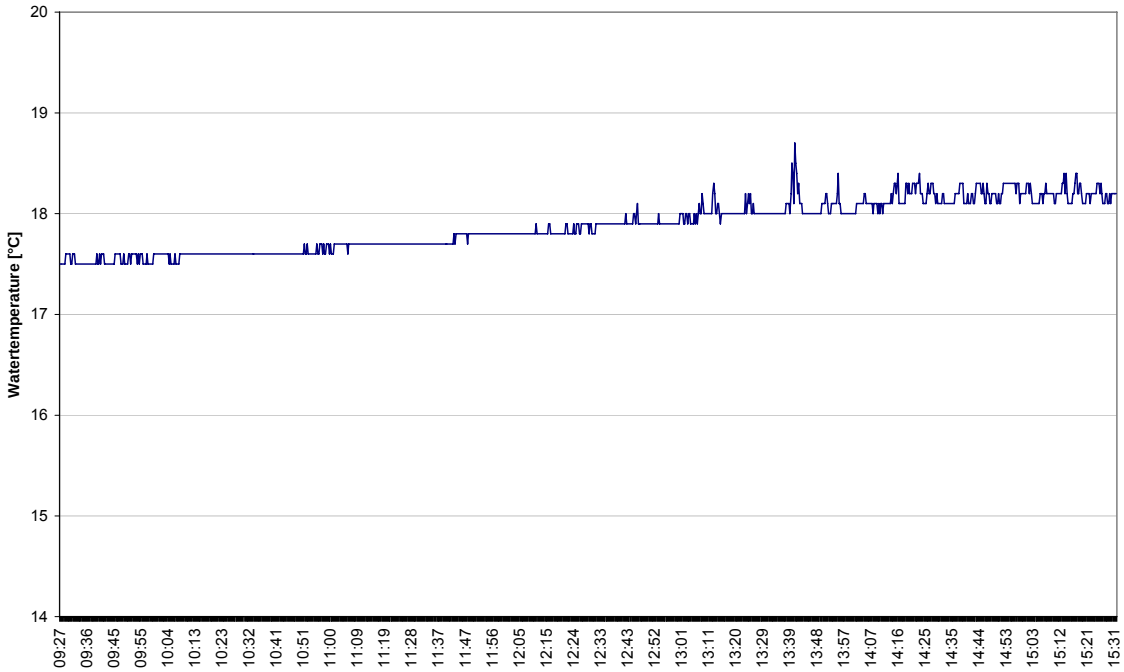


Figure 2: Po River water temperature during the exercise

The Po river temperature increased slightly, ca. 0.5 °C, during the sampling day. Conductivity and pH did not show inhomogeneity over time. Observed parameters were calibrated prior to measurement in-field and calibration was checked after the event.

4.3.2 Suspended particulate matter

Suspended particulate matter was determined gravimetrically according to European Standard Procedure prEN 872.

Table 5: Suspended particulate matter concentration during the sampling period

Time	10:00	10:15	10:30	10:45	11:00	11:07	11:11	11:15
TSM [mg/L]	33.5	43.2	46.3	42.4	49.2	48.0	41.3	47.8
Time	11:30	12:00	12:30	13:05	13:30	14:00	14:30	15:00
TSM [mg/L]	42.1	45.2	55.1	50.8	55.2	50.6	44.9	22.7

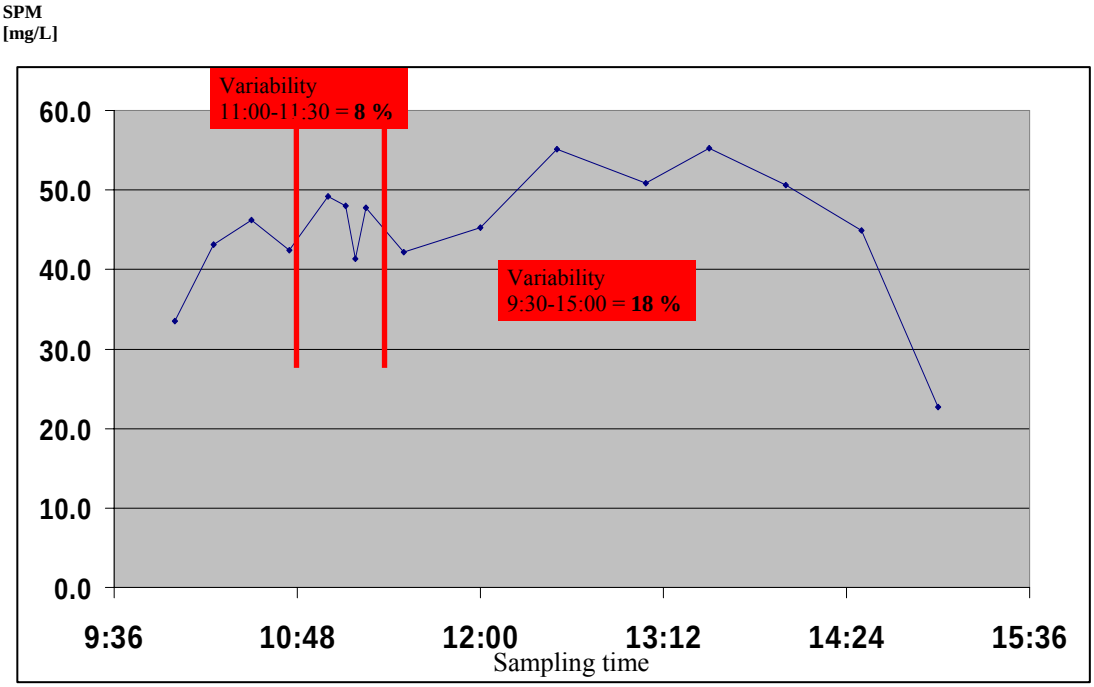


Figure 3: Suspended particulate matter concentration in water samples during sampling period

As was also confirmed by on-line turbidity measurements, the suspended particulate matter content was stable during the day and started to decrease in the afternoon. In particular during the joint sampling period the variability was low. Gravimetric determination of SPM was done with a confidence interval $< \pm$ 5%.

4.3.3 Homogeneity of PAH in river water

Table 6: PAH concentrations during sampling period

Time of sampling		10:00	11:00	11:07	11:15	11:30	13:00	14:00	15:00
PAH [ng/L]	blank								
Anthracene	0.04	0.95	1.68	7.86	5.42	1.22	0.86	1.26	0.96
Fluoranthene	0.20	4.94	4.76	13.54	5.39	4.50	5.43	6.48	5.18
Benzo(a)pyrene	0.03	2.48	2.00	25.13	2.43	2.22	2.85	3.33	2.77
Benzo(b+k)fluoranthene	0.03	3.23	2.75	14.79	0.79	2.96	3.93	4.77	3.71
Benzo(g,h,i)perylene	0.05	2.02	1.58	7.33	0.51	1.56	2.23	2.59	1.93
Indeno(1,2,3-cd)pyrene	0.06	1.92	1.39	11.84	1.55	1.40	1.96	2.39	1.69

The test for homogeneity of the river water concerning PAH concentrations revealed a substantial increase at 11:07. The increase was of short duration and could not be detected at 11:15. A GC/MS screening lead to the identification of substances deriving e.g. from various phthalates and substances used in rubber tyre production. The increase in PAH concentration could therefore either be attributed to a passing plume of a contaminant mixture, or to the contamination of the sample with water or particles released from the rubber tyres that were fixed along the quay as shock mounts.
Being measured just after the participants had finished their bottle sampling the contamination is unlikely to have influenced their results. An interference with the sample that had been collected by participant CMA01 cannot be fully excluded, although the PAH pattern was much different.

4.3.4 Homogeneity of PBDE in river water

Table 7: PBDE concentrations during sampling period

Sampling time	Blank	10:00	11:00	11:07	11:15	11:30	13:00	14:00	15:00	Average
PBDE [ng/L]										
BDE-28	0.001	0.004	0.005	0.003	0.004	0.002	0.003	0.002	0.002	0.003
BDE-47	0.031	0.056	0.041	0.063	0.056	0.058	0.127	0.050	0.080	0.066
BDE-99	0.070	0.114	0.062	0.077	0.064	0.071	0.115	0.052	0.113	0.084
BDE-100	0.013	0.023	0.014	0.018	0.016	0.014	0.025	0.013	0.023	0.018
BDE-153	0.005	0.011	0.008	0.009	0.007	0.008	0.018	0.007	0.013	0.010
BDE-154	0.006	0.007	0.006	0.008	0.008	0.008	0.014	0.006	0.009	0.008
Sum WFD PBDE	0.126	0.215	0.135	0.177	0.155	0.161	0.301	0.129	0.241	0.189

While being close to the blank of the selected procedure, 2 L liquid/liquid extraction, the results showed that no concentration peaks occurred during the monitoring period. With the results being comparable to those of more elaborated procedures, homogeneity of the sampled water body, within the method variability, concerning the PBDE has been shown (Figure 4).

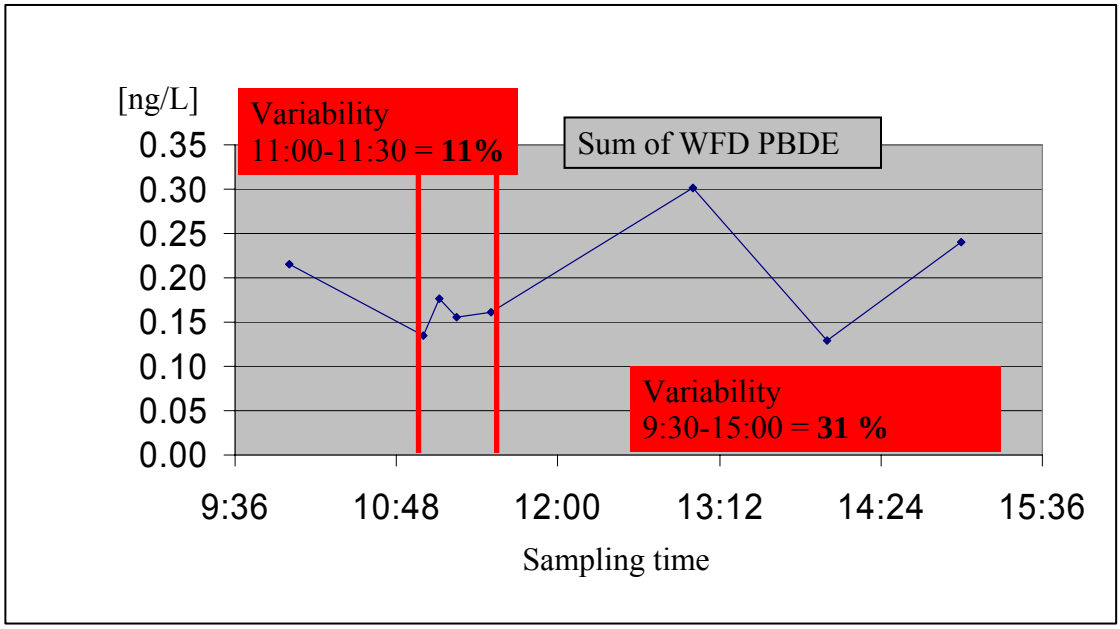


Figure 4: Sum of WFD PBDE in water samples during sampling period

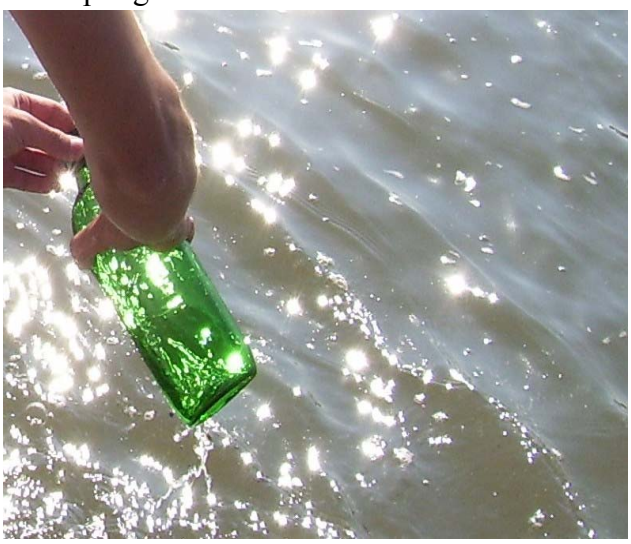
The differences in variability during the main sampling time 11:00 to 11:30 (11 % for PBDE and 8% for SPM) and during the large volume sampling 10:00 to 15:00 (31% for PBDE and 18% for SPM) confirmed homogeneity of the river for these parameters during the sampling period (see Figure 4). Determination of PBDE was done with a confidence interval < ± 20 %, as tested in a pre-campaign by analysing sample replicates.

5 Approaches for water monitoring

5.1 Methods employed by participating laboratories

A wide range of approaches has been applied by the participants: Samples were taken directly with a bottle, a bucket and then transferred to bottles. Another approach was the sampling of particulate matter with a flow-through centrifuge. Sample volumes ranged from 0.2 L to 4150 L. Samples were in some cases filtered. Sample preparation was done with liquid-liquid solvent extraction, filtration, solid phase extraction with extraction columns or extraction disks and by accelerated solvent extraction. Measurements where done by gas chromatography coupled with high- or low-resolution MS. Table 8 and Table 9, for NP/OP Table 28 give an overview about the employed methods. A detailed listing of the methods reported by the participants can be found in Annex I.

CMA On-site participants sampling on River Po



Water sampling with bucket, bottles and centrifuge

Table 8: PAH methods overview

PAH methods	CMA01	CMA02	CMA03	CMA04	CMA05	CMA06	CMA07
Sample Volume [L]	2.7	0.2	1	4150*	2.3	2.5-3	1
Filtration	no	yes	no	n.a.	yes	no	no
Extraction	LLE	SPE	LLE	Centrifuge	LLE	Disk SPE	SPE
SPE cart. / solvent		HLB 60		ASE		C_{18}	
Solvent	Ch_2Cl_2			Toluene	Ch_2Cl_2		
Analytical method	GC-MS	GC-MS	GC-MS	GC-MS	GC-MS	GC-MS	GC-MS
Ionisation	EI	EI	EI	EI	EI	EI	EI
Column	HP-5MS	DB-5	DB-5MS	HP-5MS	DB-5	Varian VF-Xms	DB-1
Length	30 m	30 m	60 m	30 m	30 m	60 m	60 m
Clean-up	Silica column	no	no	Cu, Al_2O_3, H_2O	no	no	no
Internal standard	5 i.S.	5 i.S.			5 i.S. + 7 recovery	5 i.S.	1

* SPM

Table 9: PBDE methods overview

PBDE methods	CMA01	CMA02	CMA03	CMA04	CMA05	CMA06	CMA07
Sample Volume [L]			1	4150*	2.3	2.5-3	1
Filtration			yes	n.a.	yes	no	no
Extraction			Soxhlet/LLE	Centrifuge	LLE	Disk SPE	LLE
SPE cart. / solvent				ASE		C_{18}	
Solvent				Toluene	Toluene		
Analytical method			GC-High Res. MS	GC-MS	GC-MS	GC-MS	GC-MS
Ionisation			EI	NCI	NCI	EI-MS-MS	EI
Column			DB-5, Rtx5MS	RTX CLP	DB-5	Rtx-5MS	DB-5
Length			60 m	30 m	60 m	60 m	60 m
Clean-up			Mixed layer Alumina/GPC	GPC, $SiOH/H_2SO_4$	Multi layer, Na_2SO_4, Si, H_2SO_4, Alox	no	Alox
Internal standard			12 i.s., 1 recovery std	3 F-BDE i.S., 1 recovery	5 i.S. + 7 recovery	2 i.S.	1

*SPM

A detailed table with information supplied by the participating laboratories can be found in Annex I

5.2 Methods employed by JRC IES:

The CMA on-site team from the JRC IES laboratory employed a variety of methods, aiming thus at a broad coverage of sampling and analytical methods. This method array should provide results obtained by different methodologies, comparing thus techniques that use a different principle of particle separation and extraction. Most of the methods were aiming at separation between the dissolved and the particle bound pollutant fractions. While this separation is clearly an operationally defined one, it allows comparison of results under application in a real water body.

20 L GF/F filtration + liquid/liquid extraction
This large volume version of a classical liquid/liquid extraction approach allowed the reduction of blank values in relation to sample volume. While not being easily suitable for routine analysis, due to the necessity to manually handle the 20 L sample, this method allowed the determination of contaminant partitioning.

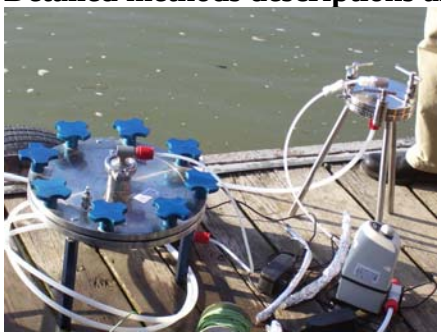
226 L filtration + 2x 250 g XAD
The large volume filtration/adsorption approach with an Infiltrex™300 device (Axys Technologies Inc., Canada) using a 2" glass fibre cartridge and subsequently 2 large, 250 g XAD cartridges has been used in analysis of dioxins in water and in ultra trace applications in marine chemistry. It was used here in parallel to the large volume water centrifugation approach used by participant CMA04.

45 L GF/F filtration + 2 x 50 g XAD
In parallel to other methods also the filtration in combination with adsorptive extraction of a medium size sample was used. With the XAD column containing 50 g adsorbent these columns are suitable for extraction of up to ca. 300 L water in inland surface water bodies.

2.3 L GF/F filtration + C_{18} extraction disk
This was a modification of a methodology used also by participants. A glass fibre filter on top of the extraction disk allowed the separate determination of contaminant in the particulate fraction. The blank situation of this method showed that experience is needed to cope with laboratory and field artefacts.

2 L liquid/liquid extraction
This method was used for homogeneity tests. It does not allow separation of particulate and dissolved contaminant fraction. It is questionable whether contaminants on particles can be monitored under all circumstances, e.g. when the substances are trapped in particles with a hydrophilic cover. The use of Dichloromethane for liquid /liquid extraction of water as routine method is not recommended due to the problematic disposal of wastewater contaminated with this chlorinated solvent.

Detailed methods descriptions are in Annex II..



Filtration manifolds, pump and infiltrex system

6 Results

6.1 JRC results

6.1.1 JRC PAH results

In order to create a set of data that would allow the comparison of results delivered by the participating laboratories, the JRC IES laboratory applied several methodologies. As the total organic priority substance content needs to be determined, the partitioning of the substances between the dissolved and the particulate phase is of importance. Separate analysis of both fractions was therefore selected in order to understand possible implications of the contaminant partitioning for the reported results.
Most of the methods are research methods, i.e. they are no standard methods and no proficiency testing scheme is available for testing their performance.

Table 10: PAH JRC method comparison

PAH	142 mm GF/F Filter + LL-Extraction		Glasfiber cartridge filter + 2x 250 g XAD		293 mm GF/F Filter + 2x 50 g XAD		GF/F Filter + 47 mm Empore C_{18}		LL-Extraction	142 mm GF/F Filtration
Sample volume	20 L		226 L		45 L		2.3 L		2 L	12 L
[ng/L]	Diss.	SPM	Diss.	SPM	Diss.	SPM	Diss.	SPM	Diss./ SPM	SPM
Anthracene	0.15	0.31	0.35	0.43	0.03	0.28	0.05	0.47	1.26	0.37
Fluoranthene	0.61	3.44	0.32	3.24	0.14	2.99	1.24	2.87	3.14	2.51
Benzo(a)pyrene	0.02	1.92	0.06	1.67	0.00	1.72	0.09	2.20	2.70	1.71
Benzo(b+k)fluoranthene	0.08	4.31	0.19	2.25	0.19	3.68	0.17	3.25	2.31	3.73
Benzo(g,h,i)perylene	0.02	1.78	0.05	1.21	0.01	1.54	0.11	1.78	1.23	1.60
Indeno(1,2,3-cd)pyrene	0.02	1.69	0.04	2.24	0.02	1.49	0.10	1.84	1.51	1.63

Sum values are shown in Table 14

The Polycyclic Aromatic Hydrocarbons, PAH, have been considered as listed in the Priority Substance List (Decision 2455/2001/EC). While the higher molecular weight PAH are predominant in the particulate fraction, significant amounts of the lowest molecular weight substances are dissolved.

6.1.2 JRC PBDE results

For PBDE analysis the sampling procedures as for PAH analysis have been applied. An aliquot of the sample extract has been used for PAH analysis, while the other was submitted to PBDE analysis. Also for PBDE analysis the partitioning of contaminants between particulate and dissolved fraction has been investigated.
In addition to the congeners listed as priority substances within the Water Framework Directive, also other PBDE have been analysed. The results will be published elsewhere.

Table 10: PBDE 20 L Method

PBDE	20 L GF/F Filter + LL-Extraction			
[ng/L]	Blank LL	LL (2x)	Filter	Total
BDE-28	0.0002	0.0010	0.0006	0.0015
BDE-47	0.0040	0.0250	0.0259	0.0509
BDE-99	0.0071	0.0624	0.0449	0.1074
BDE-100	0.0019	0.0165	0.0115	0.0281
BDE-153	0.0008	0.0015	0.0040	0.0054
BDE-154	0.0005	0.0020	0.0041	0.0061
Sum	0.0144	0.1083	0.0910	**0.1993**

Table 11: PBDE 226 L method

PBDE	226 L Glass fiber cartridge filter + 2x 250 g XAD				
[ng/L]	XAD Cartridge 1	XAD Cartridge 2	XAD Cartridge 1 +2	Filter	Total
BDE-28	0.0008	0.0001	0.0008	0.0010	0.0018
BDE-47	0.0155	0.0041	0.0195	0.0320	0.0515
BDE-99	0.0232	0.0122	0.0354	0.0464	0.0817
BDE-100	0.0048	0.0020	0.0069	0.0120	0.0189
BDE-153	0.0015	0.0009	0.0024	0.0359	0.0383
BDE-154	0.0018	0.0012	0.0030	0.0292	0.0322
Sum	0.0476	0.0204	0.0680	0.1564	**0.2244**

Table 12: PBDE 45 L method

PBDE	45 L GF/F Filter + 2x 50 g XAD				
[ng/L]	XAD Cartridge 1	XAD Cartridge 2	XAD Cartridge 1 +2	Filter	Total 45 L
BDE-28	0.0003	0.0003	0.0006	0.0357	0.0363
BDE-47	0.0156	0.0101	0.0256	0.0484	0.0741
BDE-99	0.0221	0.0132	0.0353	0.0149	0.0502
BDE-100	0.0080	0.0034	0.0114	0.0017	0.0131
BDE-153	0.0008	0.0004	0.0013	0.0032	0.0045
BDE-154	0.0020	0.0006	0.0026	0.0000	0.0026
Sum	0.0488	0.0280	0.0768	0.1039	**0.1808**

Procedural blanks of the adsorptive extraction columns, derived prior to a final cleaning of the columns, were not always satisfactory due to the use of new columns. Comparison of blanks analysed later, prior to reuse of the extraction columns and the comparison with other methods showed that the column blanks did not interfere significantly with the obtained results. Therefore blanks were not substracted.

Table 13: PBDE 2.3 and 2 L methods

PBDE	2.3 L Filter + Disk SPE				2 L Liquid/liquid extraction	
[ng/L]	Blank SPE	Disk SPE	Filter	Total	Blank	Average
BDE-28	0.0008	0.0014	0.0023	0.0038	0.0011	0.0031
BDE-47	0.0129	0.0124	0.0424	0.0548	0.0312	0.0663
BDE-99	0.0122	0.0116	0.0535	0.0651	0.0700	0.0836
BDE-100	0.0037	0.0029	0.0152	0.0181	0.0130	0.0182
BDE-153	0.0087	0.0099	0.0178	0.0277	0.0049	0.0099
BDE-154	0.0026	0.0061	0.0095	0.0156	0.0059	0.0082
Sum	0.0409	0.0443	0.1407	**0.1850**	0.1260	**0.1893**

The results showed clearly the partitioning of PBDE between particles suspended in the water body and the "so-called" dissolved phase, operationally defined as contaminant that passes a glass fibre filter with 0.7 µm particle retention (at 98% efficiency) or a glass fibre cartridge with 1 µm nominal retention.
The WFD PBDE priority substance congeners of highest abundance in the aquatic environment, BDE-47 and BDE-99 showed a substantial amount in the dissolved phase. Ca. 50-60 % of these compounds where found by liquid/liquid extraction after sample filtration. Though the experiments shown here have been performed only once, due to the nature of the experimental set-up, the different methodological approaches confirm this. Also the filtration/XAD adsorption methods show ca. 40-70 % of BDE-47 and BDE-99 present after filtration. The 2.3 L solid phase extraction had here a blank value too close to the analytical results and cannot be account for.
As the River Po showed with ca. 45 mg/L suspended particulate matter significant partitioning, it can be expected that a larger contaminant fraction will be present in the dissolved phase at lower SPM values.

6.1.3 JRC whole water results

Following the whole water approach for analysis of total contaminant content for organic trace pollutants, as described in the EQS Directive proposal and the intermediate version of the guidance document for surface water chemical monitoring, the further considerations have been made by comparing combined analysis resulting in a single result for a sample.

Table 14: JRC PAH whole water results

PAH - Whole water	GF/F Filter + LL-Extraction	Glasfiber cartridge filter + 2x 250 g XAD	GF/F Filter + 2x 50 g XAD	GF/F Filter + Empore C_{18}	LL-Extraction
Sample volume	20 L	226 L	45 L	2.3 L	2 L
PAH concentration [ng/L]					
Anthracene	0.46	0.78	0.31	0.53	0.84
Fluoranthene	4.04	3.55	3.12	4.11	2.38
Benzo(a)pyrene	1.93	1.74	1.72	2.30	1.00
Benzo(b+j+k)fluoranthene	4.39	2.44	3.87	3.43	1.38
Benzo(g,h,i)perylene	1.81	1.26	1.55	1.90	0.79
Indeno(1,2,3-cd)pyrene	1.71	2.28	1.51	1.94	0.70

Table 15: Variability of JRC PAH whole water methods

PAH concentration [ng/L]	Average of 5 methods	standard deviation	CV %
Anthracene	0.67	0.22	33.1
Fluoranthene	3.59	0.72	19.9
Benzo(a)pyrene	2.08	0.47	22.8
Benzo(b+k)fluoranthene	3.29	1.20	36.5
Benzo(g,h,i)perylene	1.55	0.45	29.1
Indeno(1,2,3-cd)pyrene	1.79	0.59	33.1

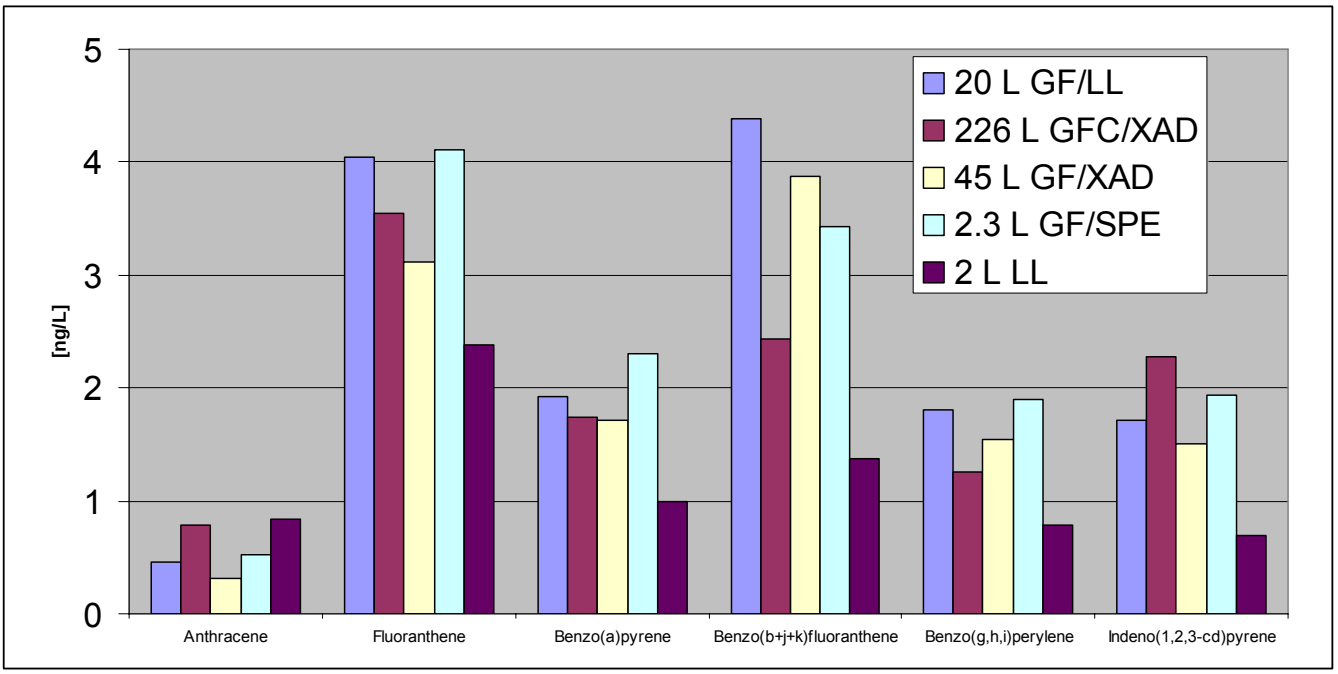


Figure 5: PAH JRC Method comparison

A comparison of the whole water PAH content measured with the different employed methods shows a good agreement (Figure 5). The liquid/liquid extraction shows a substantially lower result for all but the lowest concentrated and most hydrophilic PAH. All methods showed a variability coefficient of less or equal to 37 % (Table 15), eliminating the biased liquid/liquid extraction method even a coefficient of variability of 25 % can be achieved.

Table 16: JRC PBDE whole water results

PBDE – Whole water	LL-Extraction	GF/F Filter + Empore C_{18}	GF/F Filter + LL-Extraction	GF/F Filter + 2x 50 g XAD	Glasfiber cartridge filter + 2x 250 g XAD
Sample Volume	Average of 8 x 2.4L	2.3 L	20 L	45 L	226 L
PBDE [ng/L]					
BDE-28	0.003	0.004	0.002	0.001	0.002
BDE-47	0.066	0.055	0.051	0.039	0.052
BDE-99	0.084	0.065	0.107	0.059	0.082
BDE-100	0.018	0.018	0.028	0.017	0.019
BDE-153	0.010	0.028	0.005	0.004	0.038
BDE-154	0.008	0.016	0.006	0.005	0.032
Sum WFD PBDE	**0.189**	**0.185**	**0.199**	**0.125**	**0.224**

Table 17: Variability of JRC PBDE whole water methods

PBDE [ng/L]	average of 5 methods	standard deviation	CV %
BDE-28	0.002	0.001	47.5
BDE-47	0.053	0.010	18.4
BDE-99	0.079	0.019	23.7
BDE-100	0.020	0.005	22.6
BDE-153	0.017	0.015	89.4
BDE-154	0.013	0.011	84.0
Sum WFD PBDE	**0.184**	**0.037**	**19.8**

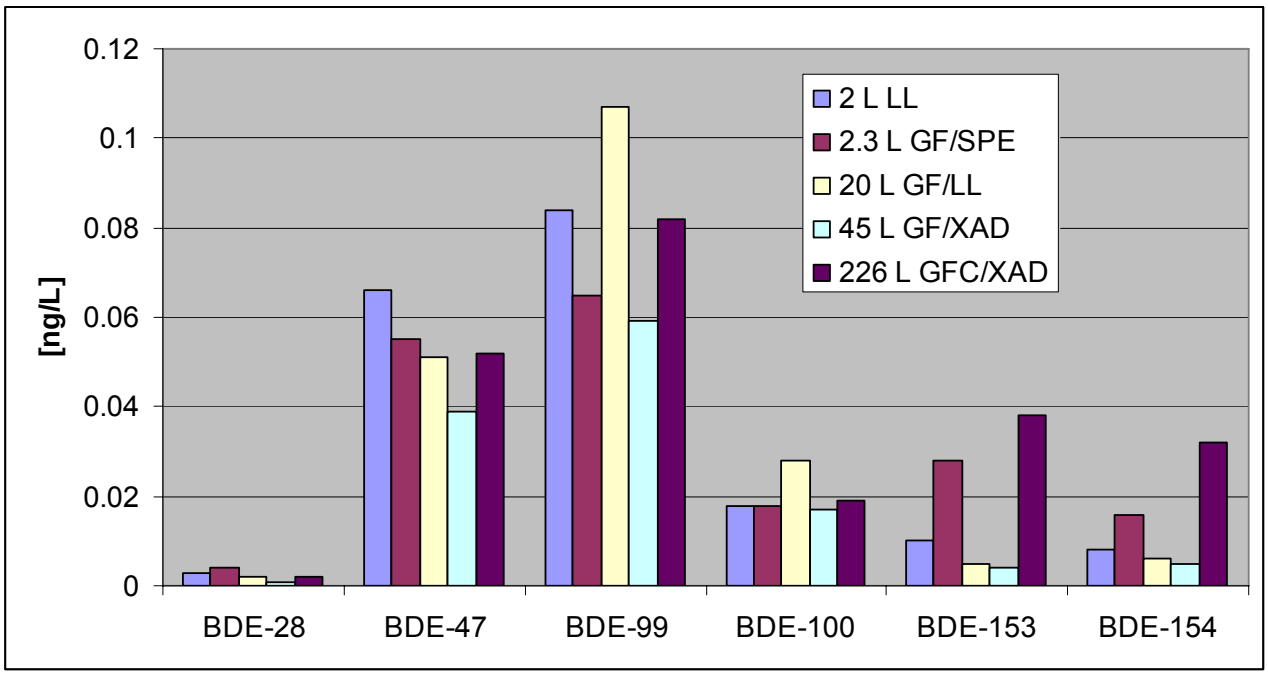


Figure 6: PBDE JRC method comparison

The 5 different methodologies used for analysis of PBDE in river water show a good agreement, considering even that the results are underlying the short term variability in a natural flowing water body, plus the analytical variability of a complex instrumental analysis at low analyte concentration.
Figure 6 shows the result comparison. While concentrations of BDE-28, BDE-153 and BDE-154 are of lower concentration and show therefore a higher variability, the 3 congeners BDE-47, BDE-99 and BDE-100 have been measured by the 5 methods obtaining very similar results. While Table 16 shows the obtained results, Table 17 shows the variability, which, for the 3 more prominent congeners, is below 25%. The basis of 5 different methodologies in good agreement with each other was then used as base for comparison with the results obtained by the participating laboratories.

6.2 PAH and PBDE results from participating laboratories

The participants transported the samples themselves back home to their laboratories. A tentative deadline for result submission on 4.12.06 was set. A reporting sheet template for collecting both analytical data and information about the applied methodologies (see Annex V.) was therefore distributed to the participants. Response time was rather variable and some results were received also in March 2007. CMA07 could not report PAH and PBDE results in standards and extracts due to an incompatibility of the standard and extract solvent with the methodology employed by the laboratory.

6.2.1 PAH results from participating laboratories

From measurement of the PAH standard S1 6 of the 7 laboratories delivered results for the extract E1 and for the river water 5 laboratories.

6.2.1.1 PAH standard results

Table18: PAH Standard S1 results

PAH results	Standard	CMA01	CMA02	CMA03	CMA04	CMA05	CMA06
Standard S1							
[ng/ml]							
Anthracene	60	27	49.6	48	32.5	70.5	60
Fluoranthene	60	36	66.4	56	34.5	61.8	66
Benzo(a)pyrene	60	24	67.9	96	40.5	105.0	54
Benzo(b)fluoranthene	60		63.7	61	20.5		59
Benzo(k)fluoranthene	60		63.3	49	15		62
Benzo(b+k)fluoranthene*		42				49.6	
Benzo(g,h,i)perylene	60	22	35.2	80	28.5	49.3	58
Indeno(1,2,3-cd)pyrene	60	15	39.0	90	24	45.4	62
Sum of WFD relevant PAH	**420**	**166**	**385**	**480**	**196**	**382**	**421**

*Sum of Benzo(b)fluoranthene and Benzo(k)fluoranthene in case of no chromatographic separation

Two laboratories reported the sum of Benzo(b)fluoranthene and Benzo(k)fluoranthene, as with their chromatographic system a separation could not be achieved.

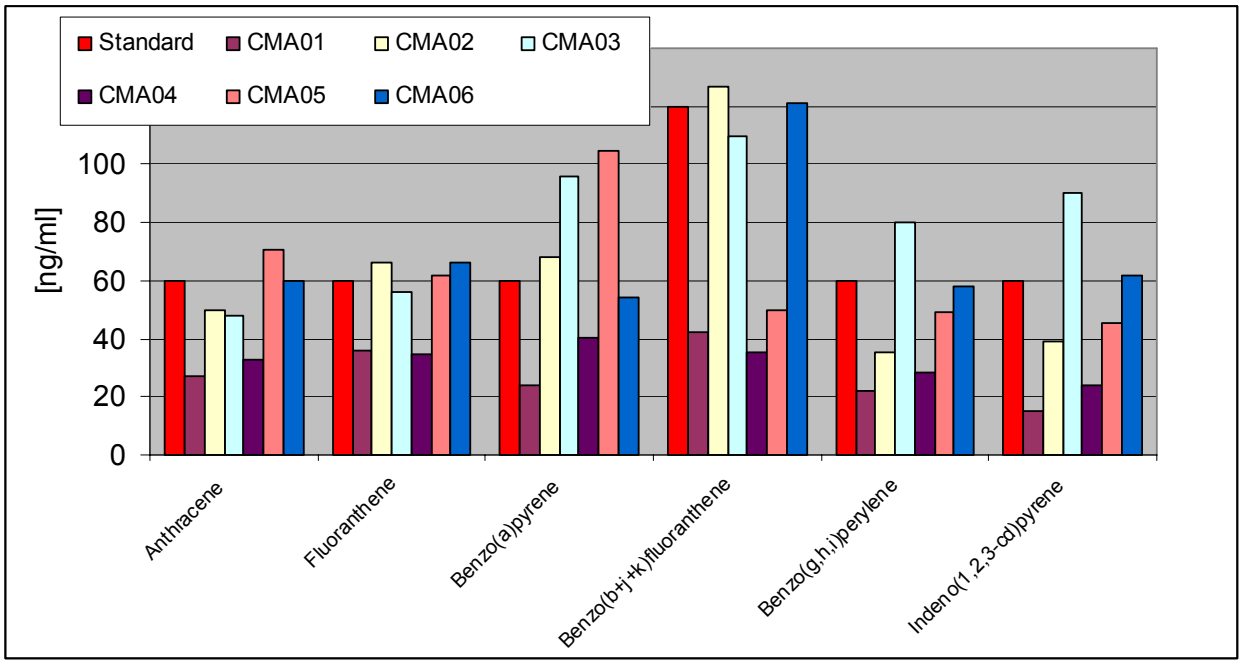


Figure 7: PAH Standard S1 results

The analysis of the PAH standard solution resulted in a coefficient of variation of 38 % for the PAH sum. No compound specific bias can be observed, while it is shown that some laboratories (CMA01 and CMA04) report data that are too low by a factor of ca. 2.

6.2.1.2 PAH extract E1 results

Table 19: PAH Extract E1 results

PAH results						
	CMA00	CMA02	CMA03	CMA04	CMA05	CMA06
Extract E1						
[ng/ml]						
Anthracene	2.6	15.0	3.7	0.3	1.8	3.8
Fluoranthene	21.3	50.8	11.0	1.9	20.8	28.8
Benzo(a)pyrene	11.1	61.2	13.0	1.6	34.6	16.3
Benzo(b)fluoranthene		57.7	11.0	0.8		19.6
Benzo(k)fluoranthene		51.9	4.6	0.7		20.0
Benzo(b+k)fluoranthene*	18.6				19.4	
Benzo(g,h,i)perylene	12.1	44.7	16.0	1.2	26.0	16.7
Indeno(1,2,3-cd)pyrene	8.1	51.0	19.0	1.1	32.9	21.0
Sum of WFD relevant PAH	**73.7**	**332.3**	**78.3**	**7.5**	**135.5**	**126.2**

As expected, the result for the matrix loaded Extract sample introduced a higher variability among the results. As this sample cannot be linked to a standard and an externally assigned value could not be derived, a comparison could only be made between the participating laboratories. Variability in analysis from a single laboratory was shown in the homogeneity study performed by JRC, leading to a coefficient of variation of below 1 % after 3 replicates for all but the lowest concentrated PAH. This shows, also in comparison with the previous result for a standard solution, that the added matrix is a

major source of variability.

Table 20: Variability in Extract E1 PAH results

[ng/ml]	Average of 6 labs	Standard deviation	CV%
Anthracene	4.53	5.29	116.7
Fluoranthene	22.43	16.74	74.6
Benzo(a)pyrene	22.97	21.63	94.2
Benzo(b+k)fluoranthene	34.05	38.97	114.4
Benzo(g,h,i)perylene	19.45	14.74	75.8
Indeno(1,2,3-cd)pyrene	22.18	17.89	80.6
Sum of WFD relevant PAH	125.58	111.09	88.5

Coefficients of variation range from 75 to 117%, indicating that this exercise was of particular complexity. Both the direct introduction of a matrix loaded sample, as also the clean-up introduce variability into the analytical procedure.

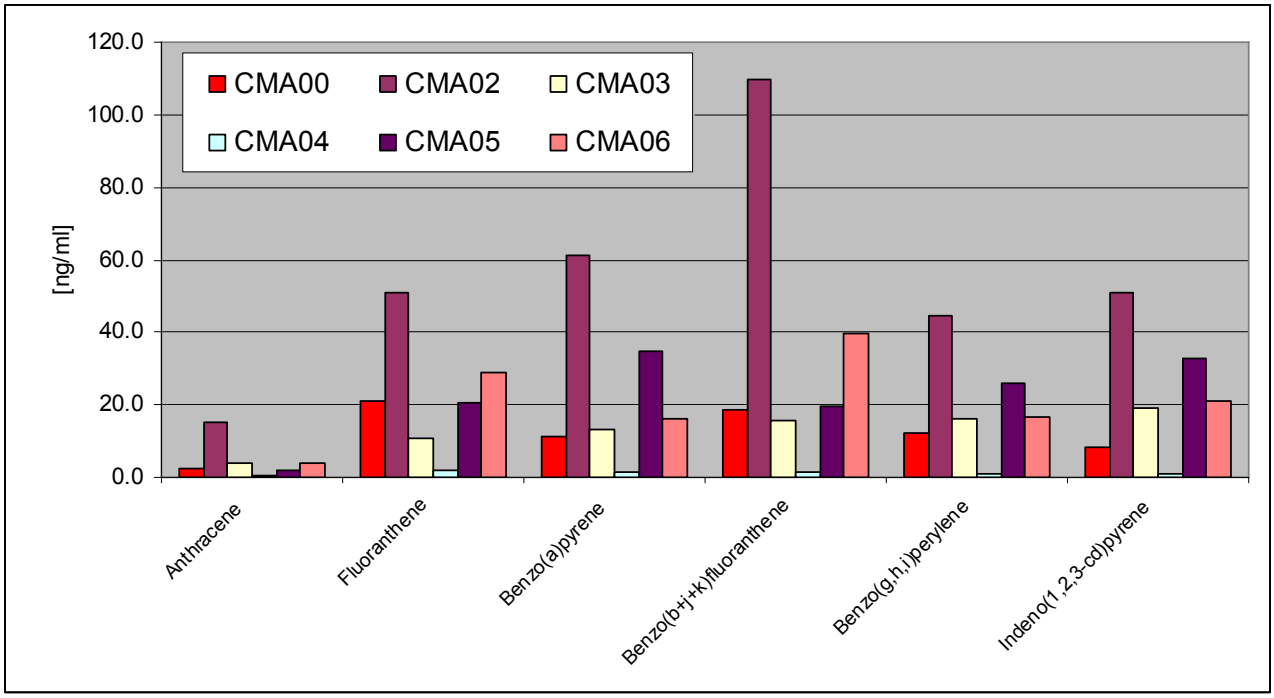


Figure 8: PAH Extract E1 results

CMA01 did not report values. The results of CMA04 appear to be particularly low, eventually this could be linked to the fact that CMA04 was the only reporting laboratory to use a clean-up procedure for PAH. The results of CMA02 are rather high in comparison.

6.2.1.3 PAH River Po results

Table 21: PAH whole water results

PAH results								
	CMA00	CMA01	CMA02	CMA03	CMA04	CMA05	CMA06	CMA07
Po whole water conc.					**			
[ng/L]								
Anthracene	0.67	19	< 1	<20	0.42	<0,5	0.9	<10
Fluoranthene	3.59	89	1	<10	3.25	2.1	3.0	<10
Benzo(a)pyrene	2.08	4	1	<10	2.43	2.6	2.1	<10
Benzo(b)fluoranthene			< 1	<10	2.33		1.9	<10
Benzo(k)fluoranthene			< 1	<10	2.53		1.8	<10
Benzo(b+k)fluoranthene*	3.29	4				1.2		
Benzo(g,h,i)perylene	1.55	18	1	<10	2.08	0.9	2.7	<10
Indeno(1,2,3-cd)pyrene	1.79	1	3	<10	2.23	0.9	1.9	<10
Sum of WFD relevant PAH	12.97	135	6		15.27	7.7	14.3	

***sum of single compounds in case of no chromatographic separation**

**** only SPM**

The main aim of the CMA on-site exercise was to compare the final results of environmental analysis performed at the same location, according to available, current protocols. For PAH analysis in River Po, 5 participants reported results, while 2 laboratories reported limits of quantification that where, for all compounds, above the observed concentrations.

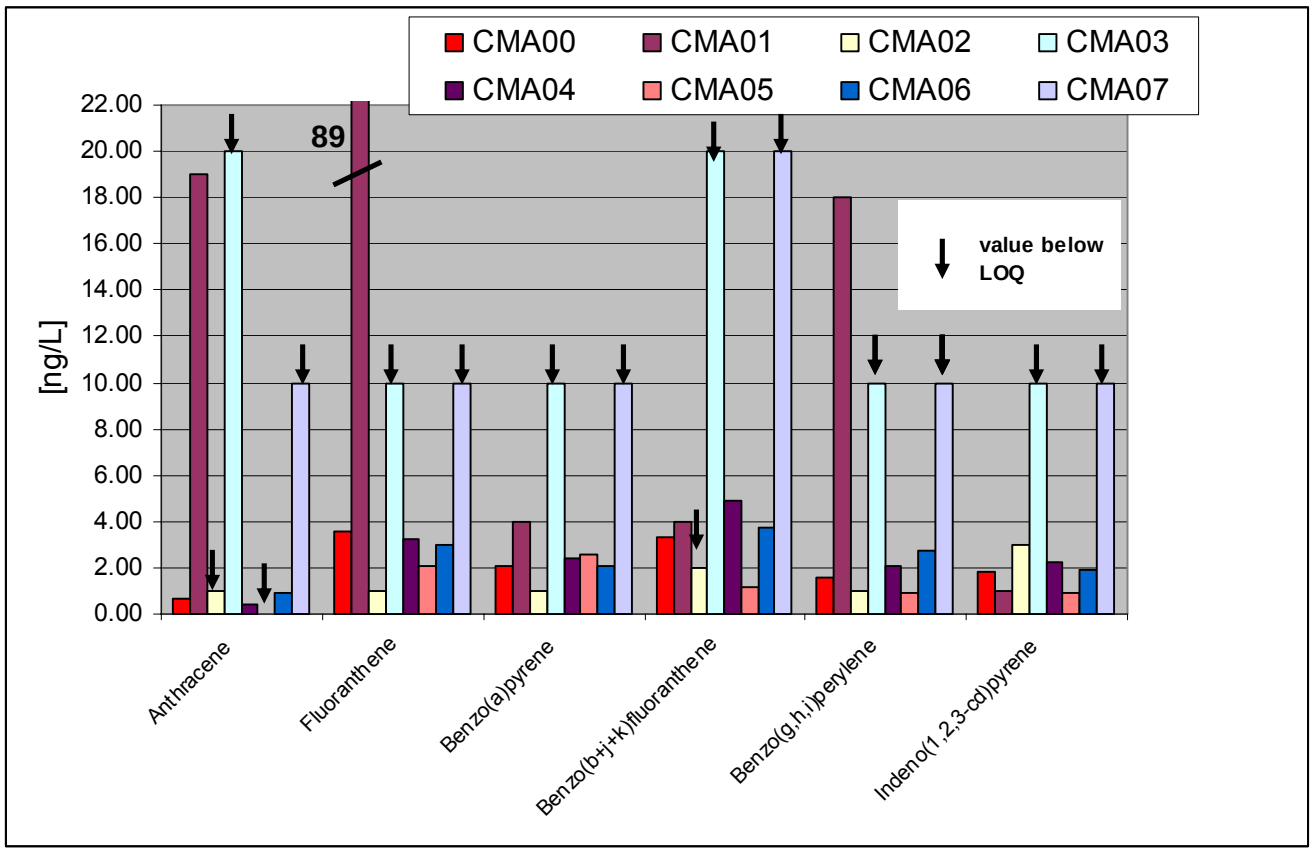


Figure 9: PAH whole water results

The results are shown in Table 21, together with the result obtained by JRC averaging 5 different analytical methods (CMA00, red column), as described in chapter 6.1.1.
Laboratory CMA01 reported outlier results that where much higher than all others, up to 89 ng/L. Though it might be possible that this sample was influenced by the spot contamination observed in the river water homogeneity studies (Chapter 4.3.3, Table 6), the PAH pattern is much distinct, with Benz(a)pyrene being the principal component in the spot contamination. It is more likely that some problems in the sample preparation and measurement occurred, although lab CMA01 performed better in the PAH standard measurement.

Table 22: Variability in river Po PAH results

[ng/L]	average from 5 labs*	standard deviation	CV %
Anthracene	0.55	0.25	45.3
Fluoranthene	2.59	1.05	40.4
Benzo(a)pyrene	2.04	0.62	30.5
Benzo(b+k)fluoranthene	2.81	1.67	59.3
Benzo(g,h,i)perylene	1.65	0.76	45.9
Indeno(1,2,3-cd)pyrene	1.96	0.76	38.7
Sum of WFD relevant PAH	11.25	4.14	36.8

*reported limits of detection have been substituted by a value half the LOQ if other PAH were quantified

The remaining participants CMA02, CMA04, CMA05 and CMA06 showed results in the same range. For CMA02 the results were very close to the reported limit of quantification (Table 23). Calculating the coefficient of variation in Table 22 results for most PAH in a value below 50%. Surprisingly therefore the performance in river water is less heterogeneous than in the river water extract and more similar to the variability observed in the standard analysis. For the calculations in Table 22 single values below the limit of quantification have been substituted by a value half of that limit.

Table 23: PAH Reported limits of Quantification

PAH – Reported LOQ in water						
[ng/L]	CMA02	CMA03	CMA04	CMA05	CMA06	CMA07
Anthracene	1	20	0.03	0.5	0.4	10
Fluoranthene	1	10	0.18	0.5	0.4	10
Benzo(a)pyrene	1	10	0.16	0.5	0.8	10
Benzo(b)fluoranthene	1	10	0.03		0.8	10
Benzo(k)fluoranthene	1	10	0.01		0.8	10
Benzo(b+k)fluoranthene*				1		
Benzo(g,h,i)perylene	1	10	0.19	0.5	0.8	10
Indeno(1,2,3-cd)pyrene	1	10	0.01	0.5	0.8	10

***sum of single compounds in case of no chromatographic separation**

The reported limits of quantification varied according to the analytical method employed. The lowest values were reached by lab CMA04 using large volume centrifugation for sampling. The limit of

quantification of CMA02 was close to the observed concentrations. CMA03 and CMA07 could not detect PAH with quantification limits of 10 ng/L for most compounds.

6.2.2 PBDE results from participating laboratories

The analysis of PBDE in environmental water samples is not common and no standard methodology exists. In preparation of the WFD implementation methodologies have been developed or adjusted that allow laboratories to analyse these compounds. Five out of seven laboratories reported results on PBDE concentrations in standards, extracts or river water.

6.2.2.1 PBDE Standards S1 results

Table 24: PBDE Standard S1 results

PBDE					
	Standard	CMA03	CMA04	CMA05	CMA06
Standard S1					
[ng/ml]					
BDE-28	10	0.94	10.0	4.71	10
BDE-47	10	0.99	8.8	3.4	11
BDE-99	10	1	9.2	4.32	9
BDE-100	10	0.99	8.8	3.37	9
BDE-153	20	2	19.9	11.25	20
BDE-154	20	2	31.2	8.51	20
Sum of WFD relevant BDE	**80**	**7.92**	**87.9**	**35.56**	**79**

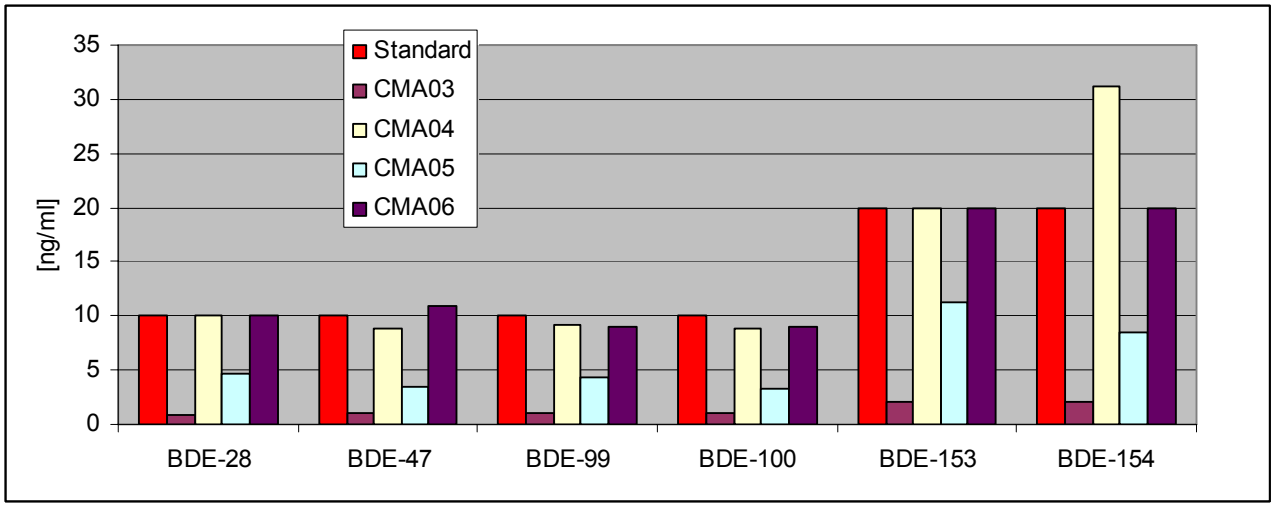


Figure 10: PBDE Standard S1 results

Four laboratories reported results for the analysis of the PBDE standard solution. With the standard concentration indicated in the red columns in Figure 10: PBDE Standard S1 resultsFigure 10, it appears that lab CMA 03 and lab CMA05 might have analysed correctly, as the ratios between the different congeners are in decent agreement, but that a bias was introduced in calculating the final result. CMA03 reports a result too low by a factor of ca. 10, while CMA05 a result that is too low by a

factor of ca. 2. The other two laboratories, CMA04 and CMA06 are in very good agreement with the concentration of the PBDE in the standard solution.

6.2.2.2 PBDE Extract E1 results

Table 25: PBDE Extract E1 results

PBDE					
	CMA00	CMA03	CMA04	CMA05	CMA06
Extract E1					
[ng/ml]					
BDE-28	0.012	0.0019	N.D.	N.D.	<0.2
BDE-47	0.444	0.073	0.30	0.29	0.6
BDE-99	0.427	0.07	0.54	0.4	0.7
BDE-100	0.112	0.017	0.14	0.1	0.3
BDE-153	0.111	0.014	0.20	0.14	<0.4
BDE-154	0.073	0.0098	0.16	0.08	<0.4
Sum of WFD relevant BDE	**1.179**	**0.1857**	**1.34**	**1.01**	**1.57**

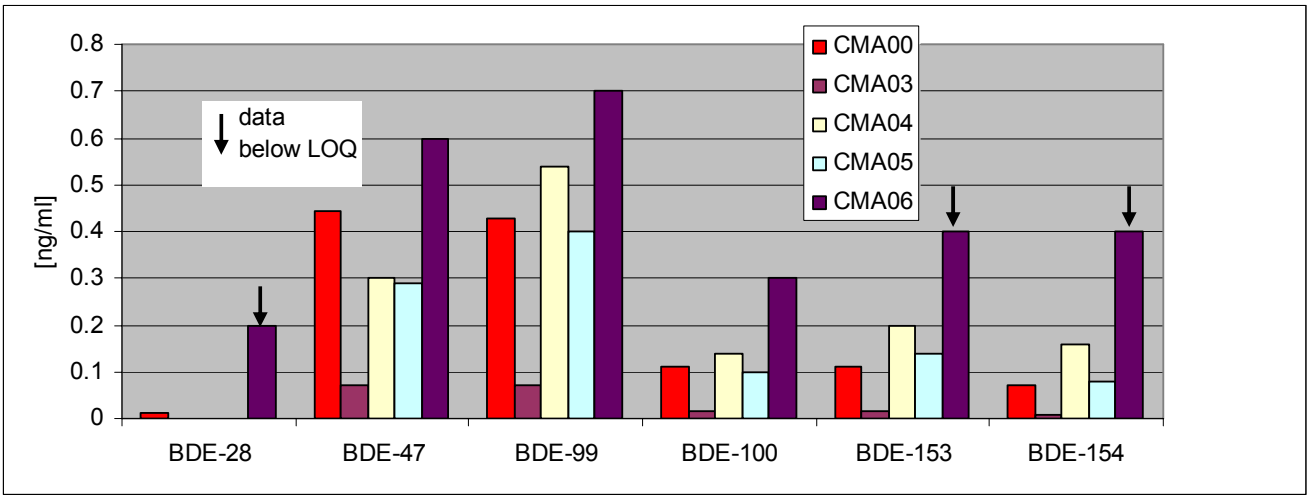


Figure 11: PBDE Extract E1 results

As evident in the graph with the results of the Extract E1 analysis Figure 11, the additional matrix makes the analysis more difficult. CMA03 shows, like in the standard, a result that is roughly a factor of 5-10 lower than other participants and it cannot be excluded that a miscalculation was the reason. The remaining 4 laboratories show a PBDE sum varying from 1.01 to 1.57 ng/ml. The variability seems to be rather low for trace organic analysis at these concentration levels, considering that the total extract received by the participants is the equivalent of 14.6 L of Po river water. The lower concentrated congeners BDE-28, BDE-153 and BDE-154 could not be quantified by lab CMA06.

6.2.2.3 PBDE river Po results

Table 26: PBDE whole water results

PBDE					
	CMA00	CMA03	CMA04	CMA05	CMA06
Po whole water conc.			*		
[ng/L]					
BDE-28	0.009	0.042	N.D.	N.D.	N.D.
BDE-47	0.060	0.45	0.022	0.036	0.3
BDE-99	0.078	0.4	0.063	0.054	0.2
BDE-100	0.019	0.035	0.011	0.018	N.D.
BDE-153	0.017	N.D.	0.015	N.D.	N.D.
BDE-154	0.013	N.D.	0.010	N.D.	N.D.
Sum of WFD relevant BDE	**0.196**	**0.927**	**0.12**	**0.108**	**0.52**

*** only spm measurement**

Four of the 7 participating laboratories reported concentration values from the analysis of PBDE in water (Table 26: PBDE whole water results). The reported concentrations are between 0.1 and 1 ng/L for the sum of PBDE listed as WFD priority substances. BDE-47 and BDE-99 were the most prominent congeners, accounting for more than 70 % of the PBDE sum in all results.

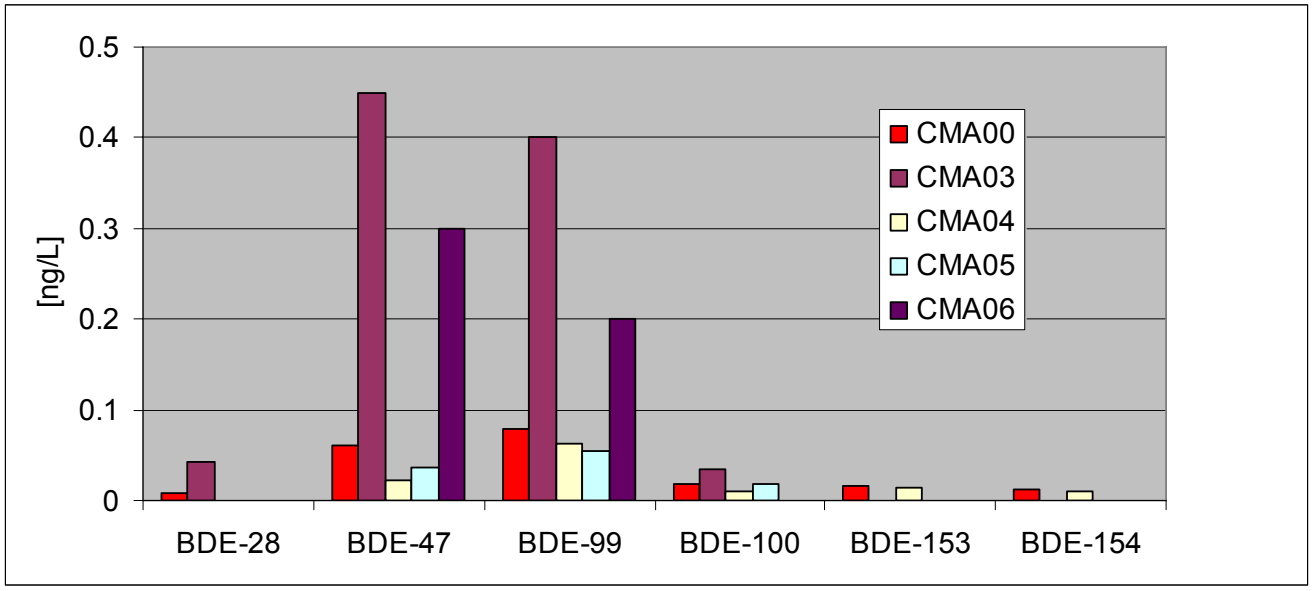


Figure 12: PBDE whole water results

The detailed results for single congeners, Figure 12, shows that, beside JRC, only laboratory CMA04, employing large volume water centrifugation, was able to detect the higher molecular weight PBDE. Laboratory CMA03, underestimating both standards and extract, reports a result that is factor 5 higher than the JRC combined results.

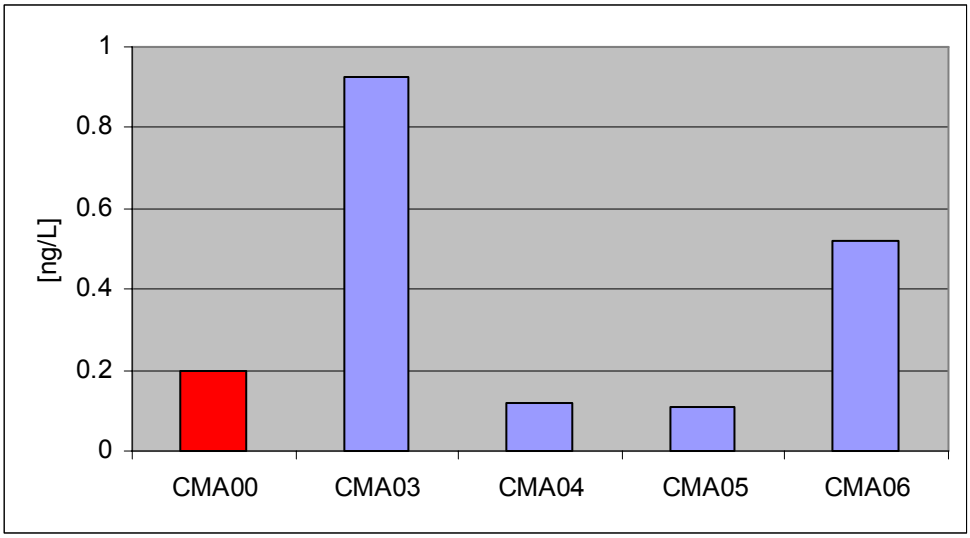


Figure 13: PBDE sum whole water results

In Figure 13 combined congener results are shown together with the average from 5 different analytical techniques, as red column, used by JRC IES. With a proposed annual average limit value of 0.5 ng/L the quantification limit for the sum of PBDE should be at 0.3 of that value, according to the proposed analytical method performance criteria. A required quantification limit for the PBDE sum of 0.15 ng/L would result. The PBDE concentration in the river Po has therefore been relevant for WFD chemical monitoring.

Table 27: PBDE reported LOQ in water

PBDE – Reported LOQ in water					
[ng/L]					
	CMA03	CMA04	CMA05	CMA06	CMA07
BDE-28	0.009	0.002	0.063	0.1	0.5
BDE-47	0.005	0.004	0.063	0.1	0.5
BDE-99	0.008	0.002	0.063	0.2	0.5
BDE-100	0.005	0.002	0.061	0.2	0.5
BDE-153	0.007	0.002	0.063	0.2	0.5
BDE-154	0.004	0.002	0.157	0.2	0.5

The reported limits of quantification were in logical agreement with the reported results. For some methods the environmental concentrations were just at the border of quantification. The lowest LOQ (CMA04) was obtained by large volume centrifugation and subsequent analysis of the collected SPM.

7 Nonylphenol / Octylphenol

For NP/OP seven laboratories reported analytical results. However, lab CMA07 did not analyse the standard and the river water extract E2, and lab CMA03 did have analytical problems, it was the only "outlier".

7.1 Experimental NP/OP

All laboratories used different analytical methods, triple-quadrupole LC-MS-MS, low resolution GC-MS without derivatisation and one Lab GC-MS with derivatisation (CMA04), and LC-fluorescence (CMA06). The Po River water sample was filtered in some labs, whereas in the others the water samples were processed directly. In addition, different extraction techniques were used for the Po River sample (Table 28). Five labs used solid-phase extraction (SPE) for the extraction of the water sample, and one lab liquid-liquid extraction (LLE). The SPE materials used were Oasis HLB (Waters), C18, and Envichrom P (Supelco). Lab CMA05 used dichloromethane (DCM) for the LLE of 2.3 L water. The elution of the SPE cartridges was as well performed with different solvents, ethylacetate (EA), DCM/EA (1:1), methanol/methyl-tert-butylether (MeOH/MTBE), and acetone.

Two labs analysed the collected suspended particle matter (SPM) material for NP/OP. In one of the labs Soxhlet extraction with acetone/hexane (2:1) was employed, whereas in the other one Randall extraction with hot MeOH was used. Lab CMA04 obtained the SPM material by on-site high volume flow-trough centrifuge sampling (4150 L), Lab CMA06 by filtration of 11.82 L water. The SPM content of the Po River water was ~ 45 mg/L.

LC separation of the analytes was performed by RP-LC using gradient elution with water-acetonitrile or water-methanol. The ions or transitions monitored by the different labs using GC-MS or LC-MS-MS are shown in Table 28. The internal standard used by most labs was 4n-NP (d8), which is available from different suppliers.

The JRC distributed to all laboratories a standard solution of the target compounds with an unknown concentration of NP and OP and a river water extract. For the standard solution technical NP (Aldrich, no. 29,085-8), and 4-OP (CAS no. 1806-26-4; mentioned in the PS EQS Directive (EC, 2006), Aldrich, no. 38,444-5) were used. They were dissolved in methanol and further diluted to a concentration of 200 ng/mL NP and 200 ng/mL n-OP, in methanol for the LC-MS labs and in hexane for GC-MS measurements.

The river water extract came from the River Seveso in the North of Milan (coordinates N 45.5380, E 9.1822). Sampling date was 4 October 2006 (11 h). A volume of 15 L of this river water was extracted by SPE using fifteen C18 cartridges (Isolute C18, 500 mg, 6 ml, International Sorbent Technology (IST), Cambridge, UK), using an AutoTrace® SPE workstation (Caliper Life Sciences). Elution was performed with 6 mL EA (for each cartridge). The eluates were merged and evaporated to 15 mL. Each laboratory received 1 mL of this extract, corresponding to a 1 L water sample of the River Seveso.

7.2 Results NP/OP

7.2.1 Octylphenol Standard

During the CMA onsite field trial it was realised that two different octylphenol isomers are being discussed in WFD working groups: linear 4n-OP with the CAS no. 1806-26-4, and branched *para-tert*-octylphenol (4-*tert*-OP) with the CAS no. 140-66-9, which is the technical used OP. Commercially available are two different OP standards, 4-OP, and 4-*tert*-OP. The 4-OP is the linear isomer, which is not technically used and thus it should not be present in the environment. The toxic isomer released to the environment is 4-*tert*-OP, mentioned in the OSPAR background document on OP (Ospar, 2003).

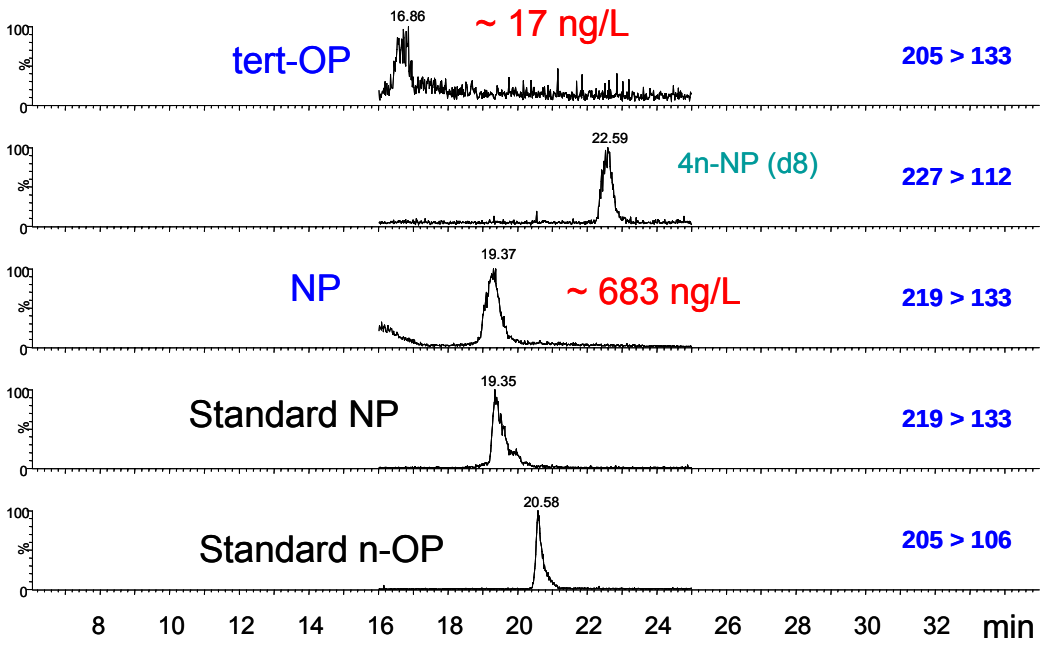


Figure 14 LC-MS-MS chromatograms for NP/OP of the river water extract (River Seveso). **Quattro Micro LC-MS-MS (Waters), C18 column; 150 × 2 mm, water – acetonitrile gradient, start with 60 % water (JRC result).**

By LC, 4-*tert*-OP is eluting earlier than 4n-OP (and before NP) and shows the characteristic mass transition 205 > 133, whereas 4n-OP has the MS-MS transition 205 > 106 with the cleavage of the alkyl chain at the β position (Figure 14). Also 4n-NP has the corresponding transition 219 > 106 (Loos et al., 2007). This indicates that the 4-OP standard is a linear isomer form of OP.

The standard solution S3 contained 4-OP, which is the linear form of OP.

7.2.2 Standard S3 and extract E2

For the NP/OP standard solution S3 and the river water extract E2 relatively good agreement was achieved for the analysis of NP by 5 labs. Lab CMA03 however, reported much lower NP concentrations for both the standard and the extract; this lab was considered as an "outlier". The reason for this could not be explained (problem with the standard or the instrument). The relative standard deviation (RSD) of the NP results from the different labs was calculated, and was between 23-29 % (excluding Lab CMA03). The laboratories were using different chromatographic detection systems. From these results it is obvious that NP and OP are being well analyzed by LC-MS-MS, LC-fluorescence as well as GC-MS (with and without derivatisation). Fluorescence detection does not have the selectivity to distinguish NP from n-OP which partially coelute on the used RP Phenylhexyl column (see Figure 14, CMA06).

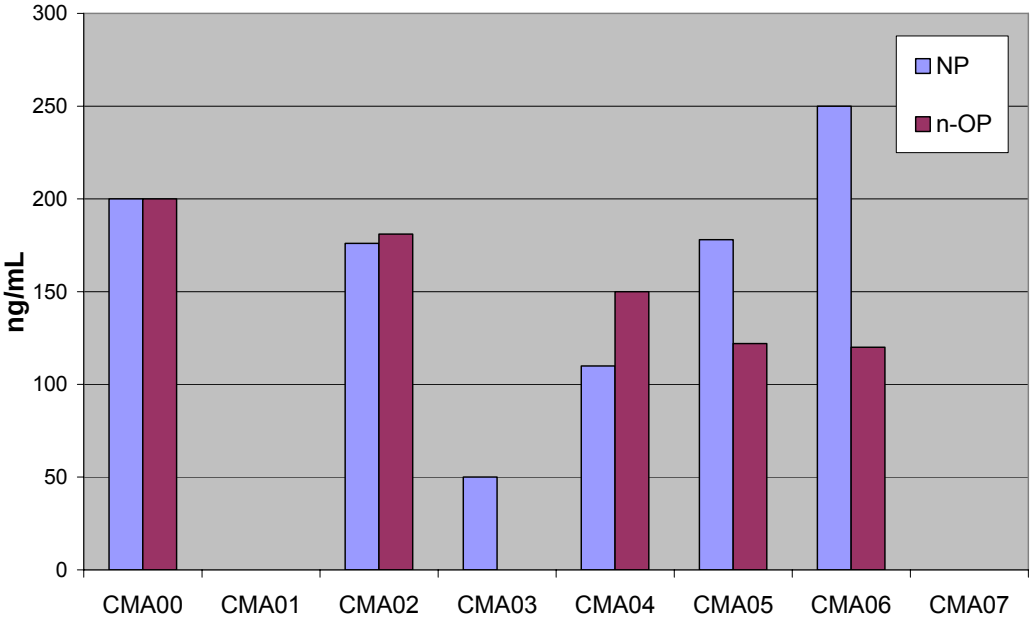


Figure 15: NP/n-OP in the standard S3

The standard solution contained 200 ng/mL NP and 4n-OP, respectively; the NP concentration in the river water extract was approx. 600 ng/mL (Table 29), which corresponds to 600 ng/L in the river water (River Seveso). In this river water extract, also some tert-OP was found by 5 labs (Figure 16).

For the river water extract the matrix effect was studied by LC-MS-MS with the standard addition method; no ion suppression was measurable for NP in this extract (by the JRC).

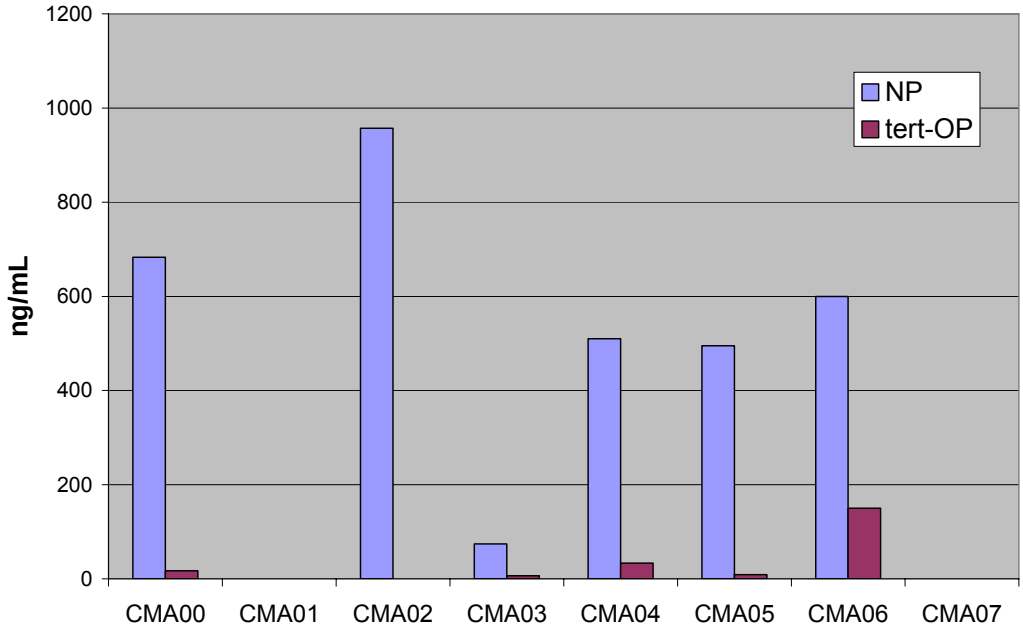


Figure 16: NP/tert-OP in the river water extract E2

Comparing the river water extract NP results of the different labs, it appears that Lab CMA02 has reported the highest concentration level (Figure 16); this might be explained by the fact that they used GC-MS detection principle without derivatisation. The ion m/z 149 monitored by this lab for the quantification of NP is not very specific (also characteristic for phthalates) and could lead to false positive findings in matrix-rich samples such as this river water extract.

The ISO method for "selected alkylphenols in water samples" from the year 2005 uses GC-MS determination (after LLE with toluene), and detection of NP without derivatisation using the ions m/z 135 and 107 (ISO, 2005). A round robin test organized by ISO with this method was not very successful (unpublished results), because the use of such low masses for quantification can lead to problems with matrix interferences. Therefore, ISO is currently developing a new method for alkylphenols using GC-MS after derivatisation (ISO/CP).

7.2.3 River Po water

The analysis of NP/OP in the River Po was difficult due to the very low concentration levels. Three labs reported a positive result for NP, 70 ng/L (CMA00), 110 ng/L (CMA02), and 80 ng/L (CMA06), respectively. Three other labs reported NP levels below the LOQ (10, 10, and 22 ng/L). One lab (CMA04) reported a NP concentration level of 5.1 ng/L in the River Po water sample. This lab was using "centrifuge large water SPM sampling", it was analyzing only the SPM and not the dissolved water phase (Table 28 and Figure 17).

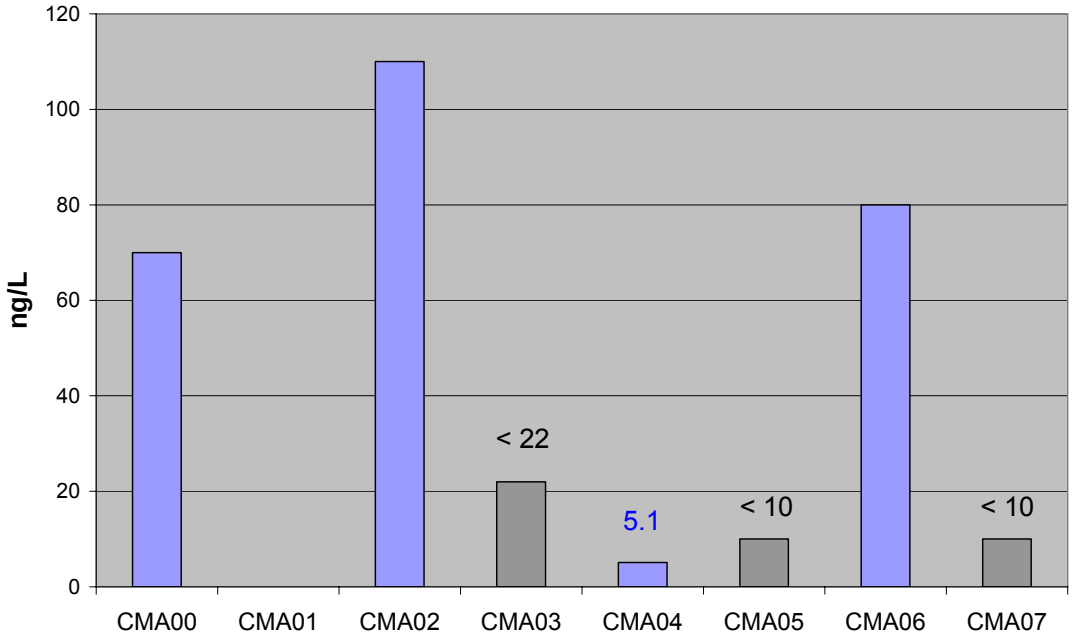


Figure 17: Nonylphenol in Po River. Grey bars are the blank value determined LOQs of the labs.

These results suggest that the three labs with the positive NP result have measured a NP blank laboratory contamination. At first glance, it appears that the NP result of Lab CMA04 (5.1 ng/L) is the most exact one (the use of a bigger amount of SPM material results in lower blank levels). However, a NP SPM concentration of 5 ng/L would imply a dissolved water concentration of ~ 40 ng/L, since it is known that most NP (~ 80 %) is present in the dissolved water phase (Isobe et al., 2001; Li et al., 2004; Xie et al., 2006a; Patrolecco et al., 2006). From this it can be concluded that also CMA04 most

likely had some problems with NP blank contamination during their SPM analysis. Apparently, not all labs were doing blank subtraction, which should be a standard routine (done by CMA03 and CMA05).

The results for the River Po analysis show that the analysis of NP in water samples at low concentrations (< 100 ng/L) is difficult due to laboratory blank problems. Apparently, the Labs CMA00, 02 and 06 reported a NP result which most likely comes from blank contamination. NP can be present in the laboratory air, the septa of the LC- or GC-vials, or the plastic SPE cartridges, which is unknown to most laboratories and was reported only recently in the literature (Xie et al., 2006b). In the JRC laboratory it was observed that a LC-MS vial with fresh MeOH left in the autosampler of the instrument can absorb in a time interval of some weeks NP from the lab air.

7.3 Conclusions for NP/OP

- During this interlaboratory study it was noted, that technical tert-OP is most relevant for environmental analysis
- All laboratories used different analytical methods, LC-MS-MS, GC-MS without derivatisation and GC-MS with derivatisation, and LC-fluorescence
- For the standard S3 and the river water extract (E2) good agreement was achieved for 5 laboratories
- Different well suited analytical methods are available for the analysis of NP/OP, LC-MS-MS, GC-MS with or without derivatisation, triple-quadrupole GC-MS-MS, and also LC with fluorescence detection
- SPE is well suited for the extraction of NP/OP from water; it can be performed with different cartridges and eluting solvents; also LLE is still used
- The internal standard used by most laboratories was 4n-NP (d8)
- The analysis of NP at concentrations < 100 ng/L is difficult due to blank laboratory contamination. Any plastic material such as plastic SPE cartridges should be avoided
- Big rivers such as the Po have low NP levels, but in smaller streams the EQS value might be exceeded (river water extract E2 ~ 600 ng/L)
- Laboratories are able to analyze NP at concentration levels ≥ 100 ng/L (one third of the EQS), but care should be taken to blank contamination in the labs. Environmental OP levels are generally much lower.

Table 28: NP/OP methods comparison

	CMA01	CMA02	CMA03	CMA04	CMA05	CMA06	CMA06	CMA07
Sample Volume [L]	0.4	0.2	0.5	4150	2.3	1.0	11.82	1.0
Filtration	no	yes	no	n.a.	no	yes	yes	no
Extraction	SPE	SPE	SPE	Centrifuge	LLE	SPE	Filtration	SPE
SPE cart. / solvent	HLB 200	HLB 60	C18	Soxhlet	DCM	C18	Randall extraction	Envichrom P
SPE elution	EA	DCM/EA	MeOH + MTBE	SPM[1]	n.a.	Acetone	SPM[2]	DCM
Analytical method	LC-MS (tq)	GC-MS	LC-MS (tq)	GC-MS (it)	GC-MS	LC-fluor	LC-fluor	GC-MS
LC solvents	H_2O-acet.	n.a.	H_2O-acet.	n.a.	n.a.	H_2O-MeOH	H_2O-MeOH	n.a.
Column	C18	DB-5	C18	ZB-5	DB-5	Phenylhexyl	Phenylhexyl	DB-1
Length	2.1 × 150 mm	30 m	2.1 × 100 mm	30 m	30 m	4.6 × 250 mm	4.6 × 250 mm	60 m
Derivatisation	n.a.	no	n.a.	MSTFA	no	no	no	no
Ions or wavelength monitored	219 > 133 227 > 112 205 > 106 205 > 133	149 (for NP) 135 (for OP) 121 107	219 > 133 219 > 106 225 > 112 205 > 133	207 > 179 221 > 179 235 > 179 278 > 179 292 > 179	135	230 nm exc. 302 nm em	230 nm exc. 302 nm em	135 107 57 220 77
Internal standard	4n-NP d8	4n-NP d8	4n-NP d6	4-Bromophenol	4n-NP d8	no	no	Atrazine d5

SPE: solid-phase extraction
HLB: Oasis HLB cartridge (Waters); 200 mg or 60 mg
EnvirchromP : Supelco
EA: Ethylacetate
SPM: suspended particle matter
it: ion trap
acet.: acetonitrile
MSTFA: methyl-N-(trimethylsilyl)trifluoroacetamide
2: Randall extraction with hot MeOH, silica clean-up

LLE: liquid-liquid extraction
MeOH: methanol
DCM: dichloromethane
MTBE : methyl-tert-butylether
tq: triple quadrupole
fluor: Fluorescence
n.a.: not applicable
1: freeze drying, extraction with acetone/hexane (2:1), silica clean-up

Table 29: NP/OP in the standard S3, the river water extract E2, and the Po River

NP/OP in standard S3	**CMA00**	**CMA01**	**CMA02**	**CMA03**	**CMA04**	**CMA05**	**CMA06**	**CMA07**
[ng/mL]								
NP	200		176	50	110	178	250	
n-OP	200		181		150	122	120	
NP/OP in extract E2								
[ng/mL]								
NP	683		957	74	510	495	600	
tert-OP	17			6.6	33	9	150	
n-OP			< 0.44		< 10			
NP/OP in River Po (whole water)								
[ng/L]								
NP	70		110	< 22	5.1*	< 10	80*[1]	< 10
tert-OP	< 5				1.5*	< 5	< 50	
n-OP			< 1		< 0.5*			

*SPM measurement

[1]: dissolved water concentration: < 50 ng L^{-1} (LOQ)

8 Conclusions

It was shown that even some of the most challenging WFD priority substances, selected on purpose for this exercise, can be measured at WFD relevant concentrations (0.3 x EQS) with methods currently applied in Member States. Obtained results were not within proposed data quality limits for most participants and therefore further development of methods and harmonisations of efforts is suggested.

Overall conclusions

- Environmental concentrations of PAH, PBDE and NP can be analysed in surface waters at concentrations taking into account the proposed EQS values and performance criteria.
- No standard methodologies for PAH and PBDE for these applications are available
- Very much differing sampling and analytical methodologies are currently in use within Member States
- Currently only few among the invited laboratories were able to deliver results at the required concentration levels
- No proficiency testing scheme or other external quality control possibility is available at present for these analyses
- In vicinity to the proposed EQS concentration levels high data quality is of importance for compliance checking
- Blank values in analytical procedures are of crucial importance, as analytical problems can lead also to an overestimation of pollutant content
- The partitioning of PBDE into the dissolved fraction, even of rather hydrophobic substances is significant, in particular in waters with a low SPM content
- Lowest limits of quantification have been reached by collecting SPM with a flow-through centrifuge
- Time integrating sampling methods would improve the reporting of annual average values

9 Outlook

Further joint on-site trials are being planned in the frame of the Chemical Monitoring Activity working group. It will be important that the exercises are reflecting the needs of Member States and help to harmonise approaches and their further development on European scale. While harmonisation of analytical methods is a key issue, also the further development of monitoring strategies is of importance.

The CMA On-site participants and organising team

10 Acknowledgements

We like to thank the Servizio Risorse Idriche e Tutela Ambientale della Provincia di Ferrara, the participants and supporters of the exercise: Silvano Bencivelli, Susanne Boutrup, Damia Barceló, Ronald de Boer, Ivanka Dimitrova, Licia Guzzella, Philipp Hohenblum, Peter Lepom, Paola Magri, Alícia Navarro Ortega, Lars Håkanson, Alain Hildebrandt, Wolfgang Moche, Olga Nitcheva, Stefano Polesello, Claudio Roscioli, Harald Schmid, Franz Leiendecker, Ole Sortkjaer, Joan Staeb, Thomas Ternes, Sara Valsecchi, Graziella Leroy and Madeleine Rizzi.

11 References

Abad E., Saulo J., Caixach, J. and Riviera, J., Evaluation of a new automated clean-up system for the analysis of polychlorinated dibenzo-p-dioxins and dibenzofurans in environmental samples. J.Chromatography A 893, 383-391

European Commission, Circa homepage, 2007, http://circa.europa.eu/Public/irc/env/wfd/-home

European Commission, COMMON IMPLEMENTATION STRATEGY FOR THE WATER FRAMEWORK DIRECTIVE (2000/60/EC), Guidance Document No. 7, Monitoring under the Water Framework Directive, Luxembourg: Office for Official Publications of the European Communities, 2003, ISBN 92-894-5127-0, ISSN 1725-1087

European Commission, COMMON IMPLEMENTATION STRATEGY FOR THE WATER FRAMEWORK DIRECTIVE (2000/60/EC), Guidance Document No. 15, Guidance on Groundwater Monitoring, Luxembourg: Office for Official Publications of the European Communities, 2007, ISBN 92-79-04558-X, ISSN 1725-1087

European Commission, Technical Guidance on Surface Water Chemical Monitoring- Interim Version 15.05.2007
(http://circa.europa.eu/Public/irc/env/wfd/library?l=/framework_directive/chemical_monitoring&vm=detailed&sb=Title)

European Commission, 2000. Off. J. Europ. Commun., L 327, 22 Dec. 2000, DIRECTIVE 2000/60/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 23 October 2000 establishing a framework for Community action in the field of water policy.

European Commission, 2001, Off. J. Europ. Commun., L 327, 22 Dec. 2000, DECISION No. 2455/2001/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 20 November 2001 establishing the list of priority substances in the field of water policy and amending Directive 2000/60/EC.

European Commission, 2006, Off. J. European Union, L 372/19, DIRECTIVE 2006/118/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 12 December 2006 on the protection of groundwater against pollution and deterioration.

European Commission, 2006, Proposal for a DIRECTIVE OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL on environmental quality standards in the field of water policy and amending Directive 2000/60/EC, internet, URL: http://ec.europa.eu/environment/water/water-dangersub/surface_water.htm

ISO 18857-1, 2005, Water quality - Determination of selected alkylphenols - Part 1: Method for non-filtered samples using liquid extraction and gas chromatography with mass selective detection.

ISO/CD 18857-2, under development, Water quality - Determination of selected alkylphenols - Part 2: Determination of alkylphenols, alkylphenol ethoxylates and bisphenol A - Method for non-filtered samples using solid-phase extraction and gas chromatography with mass selective detection after derivation.

Isobe, T., Nishiyama, H., Nakashima, A., Takada, H., 2001, Distribution and Behavior of Nonylphenol, Octylphenol, and Nonylphenol Monoethoxylate in Tokyo Metropolitan Area: Their Association with Aquatic Particles and Sedimentary Distributions, Environ. Sci. Technol. 35, 1041-1049.

OSPAR Commission, 2003, (URL: http://www.ospar.org/documents/dbase/publications/-p00273_BD%20on%20octylphenol%20_2006%20version.pdf

Quasimeme homepage, http://www.quasimeme.org/

Li, Z., Li, D., Oh, J.-R., Je, J.-G., 2004, Seasonal and spatial distribution of nonylphenol in Shihwa Lake, Korea, Chemosphere 56, 611-618.

Loos, R., Hanke, G., Umlauf, G., Eisenreich, S.J., 2007, LC-MS-MS analysis and occurrence of octyl- and nonylphenol, their ethoxylates and their carboxylates in Belgian and Italian textile industry, waste water treatment plant effluents and surface waters, Chemosphere 66, 690-399.

Patrolecco, L., Capri, S., De Angelis, S., Pagnotta, R., Polesello, S., Valsecchi, S., 2006, Partition of nonylphenol and related compounds among different aquatic compartments in Tiber River (Central Italy), Water, Air, and Soil Pollution 172, 151-166.

Xie, Z., Lakaschus S., Ebinghaus, R., Caba, A., Ruck, W., 2006a, Atmospheric concentrations and air–sea exchanges of nonylphenol, tertiary octylphenol and nonylphenol monoethoxylate in the North Sea, Environ. Poll. 142, 170-180.

Xie, Z., Selzer, J., Ebinghaus, R., Caba, A., Ruck, W., 2006b, Development and validation of a method for the determination of trace alkylphenols and phthalates in the atmosphere, Anal Chim Acta 565: 198-207.

Annex I Analytical methods employed by participating laboratories

Participant code:	**CMA00**		
	Standard	**Extract**	**Po River Water**
Alkylphenol Method information			
Sample Volume [L]			400 mL
Sampling method			Direct bottle sampling
Bottle type			Schott Duran glass 1L
Bottle preparation			Heating at 450ºC
Sample transport			Cooled
Sample pretreatment			No filtration
Water Extraction technique			SPE
SPE cartridge			Oasis HLB 200 mg; elution with ethylacetate
LC/MS system	Waters Quattro Micro triple quad		
LC/MS-MS transitions used	219-133; 219 > 106; 205 > 106, 205 > 133		
Mobile phase	Water – acetonitrile		
LC column	RP C18 2.1 x 150 mm		
Ion suppression evaluated	No ion suppression quantified in River extract E2		
^{13}C/Deuterated Internal Standards	4n-Nonylphenol		
^{13}C/Deuterated Recovery Standards			
Measurement uncertainty			
Blank values			~ 50 ng/L

Participant code:	CMA01		
	Standard	**Extract**	**Po River Water**
PAH Method information			
Volume [L]	2	14.6	2.7
Sampling method			Simple manual
Bottle type	Glass tube		Glass bottle
Sample transport	Ambient temperature		
Water Extraction technique			LLE / Methylene chloride
Clean Up			Silica column
GC column	HP-5 / MS		
Length	30 m		
Film thickness	0.25 μm		
Temperature program	Yes		
GC/MS system	Low Res.		
Ionisation	EI		
^{13}C/Deuterated Internal Standards	5 / before extraction		
Method	GC/MS self validated Hewlett Packard method		

Participant code:	CMA02		
	Standard	**Extract**	**Po River Water**
PAH Method information			
Volume [L]	2	14.6	200 mL
Sampling method			Direct bottle sampling
Bottle type			Amber glass bottle
Bottle preparation			Acetone and methanol cleaning
Sample transport			Ambient temperature
Sample pretreatment			Filtration (nylon 0.45 µm)
Water Extraction technique			SPE (OASIS HLB 60 mg)
GC column	DB-5		
Length	30 m		
Film thickness	0.25µm		
GC/MS system	Thermo, GC-MS (low resolution)		
Ionisation	EI		
^{13}C/Deuterated Internal Standards	1	1	1
^{13}C/Deuterated Recovery Standards	5	5	5
Comments			Monitoring of 3 ions/compound
Alkylphenol Method information			
Sample Volume [L]	1	1	200 mL
Sampling method			Direct bottle sampling
Bottle type			Amber glass bottle
Bottle preparation			Acetone and methanol cleaning
Sample transport			Ambient temperature
Sample pretreatment			Filtration (nylon 0.45 µm)
Water Extraction technique			SPE (OASIS HLB 60mg)
SPE cartridge			Elution with DCM/EA
GC column	DB-5		
Length	30 m		
Film thickness	0.25µm		
Temperature program	60ºC (1min), 6 K/min -> 175ºC (4min), 3 K/min -> 235ºC, 8 K/min -> 300ºC (5min)		
GC/MS system	Thermo, GC-MS (low resolution)		
Ions monitored	3 ions/compound		
Ionisation	EI		
13C/Deuterated Internal Standards	1	1	1
13C/Deuterated Recovery Standards	1	1	1

Participant code:	CMA03		
	Standard	**Extract**	**Po River Water**
PAH Method information			
Volume [L]	2	14.6	1
Sampling method			Direct bottle sampling
Bottle type			Alu bottle
Bottle preparation			Solvent cleaning, pre-rinsing
Sample transport			Cooled
Water Extraction technique			LLE
GC column	DB-5MS		
Length	60 m		
Temperature program	0.25 µm		
GC/MS system	Agilent, Low Res. MSD		
Ionisation	EI		
^{13}C/Deuterated Internal Standards	1	1	1
^{13}C/Deuterated Recovery Standards			16
Method	EN ISO 17993		
PBDE Method information			
Sample Volume [L]	20	14.6	
Sampling method			Direct bottle sampling
Bottle type			Alu bottle
Bottle preparation			Solvent cleaning, pre-rinsing
Sample transport			Cooled
Sample pretreatment			Filtration GF-8
SPM Extraction technique			Soxhlet
Water Extraction technique			LLE
Clean Up		Mixed layer, alumina column, GPC	
GC column	DB-5, Rtx5MS		
Length	60 m, 15 m		
Film thickness	0.25µm		
Temperature program	60°C (5min), 10 K/min -> 190°C (4min), 5 K/min -> 350°C (18min) (tri-hepta BDE); 60°C (5min) -> 10 K/min -> 350°C (6min) (octa-deca BDE)		
GC/MS system	High Res MS		
Ionisation	EI		
^{13}C/Deuterated Internal Standards	12	12	12
^{13}C/Deuterated Recovery Standards	1	1	1
Blank values			substracted
Alkylphenol Method information			
Sample Volume [L]	1	1	0.5
Bottle type			Direct bottle sampling
Bottle preparation			Alu bottle
Sample transport			Solvent cleaning, pre-rinsing
Sample pretreatment			Cooled
Water Extraction technique			SPE
SPE cartridge			C18, MeOH + MTBE
LC/MS system	HP1100+ Micromass quattro		
LC/MS-MS transitions used	219 - 133, 219 -106,		
Mobile phase	225 - 112, 205 - 133		
Ion suppression evaluated	yes		
^{13}C/Deuterated Internal Standards	1	1	1
^{13}C/Deuterated Recovery Standards			1

Measurement uncertainty			18%
Blank values			5 ng/L

Participant code:	**CMA 04**		
	Standard	**Extract**	**Po River Water**
PAH Method information			
Volume [L]	2	14.6	
SPM Extraction technique			ASE
Clean Up			Cu; deactivated Al_20_3 with 10% H_2O
GC column	HP5 MS		
Length	30 m		
Film thickness	0.25µm		
Temperature program	60°C (3min), 10 K/min -> 280°C, 25 K/min -> 340°C (10min)		
GC/MS system	MSD		
Ionisation	EI		
^{13}C/Deuterated Internal Standards	2,3,6 deuterated		
PBDE Method information			
Sample Volume [L]	20	14.6	
Sampling method			Centrifuge
Bottle type			Polystyrene
Sample transport			Cooled/partly frozen
Sample pretreatment			Freeze drying, grinding with ball mill
SPM Extraction technique			ASE toluene
Clean Up		GPC $SiOH/H_2SO_4$	GPC $SiOH/H_2SO_4$
GC column	RTX CLP		
Length	30 m		
Film thickness	0.25µm		
GC/MS system	GC/MSD		
Ionisation	NCI		
^{13}C/Deuterated Internal Standards	F-BDE 28,100,160		
^{13}C/Deuterated Recovery Standards	BDE 181		
Others (F,Br-BDE,…….)	^{13}C BDE 209		
Method	ISO/FDIS 22032 modified		
Blank values			BDE47: 0.002 ng/L; BDE209: 0.005 ng/L
Comments			All results for these two congeners are blank corrected
Alkylphenol Method information			
Sample Volume [L]	1	1	
Sampling method			Centrifuge
Bottle type			Polystyrene
Sample transport			Cooled/partly frozen
Sample pretreatment			Freeze drying, grinding with ball mill
SPM Extraction technique			Soxhlet with acetone/hexane 2:1
Clean Up			Silicagel with 3% water
Derivatisation	MSTFA		
GC column	ZB-5 (Phenomenex)		
Length	30 m		
Film thickness	0,25µm		

Temperature program	40°C -> 160°C (20 K/min), -> 220°C (6 K/min), -> 320°C (20 K/min)
GC/MS system	Ion trap Saturn 2000 (Varian)
Ions monitored	MS-MS: 207->179, 221->179, 235->179, 278->179, 292->179
^{13}C/Deuterated Internal Standards	4-Bromophenol used as internal standard (MS-MS: 246->229)
^{13}C/Deuterated Recovery Standards	added before derivatisation

Participant code:	**CMA05**		
	Standard	**Extract**	**Po River Water**
PAH Method information			
Volume [L]	2	14.6	2.3
Bottle type			Glass bottle
Bottle preparation			Bottles were heated at 450°C for 4 hours, Teflon lined caps were solvent cleaned with pentane
SPM Extraction technique			Soxhlet 24 h with toluene
Water Extraction technique			LLE: Dichloromethane
GC column	DB5		
Length	30 m		
Film thickness	0.15 µm		
Temperature program	90°C (1min), 10 K/min -> 240°C (4min), 20 K/min -> 270°C (18.5min)		
GC/MS system	Finnigan, LR-MS		
Ionisation	EI		
^{13}C/Deuterated Internal Standards	5	5	5
^{13}C/Deuterated Recovery Standards			7
Method			
Blank values	no	no	Yes
Comments			Correction for recovery and blank (for SMP a filter-blank) subtracted before report
PBDE Method information			
The sample was processed in two ways: *1.) Filtration and extraction of filter. 2.) Liquid-liquid extraction of the water sample.*			
Sample Volume [L]	20	14.6	
Bottle type			Glass bottle
Bottle preparation			Bottles were heated at 450°C for 4 hours, Teflon lined caps were solvent cleaned with pentane
Sample pretreatment			1.) 0.45 µm
SPM Extraction technique			1.) Soxhlet, hexane:acetone (4:1)
Water Extraction technique			2.) Liquid-liquid extraction (toluene)
Clean Up			Multi-layer column: Sodium sulphate, silica, silica + sulphuric acid, aluminium oxide.
GC column	DB-5		
Length	60 m		
Film thickness	0.25 µm		
Temperature program	90°C (2min), 50 K/min -> 220°C, 5 K/min -> 315°C (35min)		
GC/MS system	HRGC-MS		
Ionisation	NCI		
Blank values			BDE-47 subtracted
Comments	Addition of BDE-71 as	Addition of BDE-71 as	Addition of BDE-77 as recovery standard and BDE-71 as

	quantification standard.	quantification standard. Some interference on IS.	quantification standard.

Participant code:	**CMA05**		
	Standard	**Extract**	**Po River Water**
Alkylphenol Method information			
Sample Volume [L]	1	1	2.3
Bottle type			Glass bottle
Bottle preparation			Bottles were heated at 450°C for 4 hours, Teflon lined caps were solvent cleaned with pentane
Water Extraction technique			LLE: Dichloromethane
GC column	DB5		
Length	30 m		
Film thickness	0,15 µm		
Temperature program	90°C (1min), 10 K/min -> 240°C (4min), 20 K/min -> 270°C (18.5min)		
GC/MS system	Finnigan, LR-MS		
Ionisation	EI		
^{13}C/Deuterated Internal Standards	1	1	1
^{13}C/Deuterated Recovery Standards			1
Blank values	no	no	Yes
Comments			Correction for recovery and blank subtracted before report

Participant code:	**CMA06**		
	Standard	**Extract**	**Po River Water**
PAH Method information			
Volume [L]	2	14.6	2.5-3.0
Sampling method			Bucket
Bottle type			Glass Bottle
Bottle preparation			Solvent cleaning and silanization with chlorosilanes
Water Extraction technique			SPE C18 (BakerBond Speedisk)
GC column	Varian VF-Xms		
Length	60m x 0.25 mm		
Film thickness	0.25µm		
Temperature program	Inj. Splitless, 2µL (285ºC); 60ºC (2 min), 40 K/min -> 230ºC (0.1 min), 3 k/min ->285ºC (30 min); He 1.3 mL/min; transfer line 280ºC		
GC/MS system:	Thermo Electron Focus/Trace DSQ Low resolution quadruple mass spectrometer		
Ionisation	EI, SIM mode		
^{13}C/Deuterated Internal Standards	Pyrene-d10 Indeno[1,2,3-cd]pyrene-d12		
^{13}C/Deuterated Recovery Standards			Acenaphthene-d10 Phenanthrene-d10 Naphthalene-d8 Chrysene-d12 Perylene-d12
Measurement uncertainty	see report	see report	see report
Blank values		see report	see report
PBDE Method information			
Sample Volume [L]	20	14.6	2.5-3.0
Sampling method			Bucket
Bottle type			Glass Bottle
Bottle preparation			Solvent cleaning and silanization with chlorosilanes
Water Extraction technique			SPE C18 (BakerBond Speedisk)
BDE-28, 47, 99, 100, 153, 154			
GC column	Rtx-5MS		
Length	60m x 0.25 mm		
Film thickness	0.25µm		
Temperature program	PTV 2µL; 60ºC (2 min), 40 K/min ->230ºC (0.1 min), 3 K/min -> 285ºC (30 min); He 1.3 mL/min; transfer line 280ºC		
GC/MS system	Thermo Electron Trace GC/PolarisQ Ion trap mass spectrometer		
Ionisation	EI in MS-MS mode		
^{13}C/Deuterated Internal Standards	[13C12]-3,3',4,4'-BDE, [13C12]-3,3'4,4',5-BDE		
Measurement uncertainty(if available)	see report	see report	see report
Blank values		see report	see report
BDE-209			
GC column:	Rtx-5MS		
Length	7m x 0.32mm		
Film thickness	0.25µm		
Temperature program	80ºC (1 min), 40 K/min -> 285ºC (12 min); He 2.5 mL/min		
GC/ECD system	Thermo Electron Trace GC/ECD 40 Electron Capture Detector		
Other Standards (F,Br-DE,…….)	BB-209 (as syringe standard)		
Measurement uncertainty(if available)	see report	see report	see report
Blank values		see report	see report

Participant code:	CMA06		
	Standard	**Extract**	**Po River Water**
Alkylphenol Method information			
Sample Volume for water [L]	1	1	1
Sample volume for SPM [L]			11.82
Sampling method			Plastic bucket
Bottle type			Brown glass bottles
Bottle preparation			Solvent cleaning (methanol or acetone)
Sample transport			Ambient temperature
Sample pretreatment			Filtration with GF/F glass filter; 0.7 micron nominal pore size
SPM Extraction technique			Randall extraction with hot methanol
Water Extraction technique			SPE
SPE cartridge			Strata C18-Unendcapped (Phenomenex) 6 mL, 500 mg; conditioning: 10 mL acetone, 10 mL methanol; 10 mL ultrapure water. Drying time: 30 min. Elution: 10 mL acetone reduced to 0.5 mL under nitrogen stream
Clean Up			For SPM: Silica column 9 g activated at 160°C
HPLC column	Luna Phenyl-Hexyl (Phenomenex) 5 micron, 4.6x250 mm		
Gradient	Solvent water:methanol: 1 mL/min. Gradient: from 40:60 to 20:80 in 35min, then to 100% methanol at 40min		
Detector	Fluorescence: ex 230 nm; em 302 nm		
Method	Internal (proposed IRSA-APAT method)		
Measurement uncertainty	10% as standard deviation of repeatability tests on a 10 µg/L water sample		
Blank values NP	0.05 mg/L		
Blank values t-OP	0.10 mg/L		

Participant code:	CMA07		
	Standard	**Extract**	**Po River Water**
PAH Method information			
Volume [L]	2	14.6	1
Sampling method			direct bottle sampling
Bottle type			glass bottle
Bottle preparation			none
Sample transport			cooled
Sample pretreatment			none
Water Extraction technique			SPE
Clean Up			none
GC column			DB-1
Length			60m
Film thickness			0.25
Temperature program			35-320 (7ºC/min)
GC/MS system			Agilent MSD5975 single quad
Ionisation			EI
^{13}C/Deuterated Internal Standards			1
PBDE Method information			
Sample Volume [L]	20	14.6	1
Sampling method			direct bottle sampling
Bottle type			glass bottle
Bottle preparation			none
Sample transport			cooled
Sample pretreatment			none
Water Extraction technique			LLE
Clean Up			AlOx
GC column			DB-5
Length			60m
Film thickness			0.25
GC/MS system			Agilent low res MS
Ionisation			NCI
^{13}C/Deuterated Internal Standards			1
Alkylphenol Method information			
Sample Volume [L]	1	1	1
Sampling method			direct bottle sampling
Bottle type			glass bottle
Bottle preparation			none
Sample transport			cooled
Sample pretreatment			none
Water Extraction technique			SPE
SPE cartridge			Supelco envichrom P
Clean Up			none
GC column			DB-1
Length			60 m
Film thickness			0.25
Temperature program			35-320 (7ºC/min)
GC/MS system			Agilent MSD5975
ions monitored			135; 107; 57; 220; 77
Ionisation			EI

^{13}C/Deuterated Internal Standards			1

Annex II Analytical methods employed by JRC

II.1 Filtration and liquid/liquid extraction of 20 L water

The sample (20 L) was pumped at ca 1.3L/min with a LIQUIPORT® KNF NF 1.100 FT.18 S PTFE-coated diaphragm pump (KNF FLODOS AG, Switzerland) through 8 mm i.d. Teflon tubing directly from the Po river at 50 cm depth over a 293 mm (diameter) GF/F (Whatman) glass fibre filter and the filtrate collected in a 20 L pre-cleaned (rinsed with water – acetone – hexane) Schott Duran borosilicate glass bottle (Duran Produktions GmbH & Co. KG, Mainz, Germany). The sampling was started in parallel to all participants and lasted ca 15 minutes (from 11.00 to 11.15). The GF/F filter was transferred for transport and storage in a 500mL Schott Duran borosilicate bottle and frozen until further processing whereas the 20L filtrate was transported back to the laboratory (arrived on 12.10.2006 to the lab) and processed the next day by liquid-liquid extraction (LLE) with hexane:

20L LLE of filtrate:

1. 200 mL n-hexane nanograde containing PAH labeled internal standard mix (20 ng of Anthracene, Fluoranthene, Benzo(a)pyrene, Benzo(b)fluoranthene, and Benzo(ghi)perylene in Toluene) as well as PBDE labeled internal standard mixture (1 ng of BDE28, 47, 100, and 99; 2 ng of BDE 154, 153, and 183; 5 ng of BDE 209 in Toluene) was added to the 20 L filtrate directly in the 20 L glass bottle
2. 20 min. manual agitation on a lab cart
3. Waiting for phase separation
4. addition of MilliQ water for decanting hexane phase from the 20L bottle
5. removal of ca 1 litre of water from the bottle (this part was discarded)
6. another 200mL hexane added
7. 20 min. manual agitation on a lab cart
8. waiting for phase separation
9. addition of MilliQ water for decanting hexane phase from the 20L bottle
10. hexane phases combined
11. Concentration of the extract to 0.5 ml under purified N_2 using a TURBOVAP workstation (Zymark)
12. Transfer of the extract into a 2 ml conic vial
13. PBDE labeled syringe standard added (1ng of BDE-126 and 5ng of BDE-206)
14. 20 ng of PAH labeled syringe standard added (Benzo(k)fluoranthene, Benzo(e)pyrene, Pyrene)
15. Final evaporation under a gentle stream of purified N_2 to 50 µl

GF/F Filters:

1. The frozen filters stored in the 500mL glass bottles were processed directly in these bottles
2. PAH labeled internal standard mix added (20 ng of Anthracene, Fluoranthene, Benzo(a)pyrene, Benzo(b)fluoranthene, and Benzo(ghi)perylene in Toluene). PBDE labeled internal standard mixture added (1 ng of BDE28, 47, 100, and 99; 2 ng of BDE 154, 153, and 183; 5 ng of BDE 209 in Toluene)
3. 25 g prepared (baked at 450 °C and kept at >110 °C till usage) sodium sulphate was added
4. Ca 250 mL Acetone-hexane (3/22 v/v) was added so that the filters were completely covered with solvent
5. 30 minutes ultrasonication at ca 40 °C

6. Decantation of solvent and filtration over prepared (baked at 450 °C and rinsed with extraction solvent prior to usage) glass wool
7. repetition of steps 4 and 6 twice
8. Solvent phases combined
9. Concentration of the extract to 0.5 ml under purified N_2 using a TURBOVAP workstation (Zymark)
10. Transfer of the extract into a 2 ml conic vial
11. 20 ng of PAH labeled syringe standard added (Benzo(k)fluoranthene, Benzo(e)pyrene, Pyrene)
12. Final evaporation under a gentle stream of purified N2 to 50 µl
13. instrumental analysis for PAH
14. The sample was submitted to clean-up for PBDE (see Clean-up Suspended Particulate Matter of samples 20 L, 45 L and Infiltrex: paragraph II.5)

II.2 Filtration and adsorptive extraction of 45 L water

The sample (45L) was pumped at ca 200mL/min with a LIQUIPORT KNF NF 1.100 FT.18 S PTFE-coated diaphragm pump (KNF FLODOS AG, Switzerland) through 8 mm i.d. Teflon tubing directly from the Po river over a 293 mm (diameter) GF/F glass fibre filter and the filtrate extracted online by two 50g XAD cartridges connected in series. The sampling was started after all participants had finished except the centrifugation and lasted ca 3.5 hours (from 11:45 till 15:05). The GF/F filter was transferred for transport and storage in a 500mL Schott Duran borosilicate bottle and frozen until further processing whereas the XAD cartridges were put in a fridge and was transported back to the laboratory (arrived on 12.10.2006 to the lab) and processed (27 February 2007) by pressurized liquid extraction (PLE) using a Dionex accelerated solvent extractor (ASE® 300, Dionex Cooperation, USA):

50g XAD ASE cartridges:

1. The two 100mL ASE cartridges containing each 50g XAD and the absorbed contaminants were extracted using the Dionex ASE®300 applying in a 1st extraction methanol (3 cycles each with a static time of 5 min at 75 °C , heat-up time of 5 min, a flush volume of 100%, a purging time of 60s and a pressure of 1500 psi) and in a 2nd extraction hexane (same parameters as for methanol), respectively
2. PAH labeled internal standard mix (20 ng of Anthracene, Fluoranthene, Benzo(a)pyrene, Benzo(b)fluoranthene, and Benzo(ghi)perylene in Toluene) as well as PBDE labeled internal standard mixture (1 ng of BDE28, 47, 100, and 99; 2 ng of BDE 154, 153, and 183; 5 ng of BDE 209 in Toluene) were added to the hexane phase of the ASE
3. The methanol and hexane phases were combined in a separatory funnel and ca 60-80mL (ca 1/3 of the volume of the methanol phase) MilliQ water added for improved phase separation
4. After phase separation the methanol phase was collected in the ASE bottles and the hexane phase transferred into Zymark vials for concentration
5. The methanol phase was extracted three more times with ca 20 mL hexane and the hexane phases combined with the first extract
6. Concentration of the extract to 0.5 ml under purified N_2 using a TURBOVAP® workstation (Zymark)
7. Transfer of the extract into a 2 ml conic vial
8. PBDE labeled syringe standard added (1ng of BDE-126 and 5ng of BDE-206)
9. 20 ng of PAH labeled syringe standard added (Benzo(k)fluoranthene, Benzo(e)pyrene, Pyrene)
10. Final evaporation under a gentle stream of purified N_2 to 50 µl

Planar GF/F Filters: See above procedure for 20L sample

II.3 Filtration of 11 L water on glasfiber filter

The sample (11L) was pumped at ca 0.8-1.L/min with a LIQUIPORT® KNF NF 1.100 FT.18 S PTFE-coated diaphragm pump (KNF FLODOS AG, Switzerland) through 8 mm i.d. Teflon tubing directly from the Po river over a 142 mm (diameter) GF/F glass fibre filter and the filtrate collected in 1L pre-cleaned (Schott Duran® borosilicate bottles for dissolved nonylphenols and octylphenol analyses. The sampling was started in parallel to all participants and lasted ca 15 minutes (from 11:00 until 11:15). The GF/F filter was transferred for transport and storage in a 500mL Schott Duran® borosilicate bottle and frozen until further processing.

Planar GF/F Filters: See above procedure for 20L sample

II.4 Filtration and adsorptive extraction of 226 L water

The large volume continuous filtration and extraction of 226 L of river water was performed with a Infiltrex™ 300 system (Axys Technologies Inc., Canada). Flowrate was ca. 1 L/min. The system consists of two filterholders for cylindrical glass fiber filter cartridges and two 250 g XAD filled stainless steel cartridges.

In order to avoid contamination particularly with PBDEs the filters and adsorbents were Soxhlet extracted without any attempt to dry them before. After using MeOH for removal of water the extraction was continued with adding n-Hexane to the reservoir for further extraction. After the Soxhlet extraction was finished, partitioning of the analytes in the hexane fraction was forced by adding water to the batch. Only the Hexane fraction was processed for further analysis.

Filters:

1. PAH labeled internal standard mix added (10 ng of Anthracene, Fluoranthene, Benzo(a)pyrene, Benzo(b)fluoranthene, and Benzo(ghi)perylene in Toluene). PBDE labeled internal standard mixture added (1 ng of BDE28, 47, 100, and 99; 2 ng of BDE 154, 153, and 183; 5 ng of BDE 209 in Toluene)
2. 24 h Soxhlet extraction in 800 ml MeOH pesticide grade for the removal of water
3. Addition of 500 ml n-Hexane
4. 48 h Soxhlet
5. Addition of 500 ml of Millipore water and separation of the hexane fraction
6. Partial concentration of the extract to ca. 30 ml under purified N_2 using a TURBOVAP workstation (Zymark)
7. Removal of the visible water fraction using a pipette
8. Final concentration of the extract to ca 0.5 ml under purified N_2 using a TURBOVAP workstation (Zymark)
9. Removal of the residual water traces by filtration through a glass column with pre-cleaned Na_2SO_4
10. Filter extract was submitted to Clean up FMS (see below "Clean-up of Suspended Particulate Matter")
11. Transfer of the extract into a 2 ml conic vial and further evaporation under a gentle stream of purified N_2 to 30 µl
12. 20 ng of PAH labeled syringe standard added (Benzo(k)flouranthene, Benzo(e)pyrene, Pyrene)
13. PBDE labeled syringe standard added (1ng of BDE-126 and 5ng of BDE-206).

XAD: As above except that no clean up procedure was applied

II.5 Clean-up of Suspended Particulate Matter

The extracts coming from different sampling methods, containing a lot of particulate matter were submitted to treatment with. H_2SO_4 concentrate and successively the clean-up was executed with an automated clean-up system (Power-Prep P6, Fluid Management Systems (FMS) Inc., Watertown, MA, USA). This system was previously described (Abad et al., 2000) and uses a multi-layer silica column, basic alumina and carbon column combination. Two fractions were collected, one containing PCBs and PBDEs and one for PCDD/Fs. Before analysis a syringe standard was added to recognize the procedure recovery (13C-labelled internal standards BDE-126 and BDE-206).

Extraction and clean-up analytical blanks were carried out to check the background level of PBDE.

II.6 Liquid/liquid extraction of 2 L water

Samples were collected in 2.5 L brown glass bottles pre-cleaned with n-Hexane nanograde and arrived in the laboratory on 12.10.2006.

1. 100 ml n-Hexane nanograde added into the sampling bottle
2. PAH labelled internal standard mix added (10 ng of Anthracene, Fluoranthene, Benzo(a)pyrene, Benzo(b)fluoranthene, and Benzo(ghi)perylene in Toluene)
3. PBDE labelled internal standard mixture added (1 ng of BDE28, 47, 100, and 99; 2 ng of BDE 154, 153, and 183; 5 ng of BDE 209 in Toluene)
4. 2 min. manual agitation
5. 24 h horizontal shaking at 100/min
6. Separation of the Hexane phase using a pipette
7. Repetition of steps 4 – 6 with 100 ml n-Hexane
8. 100 ml Ch_2Cl_2 nanograde added
9. 15 min of ultrasonic treatment
10. Separation of the Ch_2Cl_2 phase using a pipette
11. Ch_2Cl_2 and Hexane phases combined
12. Drying of the extract using a glass column with pre-cleaned Na_2SO_4
13. Concentration of the extract to 0.5 ml under purified N_2 using a TURBOVAP workstation (Zymark)
14. Transfer of the extract into a 2 ml conic vial and further evaporation under a gentle stream of purified N_2 to 30 µl
15. PBDE labelled syringe standard added (1ng of BDE-126 and 5ng of BDE-206)
16. 20 ng of PAH labelled syringe standard added (Benzo(k)fluoranthene, Benzo(e)pyrene, Pyrene)

II.7 Filtration and disk-SPE of 2 L water

The sample was collected during the CMA on-site exercise in a 2.5 L brown glass bottle pre-cleaned with n-hexane.

The objective of this method was to use low water volume (about 2 L) for the analysis, as 2 L liquid/liquid extraction, with the difference to get the dissolved and SPM phase differentiated.

The approach chosen was a solid phase extraction using the C-18 Empore disk with a pre-filtration < 0.7µm on glass fiber filter GF/F (Whatman). The apparatus, the C-18 Empore disk and the filter were pre-cleaned with 40 ml of toluene, rinsed with 20 ml of methanol and eluted with 40 ml of toluene to obtain the blank.

The apparatus was rinsed again with 20 ml of methanol to eliminate the toluene and other 20 ml of methanol to activate the C-18 phase. Subsequently 2.43 L of water sample was loaded on the apparatus and filtrated/extracted. Before extraction both filter and C-18 were spiked with labelled PBDE and PAH (1 ng of BDE28, 47, 100, and 99; 2 ng of BDE 154, 153, and 183; 5 ng of BDE

209 and 10 ng of Anthracene, Fluoranthene, Benzo(a)pyrene, Benzo(b)fluoranthene, and Benzo(ghi)perylene in Toluene)
Afterwards the filter was extracted twice in an ultrasonic bath for 30min with a mixture of n-hexane/acetone (220/30). The C-18 was eluted twice with 20ml of toluene.
Both fraction were concentrated to 100µl and spiked with syringe labeled syringe standard (1ng of BDE-126 and 5ng of BDE-206 for PBDE and 20 ng of Benzo(k)fluoranthene, Benzo(e)pyrene and Pyrene for PAH).
The fractions were submitted to analysis with HRGC-HRMS.

II.8 Instrumental GC/MS analyses

II.8.1 HRGC-LRMS of PAH:

Instrumental analysis of PAHs was carried out using a HP 6890 high resolution gas chromatograph equipped with a HP MSD 5973 mass selective detector (all Agilent, Waldbronn, Germany) and a Gerstel CIS 4 PTV injection system (Gerstel GmbH, Germany) utilising helium as carrier gas (1.3 ml/min). The GC separation was performed on a SGE HT8 capillary column (SGE Italy Srl:, 25 m length, 0.32 mm I.D., film thickness 0.25 µm). Electron impact (EI) ionisation was used with an ionisation potential of 70 eV. The transfer line to the MSD was operated at 320 °C.
The GC oven temperature program was held at 110 °C for 1 min and ramped from 110 °C to 320 °C at 10 °C /min and was held at 320 °C for 5 min. The total run time of the GC oven was 32 min. The Gerstel Cooled Injection System (CIS4) was operated as follows: initial temperature, 100 °C ; initial time, 0.05 min; rate, 12 °C /min; final temperature, 340 °C held for 5 min; cryo cooling was applied; equilibration time, 0.05 min. The sample volume injected was 1 µl in pulsed splitless mode.
The mass spectrometer operated in Selecting Ion Monitoring. For both native and labelled PAH isomers the molecular ion was reordered. Quantification was done by isotope dilution method.

II.8.2 HRGC-HRMS of PBDEs

Instrumental analysis of PBDEs was based on isotope dilution using HRGC-HRMS (high resolution gas chromatography – high resolution mass spectrometry) for quantification on the basis of EPA1614 method, The GC (Ultra Trace, Thermo, Germany), was coupled with a DFS mass spectrometer (Thermo, Germany) operating in the EI-mode at 45 eV with a resolution of >10000. For tri- to hepta-brominated congeners two ions of the isotopic molecular cluster were recorded for both native and labelled congeners. For the deca-brominated congener two isotopic ions of the cluster M+-2Br were recorded for both native and labeled congeners. The quantified isomers were identified through comparison of retention times of the corresponding internal standard and the isotopic ratio of the two ions recorded.
The samples were analyzed on a Sol-Gel-1ms, 15 m with 0.25 mm i.d. and 0.1 µm film GC column (SGE, Victoria, Australia). The following gas-chromatographic conditions were applied: PTV injector from 130 to 300 °C at 14.5 °C s-1, constant flow at 1.0 ml min-1 of He, GC-MS interface at 300 °C and a GC program rate: 110 °C with a 1 min. hold, then 20 °C min-1 to 300 °C and a final hold at 300 °C for 6 min.

II.9 Quality assurance/Quality control

The quality assurance/quality control, of the routinely applied analytical methodologies, is checked by successful participation in different intercalibration exercises.

PAH: POPs in environmental matrix, 12. cycle, 2007, organised by UNICHIM , Milan, Italy

PBDE: Quality Assurance of Information for Marine Environmental Monitoring in Europe – QUASIMEME (Wageningen UR, The Netherlands)
- Exercise 719 -R45 Brominated Flame Retardant DE8: Apr-Jul 2006
- Exercise 748 -R48 Brominated Flame Retardant BS1: Jan-Apr 2007

PBDE: 12th International Intercalibration Study organised by Prof. Bert van Bavel (Intercal AB, Dyltbryk, Sweden)

Annex III CMA on-site Invitation Document

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

Servizio Risorse Idriche e
Tutela Ambientale
Provincia di Ferrara

Ispra, 1st September 2006

The Joint Research Centre (JRC) together with the Servizio Risorse Idriche e Tutela Ambientale, Provincia di Ferrara is pleased to invite you to the

Technical On-Site Workshop on Chemical Monitoring for the Water Framework Directive to be held on 10-11 October 2006 in Ferrara, Italy

The technical issues concerning analysis and monitoring of chemical pollutants within the Water Framework Directive have been discussed intensively in European expert groups during the last years. This consultation process should ensure harmonised monitoring of water bodies in Europe. In this context the JRC IES is organising an exercise that should help in developing guidance for monitoring, based on existing scientific know-how and technical competence in Member States.

As the selection of approaches for the monitoring of organic hydrophobic pollutants in water was an important issue in these discussions, specific compounds from the WFD priority substance list have been selected for this practical exercise in which individual European laboratories apply their approach in monitoring of PBDEs, Nonylphenols, Octyphenol and PAHs.

The Workshop will start on Tuesday 10 October 2006 in the *Castello Estense di Ferrara* with presentations and discussions. In the morning of Wednesday 11 October 2006 the sampling exercise will take place at a selected site on the river Po.

The JRC will reimburse travel and accommodation costs according to Commission regulations for up to two experts per participating laboratory.

Please confirm your interest and send contact details of the participating persons by 14. September 2006 to georg.hanke@jrc.it.

Paola Magri
Servizio Risorse Idriche e Tutela Ambientale
Provincia di Ferrara

Giovanni Bidoglio
RWER Head of Unit
JRC IES

Joint Research Centre · I-21020 Ispra (VA), Italy · TP 460
Telephone: direct line +39 - 0332 78 93 63, secretariat +39 – 0332 78 99 57 · Telefax: +39 – 0332 78 56 01
E-mail internet: giovanni.bidoglio.@jrc.it

Annex IV CMA on-site Technical Annex

Technical On-Site Workshop on Chemical Monitoring for the Water Framework Directive jointly organised by JRC IES and the Servizio di Risorse Idriche e Tutela Ambientale of the Provincia di Ferrara

Background

The Water Framework Directive WFD shall provide regulation also for the contamination of European water bodies through chemical pollutants. This is done via the Priority Substance list and establishing of Environmental Quality Standards on European level. As a unique effort to assess the chemical quality of the aquatic environment in order to identify risks, priority issues and needs for action, the Member States will set-up monitoring programs that cover a wide range of possible contaminants in a spatial coverage that includes whole Europe.

Technical discussions about chemical monitoring have been held in the *Analysis and Monitoring of Priority Substances* AMPS working group and the *Chemical Monitoring Activity* CMA in order to arrive at a common view on the necessary monitoring for the WFD.

Member States are currently preparing the monitoring programs. Therefore it is important to harmonise the approaches and guarantee comparable results, starting from the setting up of the monitoring networks, via the sampling and sample preparation to the chemical analysis.

As with other European directives a close communication between the European Commission and the Member States as well as among Member States will be crucial for the successful preparation and implementation of the Directive. This process should therefore be accompanied by a series of practical exercises that provide results in order to help adjusting monitoring strategies in a harmonised way.

The technical on-site CMA workshop is aiming at comparison of different approaches in monitoring from the sampling of single samples to the acquisition of analytical results for single samples. The compound groups for this exercise have been selected as their monitoring results are expected to be possibly influenced by the sampling methodology that is applied.

The strategy of the on-site workshop comprises 3 different steps:

- Distribution of analytical standard solutions to estimate contribution of instrumental analysis to total variations
- Distribution of homogenised sample extracts in order to estimate contribution of sample preparation and matrix effects to total variations.
- Simultaneous sampling of a real river water sample

Please note that the scope is a joint scientific event that should help to compare different approaches in view of the obtained results. While we would limit this first exercise to a rather simple design, just aiming at a first comparison of approaches, such activities can accompany the WFD EQS implementation throughout the next years and provide a practical platform on European level for knowledge exchange concerning sampling approaches, alternative measurement techniques, emerging contaminants, etc..

WFD PS Target Substances selected for the CMA exercise
(Compound description from WFD PS proposal and CMA guidance draft version 2.0)

Nonylphenol

Nonylphenol	All 4-nonylphenol isomers	Total concentration of all isomers to be reported. Technical nonylphenol consists mainly (~ 90 %) of para substituted 4-nonylphenol and comprises theoretically 211 chain isomers; only 4-nonylphenol is of toxicological relevance

Octylphenol

Octylphenol	4-octylphenol	Octylphenol is a single isomeric compound: 4-(1,1',3,3'-tetramethyl-butyl)-phenol (4-tert-octylphenol)

PBDE

Pentabromodiphenyl Ether	BDE congener numbers 28, 47, 99, 100, 153, 154	These congeners constitute approximately 85% of technical Penta – BDE formulations; Concentrations of individual isomers and arithmetic sum of all components to be reported.

PAH

PAH	Anthracene Fluoranthene Benzo(a)pyrene Benzo(g,h,i)perylene Indeno(1,2,3-cd)pyrene Benzo[b]fluoranthene / Benzo[k]fluoranthene	Benzo[j]fluoranthene interferes with the determination of either Benzo [b]fluoranthene or Benzo[k]fluoranthene. Total concentration to be reported.

Proposed EQS values of WFD PS Target Substances selected for the CMA exercise

(Values from the Proposal for a DIRECTIVE OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL on environmental quality standards in the field of water policy and amending Directive 2000/60/EC; COM(2006)398; SEC(2006)947; **ANNEX I : ENVIRONMENTAL QUALITY STANDARDS FOR PRIORITY SUBSTANCES AND CERTAIN OTHER POLLUTANTS)**

AA: annual average;
MAC: maximum allowable concentration.
Unit: [µg/l].

(1)	(2)	(3)	(4)	(5)	(6)	(7)
N°	**Name of substance**	**CAS number**	**AA-EQS Inland surface waters**	**AA-EQS Other surface waters**	**MAC- EQS Inland surface waters**	**MAC-EQS Other surface waters**
(2)	Anthracene	120-12-7	0.1	0.1	0.4	0.4
(5)	Pentabromodiphenylether	32534-81-9	0.0005	0.0002	*not applicable*	*not applicable*
(15)	Fluoranthene	206-44-0	0.1	0.1	1	1
(24)	Nonylphenol	25154-52-3	0.3	0.3	2.0	2.0
(25)	Octylphenol	1806-26-4	0.1	0.01	*not applicable*	*not applicable*
(28)	Polyaromatic hydrocarbons (PAH)	*not applicable*	*not applicable*	*not applicable*	*not applicable*	*not applicable*
	Benzo(a)pyrene	50-32-8	0.05	0.05	0.1	0.1
	Benzo(b)fluoranthene	205-99-2	Σ=0.03	Σ=0.03	*not applicable*	*not applicable*
	Benzo(k)fluoranthene	207-08-9				
	Benzo(g,h,i)perylene	191-24-2	Σ=0.002	Σ=0.002	*not applicable*	*not applicable*
	Indeno(1,2,3-cd)pyrene	193-39-5				

Sampling location

The water samples will be taken simultaneously (as far as technically possible) from the river Po in the vicinity of Ferrara in northern Italy. Data of pH, temperature, conductivity and SPM content will be provided by JRC IES in order to monitor homogeneity of the water body. In addition JRC will take water samples for analysis of the target compounds in order to control homogeneity during the whole sampling period.

IMPORTANT: Please indicate to us the principle of your sampling technique and the approximate time you will need for sampling!

Samples
Concentrations will be at levels relevant for WFD proposed surface water limit values. Pre-campaigns have established values in the river Po, but hydrological and pollutant situation can lead to significant changes which cannot be foreseen.

- **Standard solution**
  Ampoules with standards solution for each compound group (NP/OP, PBDE, PAH) will be distributed to the participating teams.
- **Homogenised sample extract**
  A large volume water sample will be taken from river Po prior to the workshop. The sample will be extracted at JRC IES, the extract homogenised, divided into ampoules and distributed to the participating teams.
- **Water sample**
  Every participating team will take water samples according to their protocols for the analysis of the 3 compound groups. The methodologies can comprise all different sorts of applied techniques.

It is planned to prepare the NP/OP standards and extracts in Methanol, while the PBDE and PAH standards/extracts would be prepared in n-Hexane.

Sampling Equipment
Please bring the necessary equipment for your sampling. In case you need a clean working environment we will have a laboratory truck available on-site, which is equipped with fume hoods and 230 V current.
Please let us know if you have any specific technical on-site requirements!

Sample transport
For the teams travelling by airplane we would kindly ask you to verify the possibility to transport the samples as hand luggage or as checked luggage. To our current information there should be no problem in doing so. In case you encounter difficulties, please contact us so we can look for alternative solutions.
Please indicate in any case to us the number and volume of samples you intend to take!

For further technical information please contact georg.hanke@jrc.it (0039-0332-785586)

Annex V CMA on-site reporting sheet templates

Templates for the reporting of methods and results

PBDE Method information

Participant code:	

	Standard	Extract	Po River Water	
Sample Volume [L]	20	14.6		
Sampling method				pumping, bucket, direct bottle sampling,..
Bottle type				Glass Bottle, Solvent bottle, …
Bottle preparation				Solvent cleaning, pre-rinsing, …
Sample transport				Ambient temperature, cooled
Sample pretreatment				(Filtration,….)*
SPM Extraction technique:				(soxhlet, SFE, ASE,…)**
Water Extraction technique:				(LLE, SPE,…)*
Clean Up:				Silica column, Acid treatment,….
GC column:				DB-5, SP2330,…
Length				15m, 30m, 60m, …
Film thickness				
Temperature program				0.1μm, 0.25μm….
GC/MS system:				Supplier, High Res/Low Res/MS-MS
Ionisation				EI, NCI,….
^{13}C/Deuterated Internal Standards				Number used 1-8, when added
^{13}C/Deuterated Recovery Standards				Number used 1-8, when added
Others (F,Br-BDE,…….)				
Method:				ISO, CEN,EPA ...
Measurement uncertainty(if available)				Please specify methodology
Blank values				
Comments:				

(*): Specified filter type and cut-off size
(**): Specified adsorbent and/or solvent used

PBDE Report

Participant code:	

	Standard S1	Extract E1	Po dissolved conc.***	Po SPM conc.***	Po whole water conc.	LOQ**
	(ng/ml)	(ng/ml)	(ng/l)	(ng/l)	(ng/l)	(ng/l)
Date Received:						
Volume Analysed:						
Date Analysed:						
BDE-28*						
BDE-47*						
BDE-99*						
BDE-100*						
BDE-153*						
BDE-154*						
BDE-183						
BDE-209						
Total PentaBDE according to WFD: BDE congener numbers 28, 47, 99, 100, 153, 154						

(*): compulsory
(**): LOQ for the method applied for water analysis.
(***): Fill the corresponding column if fractions have been analysed spearately

PAH Method information

Participant code:	

	Standard S2	Extract E1	Po River Water	
Volume [L]	2	14.6		
Sampling method				pumping, bucket, direct bottle sampling,..
Bottle type				Glass Bottle, Solvent bottle, ...
Bottle preparation				Solvent cleaning, pre-rinsing, ...
Sample transport				Ambient temperature, cooled
Sample pretreatment				(Filtration,....)*
SPM Extraction technique:				(soxhlet, SFE, ASE,...)**
Water Extraction technique:				(LLE, SPE,...)*
Clean Up:				Silica column, Acid treatment,....
GC column: Length Film thickness Temperature program				(DB-5, SP2330,...) (15m, 30m, 60m, ...) (0.1μm, 0.25μm....)
GC/MS system:				(Supplier, High Res/Low Res/MS-MS)
Ionisation				(EI, NICI,....)
^{13}C/Deuterated Internal Standards ^{13}C/Deuterated Recovery Standards				(Number used 1-7), when added (Number used 1-7), when added
Method: Measurement uncertainty(if available)				(ISO, CEN, EPA ...) Please specify methodology
Blank values				
Comments:				

(*): Specified filter type and cut size
(**): Specified adsorbent and/or solvent used

PAH Report

Participant code:	

	Solution S2	Extract E1	Po dissolved conc.***	Po SPM conc.***	Po whole water conc.	LOQ**
	(ng/ml)	(ng/ml)	(ng/l)	(ng/l)	(ng/l)	(ng/l)
Date Received:						
Volume Analysed:						
Date Analysed:						
Anthracene						
Fluoranthene						
Benzo(a)pyrene						
Benzo(b)fluoranthene						
Benzo(k)fluoranthene						
Benzo(b+j+k)fluoranthene*						
Benzo(g,h,i)perylene						
Indeno(1,2,3-cd)pyrene						

(*): If your chromatographic method does not perform the separation of the Benzo-fluoranthene isomers report the sum of them
(**): LOQ for the method applied for water analysis.
(***): Fill the corresponding column if fractions have been analysed spearately

Alkylphenol Method information

Participant code:	

	Standard	Extract	Po River Water	
Sample Volume [L]	1	1		
Sampling method				pumping, bucket, direct bottle sampling,..
Bottle type				Glass Bottle, Solvent bottle, …
Bottle preparation				Solvent cleaning, pre-rinsing, …
Sample transport				Ambient temperature, cooled
Sample pretreatment				(Filtration,….)*
SPM Extraction technique:				(soxhlet, SFE, ASE,…)**
Water Extraction technique:				(LLE, SPE,…)*
SPE cartridge				SPE conditions, solvents, …
Clean Up:				Silica column, Acid treatment,….
SPE cartridge				
Derivatisation				
GC column:				DB-5, SP2330,…
Length				15m, 30m, 60m, …
Film thickness				
Temperature program				0.1μm, 0.25μm….
GC/MS system:				Supplier, High Res/Low Res/MS-MS
LC/MS system				Supplier, Type
ions monitored				
LC/MS-MS transitions used				
mobile phase				
Ionisation				EI, NCI, APCI
ion suppression evaluated				
^{13}C/Deuterated Internal Standards				Number used, when added
^{13}C/Deuterated Recovery Standards				Number used, when added
Method:				ISO, CEN, EPA ...
Measurement uncertainty(if available)				Please specify methodology
Blank values				
Comments:				

(*): Specified filter type and cut-off size
(**): Specified adsorbent and/or solvent used

Alkylphenol Report

Participant code:	

	Standard S3	Extract E2	Po dissolved conc.**	Po SPM conc.**	Po whole water conc.	LOQ*
	(ng/ml)	(ng/ml)	(ng/l)	(ng/l)	(ng/l)	(ng/l)
Date Received:						
Volume Analysed:						
Date Analysed:						
Nonylphenol						
Octylphenol						

(*): LOQ for the method applied for water analysis.
(**): Fill the corresponding column if fractions have been analysed spearately

European Commission

EUR 22922 EN– Joint Research Centre – Institute for Environment and Sustainability
Title: Comparison of Monitoring Approaches for Selected Priority Pollutants in
Surface Water - An Initiative in support to the Water Framework Directive Chemical Monitoring Activity

Author(s): Georg Hanke, Jan Wollgast, Robert Loos, Javier Castro Jiménez, Gunther Umlauf,
Giulio Mariani, Anne Müller, Tania Huber, Eugen H. Christoph, Giovanni Locoro,
José Manuel Zaldívar and Giovanni Bidoglio

Luxembourg: Office for Official Publications of the European Communities
2007 – 73 pp.
EUR – Scientific and Technical Research series – ISSN 1018-5593
ISBN: 978-92-79-06945-1

Abstract
The report on the Chemical Monitoring Activity On-Site event describes the comparison of different methodologies currently applied in European laboratories for the analysis of pollutants that shall be regulated within the Water Framework Directive

The mission of the JRC is to provide customer-driven scientific and technical support for the conception, development, implementation and monitoring of EU policies. As a service of the European Commission, the JRC functions as a reference centre of science and technology for the Union. Close to the policy-making process, it serves the common interest of the Member States, while being independent of special interests, whether private or national.

JRC
EUROPEAN COMMISSION

LB-NA-22922-EN-C

ISBN 978-92-79-06945-1

Publications Office
Publications.eu.int