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NORMAN interlaboratory study (ILS) on passive sampling of emerging pollutants

*A Chemical Monitoring On Site (CM Onsite)
organised by NORMAN Association and JRC in
support of the Water Framework Directive*



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NORMAN interlaboratory study (ILS) on passive sampling of emerging pollutants

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Table of contents

Acknowledgements	9
Abstract	10
1. Introduction.....	12
1.1 EU legislation for control of chemical pollutants in aquatic environment	12
1.2 Directives on Environmental Quality Standards.....	12
1.3 Method performance criteria.....	13
1.4 Chemical monitoring and emerging pollutants (CMEP) expert group	13
1.5 Previous Chemical Monitoring on-site exercises	13
1.5.1 First on-site chemical monitoring and analysis exercise (CMA on-site 1) .	13
1.5.2 Second on-site chem. monitoring and analysis exercise (CMA on-site 2).	13
1.5.3 Third on-site chemical monitoring exercise (CM on-site 3)	14
1.6 Emerging substances – NORMAN network	14
1.7 Passive sampling	14
2. Study objectives.....	16
3. Design of the study	16
4. Standard solution	17
4.1 Provided passive sampler.....	17
4.2 Participant passive samplers	18
4.3 Composite water sample.....	20
5. Target compounds.....	20
6. Steering group	23
7. Participants	24
7.1 Registration	24
7.2 Participating laboratories	27
8. Sampling station	30
8.1 Site description.....	30
8.2 Initial sampling site characterisation	32
8.3 Passive sampling homogeneity test.....	32
8.4 Sampler exposure.....	36
8.5 Field parameters.....	36
8.5.1 Current velocities	38
8.6 Water sampling	39
8.6.1 Preparation of a 7-day composite sample	39
8.6.2 Preparation of 7-day composite blank samples	39
9. Tested materials	41
9.1 Standard solutions	41
9.1.1 Polar pesticides	42

9.1.2	Pharmaceuticals	43
9.1.3	Steroid hormones	43
9.1.4	Brominated diphenyl ethers - PBDEs	43
9.1.5	Fluorinated surfactants.....	44
9.1.6	Bisphenol A and Triclosan	44
9.2	Provided samplers.....	44
9.2.1	POCIS - provided samplers for polar compounds	44
9.2.2	Silicone rubbers - provided samplers for PBDEs.....	45
9.3	Participant samplers.....	45
9.4	Spot samples	46
10.	Data evaluation approach.....	46
10.1	Box-and-whisker plots.....	46
10.2	Bar graphs	46
10.3	Biplot graphs.....	48
10.4	Expression of data variability as coefficient of variation	49
10.5	Contribution of the calculation procedure to data variability	49
10.6	Sampler designs employed by participating laboratories	50
11.	Results.....	51
11.1	Polar pesticides	51
11.1.1	Overall data variability.....	52
11.1.2	Results by laboratories – polar pesticides	53
11.1.3	Sample variability	60
11.1.4	Standard solution.....	61
11.1.5	Provided sampler	61
11.1.6	Field blanks	61
11.1.7	Sampling variability	61
11.1.8	Contribution of the calculation procedure to data variability.....	62
11.1.9	Participant samplers	64
11.1.10	Field blanks	64
11.1.11	Sampling variability	64
11.1.12	Water samples.....	66
11.1.13	Conclusions for polar pesticides.....	66
11.2	Pharmaceuticals	67
11.2.1	Overall data variability.....	67
11.2.2	Results by laboratories - pharmaceuticals.....	68
11.2.3	Sample variability	76
11.2.4	Standard solution.....	77
11.2.5	Provided sampler	77

11.2.6	Field blanks	77
11.2.7	Sampling variability	77
11.2.8	Contribution of the calculation procedure to data variability	78
11.2.9	Participant sampler.....	79
11.2.10	Field blanks	80
11.2.11	Sample variability	80
11.2.12	Water samples	81
11.2.13	Conclusions for pharmaceuticals	82
11.3	Steroid hormones	83
11.3.1	Overall data variability	83
11.3.2	Results by laboratories – steroid hormones	84
11.3.3	Sample variability	89
11.3.4	Standard solution.....	89
11.3.5	Provided sampler	90
11.3.6	Field blanks	90
11.3.7	Sample variability	90
11.3.8	Contribution of the calculation procedure to data variability.....	90
11.3.9	91
11.3.10	Participant sampler.....	92
11.3.11	Field blanks	92
11.3.12	Sample variability	92
11.3.13	Spot samples.....	93
11.3.14	Conclusions for steroids	95
11.4	Brominated diphenyl ethers – PBDEs.....	96
11.4.1	Overall data variability.....	96
11.4.2	Results by laboratories - PBDEs	97
11.4.3	Sample variability	103
11.4.4	Standard solution.....	104
11.4.5	Provided sampler	104
11.4.6	Field blank	104
11.4.7	Spiked field blank.....	104
11.4.8	Sampling variability	104
11.4.9	Contribution of the calculation procedure to data variability.....	105
11.4.10	Participant sampler.....	107
11.4.11	Field blank	108
11.4.12	Sample variability	108
11.4.13	Water samples.....	109
11.4.14	Conclusions for PBDEs	109

11.5	Fluorinated surfactants	110
11.5.1	Overall data variability	110
11.5.2	Results by laboratories – fluorinated surfactants	111
11.5.3	Sample variability	113
11.5.4	Standard solution	113
11.5.5	Provided sampler	113
11.5.6	Field blanks	114
11.5.7	Sample variability	114
11.5.8	Contribution of the calculation procedure to data variability.....	114
11.5.9	Participant sampler.....	114
11.5.10	Field blank	115
11.5.11	Sample variability	115
11.5.12	Water samples.....	116
11.5.13	Conclusions for fluorinated surfactants.....	116
11.6	Bisphenol A and Triclosan	117
11.6.1	Overall data variability	117
11.6.2	Results by laboratories – bisphenol A and triclosan.....	118
11.6.3	Sample variability	120
11.6.4	Standard solution.....	121
11.6.5	Provided sampler	121
11.6.6	Field blanks	121
11.6.7	Sample variability	121
11.6.8	Contribution of the calculation procedure to data variability.....	121
11.6.9	Participant sampler.....	121
11.6.10	Field blanks	122
11.6.11	Sample variability	122
11.6.12	Water samples.....	123
11.6.13	Conclusions for bisphenol A and triclosan	123
12.	Variability of DIA-D5 dissipation from <i>Provided samplers</i>	125
13.	Correlation between result deviation from median and level of expertise of participating laboratories	126
	Conclusions	131
	Recommendations	132
	Accuracy of analysis of complex samples using LC/MS methods	132
	Availability of accurate calibration data for adsorption based PS.....	132
	Experience with state-of-the art approaches to evaluate data from partition-based PS of hydrophobic compounds.....	133
	Organisation of future interlaboratory studies	133
	List of Tables	135

List of Figures 137
References 141
Annexes 144

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Abstract

Passive samplers can play a valuable role in monitoring water quality within a legislative framework such as the European Union's Water Framework Directive (WFD). The time-integrated data from these devices can be used to complement chemical monitoring of priority and emerging contaminants which are difficult to analyse by spot or bottle sampling methods, and to improve risk assessment of chemical pollution. In order to increase the acceptance of passive sampling technology amongst end users and to gain further information about the robustness of the calibration and analytical steps, several inter-laboratory field studies have recently been performed in Europe. Such trials are essential to further validate this sampling method and to increase the confidence of the technological approach for end users. An inter-laboratory study on the use of passive samplers for the monitoring of emerging pollutants was organised in 2011 by the NORMAN association (Network of reference laboratories for monitoring emerging environmental pollutants; www.norman-network.net) together with the European DG Joint Research Centre to support the Common Implementation Strategy of the WFD. Thirty academic, commercial and regulatory laboratories participated in the passive sampler comparison exercise and each was allowed to select their own sampler design. All the different devices were exposed at a single sampling site to treated waste water from a large municipal treatment plant. In addition, the organisers deployed in parallel for each target analyte class multiple samplers of a single type which were subsequently distributed to the participants for analysis. This allowed an evaluation of the contribution of the different analytical laboratory procedures to the data variability. The results obtained allow an evaluation of the potential of different passive sampling methods for monitoring selected emerging organic contaminants (pharmaceuticals, polar pesticides, steroid hormones, fluorinated surfactants, triclosan, bisphenol A and brominated flame retardants). In most cases, between laboratory variation of results from passive samplers was roughly a factor 5 larger than within laboratory variability. Similar results obtained for different passive samplers analysed by individual laboratories and also low within laboratory variability of sampler analysis indicate that the passive sampling process is causing less variability than the analysis. This points at difficulties that laboratories experienced with analysis in complex environmental matrices. Where a direct comparison was possible (not in case of brominated flame retardants) analysis of composite water samples provided results that were within the concentration range obtained by passive samplers. However, in the future a significant improvement of the overall precision of passive sampling is needed. The results will be used to inform EU Member States about the potential application of passive sampling methods for monitoring organic chemicals within the framework of the WFD.

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1. Introduction

1.1 EU legislation for control of chemical pollutants in aquatic environment

The Water Framework Directive 2000/60/EC (WFD) [1] provides for the protection of European water bodies from contamination by chemical pollutants. For surface waters, this protection is partly achieved by the identification of Priority Substances and the establishment of Environmental Quality Standards at European level in the daughter Directive 2008/105/EC [2], as recently amended by Directive 2013/39/EU [3]. In addition, the WFD includes the obligation for Member States to identify pollutants of national concern as river basin specific pollutants and to set environmental quality standards for them at national level. According to their analysis of pressures and impacts, Member States need to set up monitoring programs for surface waters covering a wide range of contaminants in order to characterise the risks, and the need for action. The new Watch List mechanism, introduced by Commission Decision (EU) 2015/495 [4] requires the monitoring of substances that might pose a risk at EU level for which monitoring data are not yet sufficient to confirm the risk.

1.2 Directives on Environmental Quality Standards

The Environmental Quality Standards Directive (EQSD) 2008/105/EC [2] of the European Parliament and the Council on environmental quality standards (EQS) in the field of water policy, amending and subsequently repealing Council Directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/491/EEC, 86/280/EEC and amending Directive 2000/60/EC, was published in the Official Journal on 24 December 2008.

The EQS directive established:

- in Annex I, limits on concentrations of 33 priority substances and 8 other historic pollutants in surface waters;
- the list of 33 priority substances in Annex II as Annex X of the WFD, including the identification of priority hazardous substances;
- the possibility of applying EQS for sediment and biota, instead of those for water;
- the possibility of designating mixing zones adjacent to discharge points where concentrations of the substances in Annex I might be expected to exceed their EQS;
- a requirement for Member States to establish an inventory of emissions, discharges and losses of the substances in Annex I;
- an obligation to review the list of priority substances every 4 years.

The identified 33 substances or group of substances were shown to be of major concern for European waters. Within this list, 11 substances were identified as priority hazardous substances and are therefore subject to a requirement for cessation or phasing out of discharges, emissions and losses within an appropriate timetable not exceeding 20 years.

The recently published Directive 2013/39/EU [3] added the following 12 substances to Annex X of the WFD:

dicofol, perfluorooctane sulfonic acid and its derivatives (PFOS), quinoxifen, dioxins and dioxin-like compounds, aclonifen, bifenoxy, cybutryne, cypermethrin, dichlorvos, hexabromocyclododecanes (HBCDD), heptachlor and heptachlor epoxide and terbutryn.

In addition, Article 8b of Directive 2013/39/EU introduced the requirement for a watch list of substances for which Union-wide monitoring data are to be gathered for the purpose of supporting future prioritisation exercises in order to break the so-called vicious cycle of no monitoring – no regulation. The first watch list, in Commission Decision (EU) 2015/495 [4], includes the following substances: diclofenac; 17-beta-

estradiol (E2); 17-alpha-ethinylestradiol (EE2); estrone (E1); 2,6-ditert-butyl-4-methylphenol; 2-ethylhexyl 4-methoxycinnamate; macrolide antibiotics; methiocarb; neonicotinoids; oxadiazon; and tri-allate. The Directive also highlights 11 priority substances for which an EQS_{biota} has been derived.

The Directive 2013/39/EU [3] **recommends further development of passive sampling techniques as a promising tool for future application in compliance checking and trend monitoring of priority substances.**

This interlaboratory study represents an important step in evaluating the performance of currently available passive sampling (PS) techniques with the main focus on polar (emerging) organic pollutants (pharmaceuticals, polar pesticides, steroid hormones, fluorinated surfactants, triclosan, bisphenol A) and brominated flame retardants and provides a basis for identifying tools that could be suitable for regulatory monitoring. It also should help the scientific community to identify further research needs to improve performance characteristics of PS in the aquatic environment.

1.3 Method performance criteria

The method performance criteria and technical specifications for analytical measurements in chemical analysis and monitoring of water status have been set in the Directive 2009/90/EC [5]. In the directive, minimum performance criteria for all methods of analysis applied for WFD compliance checking are based on an uncertainty of measurement of 50 % or below ($k= 2$) estimated at the level of an EQS and a limit of quantification equal or below a value of 30 % of an EQS.

1.4 Chemical monitoring and emerging pollutants (CMEP) expert group

During the years 2011-2012, technical discussions with Member States delegates on chemical monitoring issues were held in the then Chemical Monitoring and Emerging Pollutants (CMEP) expert group in order 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, to arrive at a common view on the necessary monitoring for the WFD. Chemical water analysis is done on a routine basis in the Member States according to their national regulations and it is crucial that currently applied approaches merge into a common strategy which results in comparable assessments throughout Europe. The CMEP's mandate was established in the context of the work of WG Chemicals (under the Common Implementation Strategy for the WFD).

1.5 Previous Chemical Monitoring on-site exercises

1.5.1 First on-site chemical monitoring and analysis exercise (CMA on-site 1)

A first field trial, "chemical monitoring and analysis" (CMA on-site 1) was organised by JRC IES in 2006 on the Po River in Ferrara, Italy [6].

1.5.2 Second on-site chem. monitoring and analysis exercise (CMA on-site 2)

While the first trial had been limited to 7 invited laboratories, the second CMA on-site event in 2008 was open to all laboratories nominated through the CMA group. In the second CMA on-site exercise 27 analytical laboratories from 11 EU Member States and 2 non-EU countries participated in a technical on-site event during which sampling and analytical methodologies for chemical monitoring according to proposed WFD provisions were compared [7]. Coordination of the project was provided by the European Commission Joint Research Centre in collaboration with the Italian Water Research Institute, the Hungarian Ministry of Environment and Water and the Serbian Ministry for

Environment and Spatial Planning. The laboratories had been invited to take samples from the Danube River according to their standard protocols and to analyse them for PAHs, PBDE and nonyl-, octylphenols. It was shown that even some of the most challenging WFD priority substances, selected specifically for this exercise, can be measured at WFD relevant concentrations ($0.3 \times$ EQS) with methods currently applied in Member States. Depending on the analyte group, the obtained results were, however not within proposed data quality criteria for some participants and therefore further development of methods and harmonisations of efforts was suggested.

1.5.3 Third on-site chemical monitoring exercise (CM on-site 3)

In 2010 the European Commission Joint Research Centre organised, together with the Italian Water Research Institute IRSA and the Rijkswaterstaat Centre for Water Management in the Netherlands, the third edition of the CM on-site campaign. The scope was to give Member States an opportunity to compare their monitoring approaches for WFD compliance checking. The campaign took place on 5/6 October 2010 in Eijsden at the Meuse River. The event was hosted at the Rijkswaterstaat Measuring Station Eijsden. Member States were invited to send laboratory teams for a joint sampling on the Meuse river. The laboratories were expected to measure EU priority pollutants of their choice in the river water and to share their measurement results, including data quality metadata. For selected pollutants (PAHs and PBDEs) standards were distributed and also homogenised river water extracts were available for intercomparison [8].

1.6 Emerging substances – NORMAN network

Out of several million known substances, over 150,000 substances are produced in amounts over 10 t/year (REACH registry), which may enter the environment and eventually penetrate the food chain. An understanding of which of these substances or their mixtures are potentially harmful to the living environment or humans represents one of the biggest challenges for present environmental research. From a legal point of view, the WFD is requesting each EU Member State to list so-called river basin specific pollutants (not regulated by the WFD at the EU scale), which are recognised to pose a risk to river biota and monitor them next to the WFD PS. The NORMAN database of emerging substances [9] lists over 700 non-regulated environmental contaminants with potentially harmful effects. The NORMAN prioritisation scheme ranks compounds based on their occurrence (local or European problem), toxicity (PNEC and EQS values from laboratory studies/ literature or predicted by Read Across QSAR-based models) and use (amounts produced/applied). In the NORMAN scheme none of the substances is discarded from the prioritisation because of lack of monitoring or toxicity data. Categories of substances are defined with a clear indication of which substances need, e.g., more occurrence or more toxicity data or improved analytical performance, etc. Each of the basic parameters (occurrence, toxicity and use) and numerous sub-parameters (e.g. information on whether the substance is an endocrine disruptor, belonging to the category of persistent, bioaccumulative and toxic (PBT)) has a “weight” factor contributing to the final ranking.

The JRC as the European Commission’s in-house science service took on in 2014, led by DG Environment, the technical work on the prioritisation process under the WFD. Chemical substances are being ranked according to their production volumes, use patterns, intrinsic properties, concentrations in the environment, toxic effects, and relevance to drinking water.

1.7 Passive sampling

The potential of PS to support WFD monitoring requirements was recognized in an ad hoc expert meeting organised by the NORMAN association in 2009 [10]. This resulted in a position paper on PS of emerging substances in 2010 [11], followed by the performance of the inter-laboratory study presented in this report in 2011.

Other initiatives to investigate the possible application of PS in screening and compliance monitoring were the "Utrecht workshop" organized by Deltares [12], the SETAC Pellston workshop on PS methods in sediments, [13] and the ICES Workshop on Passive Sampling and Passive Dosing [14].

The general outcome of these workshops was that partition-based PS for hydrophobic substances is sufficiently mature to play a role in regulatory monitoring for quantitative compliance checking. In contrast, it has been recognised that PS of hydrophilic substances using adsorption-based samplers needs further development.

An ISO standard has been published that specifies procedures for the determination of time-weighted average concentrations and equilibrium concentrations of dissolved organic, organo-metallic and inorganic substances, including metals, in surface water by PS, followed by analysis [15].

The recently published EU Technical report on aquatic effect-based monitoring tools [16] highlights that by combining passive sampling with effect based tools an integration of exposure and effects monitoring can be achieved. Such approach is considered to facilitate more cost effective monitoring programmes as well as forming the basis of a risk-based pollution control strategy.

Two working principles of PS must be considered, partitioning and adsorption.

Partitioning-based PS devices (p-PSD) are made from hydrophobic polymeric materials with high permeability for the compounds to be sampled. p-PSDs absorb (or, more accurately, dissolve) substances from water because of much better solubility of the substances in the sampler material compared to water. Consequently, hydrophobic substances with low solubility in water are strongly accumulated in p-PSDs, while hydrophilic substances are concentrated to a much smaller extent. Following a sufficiently long exposure in the environment the absorbed concentration in the p-PSDs will eventually attain equilibrium with the concentrations outside the sampler, e.g. water. From the equilibrated concentration in the p-PSD an aqueous phase concentration can be estimated using the sampler-water partition coefficients (K_{PW}). This is a freely dissolved concentration (C_{free}) that is not influenced by variable concentration of the substance bound to the suspended particulate (organic) matter (SPM). C_{free} is considered to play a key role in chemical uptake by aquatic organisms and its distribution between environmental compartments, since it is proportional to the chemical activity in water.

Equilibrium is assumed for the partitioning PS but, in practice, with application of p-PSDs in water, equilibrium is only attained for substances with a log K_{PW} up to 5.5. For more hydrophobic substances the uptake is too slow (or actually the sampler uptake capacity too large) to attain equilibrium in typical exposure periods (2-8 weeks). In that case the estimated C_{free} relies on the measurement of the in-situ water volume extracted by the p-PSD during the exposure period. This volume (or the sampling rate, when expressed per time unit) is derived from the release of selected substances dosed to the p-PSD prior to exposure. Basically, the rate of release, controlled by the diffusion through the water boundary layer at the sampler surface, is determined. The first order rate constant of the release under the given sampling conditions (temperature and turbulence) is equal to that of the uptake and can consequently be used for calculating C_{free} also in situations when equilibrium is not attained. Models and methods have been developed to estimate sampling rates [17] [18], as well as K_{PW} [19], to derive C_{free} from sampler uptake. Uncertainties in results obtained by application of p-PSDs are believed to range by a factor 2 depending on the level of experience of the laboratory. Different aspects of uncertainty are discussed in (Lohmann et al., 2012).

Adsorption PS devices (a-PSD) generally contain adsorptive materials that are also applied in solid phase extraction of hydrophilic substances from water. In an a-PSD a thin layer of such material is applied separated from the water phase by a filter or a membrane. As for a p-PSD the substances diffuse through the water boundary layer and

the membrane or filter, but accumulation in the binding material is by an adsorption process and not by dissolution. Adsorption of strongly hydrophilic substances is possible since binding can take place by a number of interactions between the surface of the material and the chemical, e.g. van der Waals, π - π interactions, hydrogen bonding, and Coulomb forces. After extended exposure, the uptake rate is reduced not only by equilibration but it can be limited also by saturation of the sorption sites of the adsorbent applied. Also uptake of non-target compounds and other interfering natural compounds contributes to saturation and competes for sorption sites with target substances. To avoid or reduce this effect, exposure periods are kept shorter than with partition PS. Although extensive laboratory derived calibration datasets have been reported for a-PSDs, literature shows limited agreement (Harman et al., 2011, 2012). The uptake process is not yet well understood, nor is translation of laboratory calibrations to the field, which complicates the determination of water concentrations for compliance checking. In spite of these shortcomings, a-PSDs samplers can give valuable results with regards to substance screening to determine whether water bodies are potentially at risk and as an alternative method in situations where classical monitoring approaches based on low frequency spot sampling fail, or, in situations where the classical monitoring approaches have insufficient low LOD.

2. Study objectives

In comparison with a typical collaborative trial, this interlaboratory study can be characterised by several specifics. The study ambition was not to validate the passive sampling method or to demonstrate the fitness of the method for routine monitoring under the regulatory framework, but rather to identify the current weak points and needs for future development of adsorption based passive samplers (a-PSD) in particular and also for development of procedures for future method validation. Thus, the overall performance of passive sampling technology must not be judged based on this single exercise. For example, it is known that the uncertainty of partition based passive samplers (p-PSDs) is lower than that of a-PSDs (Lohmann et al., 2012). The study was a **learning exercise** with the objective to assess the current variability of passive sampling methods for a range of emerging pollutants. The study addressed a relatively wide variety of **emerging pollutants** from several substance classes that are (with several exceptions) not yet regulated, and also some priority compounds that are problematic in terms of sampling and analysis, or compounds that are currently on the WFD watchlist. The focus of the study was thus intentionally on those compounds for which the current performance of passive sampling has not yet been fully explored.

The exercise addressed sampling in treated wastewater, which is a highly relevant matrix for future monitoring of the compounds of interest, but also a **complex matrix** that presented another challenge for methods used in analysis.

When taking into account the ambitious selection of target compounds, analysed matrices and the rather limited number of laboratories that currently apply passive samplers, organisers decided that the participation in the study was not restricted based on the level of laboratory expertise. The main objective of the present study is to characterise the variability of results when using PS for estimating aqueous concentrations of several groups of emerging polar contaminants and brominated diphenyl ethers.

3. Design of the study

The core of the study was a sampler comparison exercise that has been extended to include several steps covering individual aspects in the PS process, including analytical comparability and comparison of PS with spot sampling. All samplers were exposed in parallel to water at a single site. The levels in the study design were:

1. To verify that analytical standards applied in each laboratory agree with each other. For this purpose a standard solution of target analytes was distributed to the participating laboratories to be analysed in parallel with the various sampler extracts.
2. For each target analyte class, in parallel with the various types of *participant samplers (PPS)*, passive samplers of a single type "*NORMAN provided samplers (NPS)*" were exposed, that were also provided to each participant. These *provided samplers* needed to be analysed together with their own "*Participant's Passive Samplers (PPS)*".
3. These steps were performed to support the interpretations of the main activity of the exercise to evaluate the present data variability from various passive samplers selected by the individual participating laboratories.
4. Data from the analysed passive samplers were (with exception of brominated diphenyl ethers) compared with contaminant concentrations in composite spot water samples collected at the study site during sampler exposure.

The stepwise design helped to identify sources of variation such as instrumental analytical bias (step 1) and the analytical component of variability in the presence of matrix (step 2). Variation additionally to that of sampler processing + analysis, can be attributed to the variability/differences between samplers.

4. Standard solution

The comparison of the participant's analytical standards with a common analytical standard provided by the central laboratories showed the variability of applied instrumental methods, bias in analysis of standards, and was the first simple step to identify analytical variability.

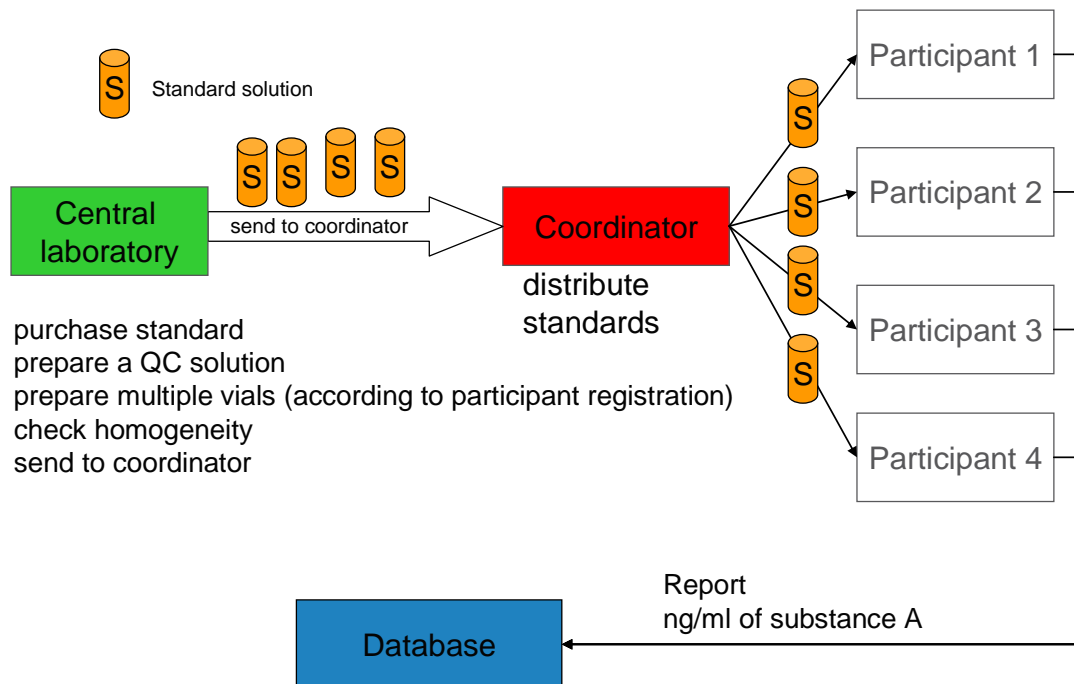


Figure 1 Analysis of standard solution. Result shows the variability of applied instrumental methods and is a first simple step to allow correction of data for analytical deviations.

4.1 Provided passive sampler

The replicate (3 replicates + blank) *provided samplers* and their analysis by participating laboratories allowed an intercalibration of the analysis of passive samplers and an estimate of the contribution of the analytical (sampler extraction + analysis) component to total variability.

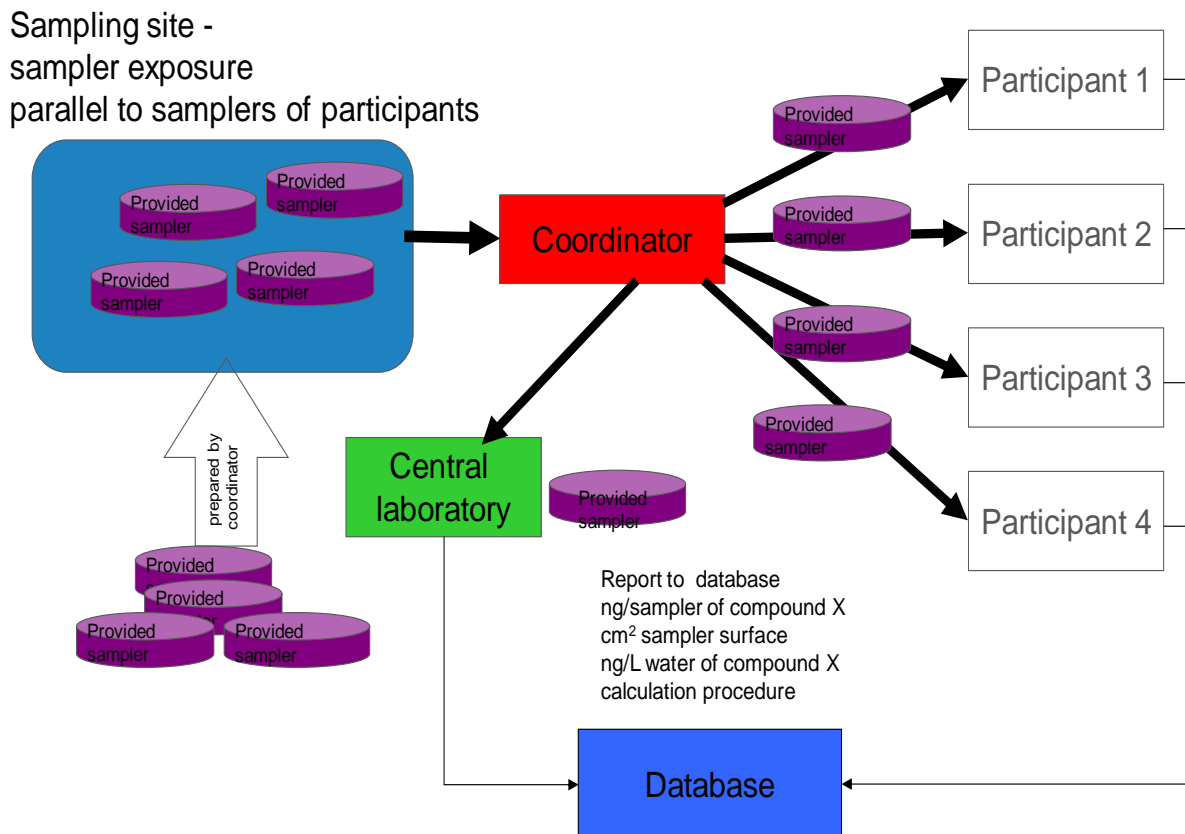


Figure 2 Provided passive sampler. The replicate (3 replicates + blank) provided samplers and their analysis by participating laboratories allows an intercalibration of the analysis of passive samplers. An estimate can be made of the contribution of the analytical (sampler extraction + analysis) component to total variability.

4.2 Participant passive samplers

The study consisted of passive samplers (3 replicates + blank for each laboratory) deployed to sample the water phase at a single sampling site. Participating laboratories were free and encouraged to deploy all recently available types/designs of passive samplers that are suitable for sampling selected target analytes at the sampling site. For this step in the exercise participants were requested to supply for each target compound the amount sampled by their sampler and the aqueous phase concentration they derived (using a calculation method of their choice) from the sampler uptake.

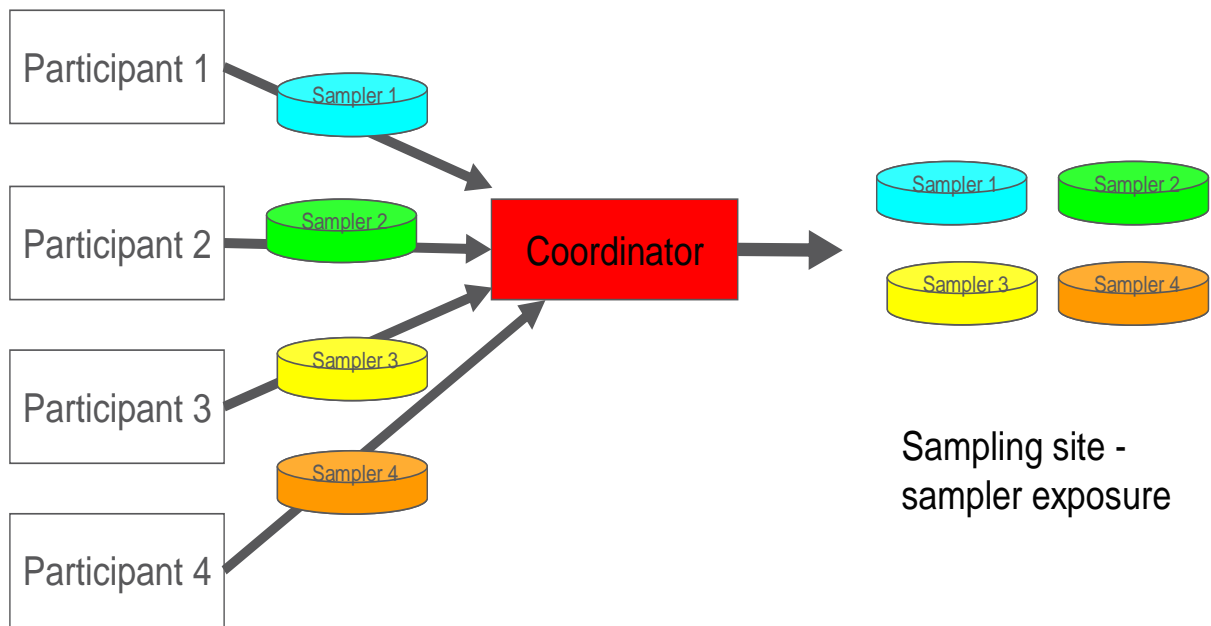


Figure 3A Participant passive samplers. The study consisted of passive samplers deployed to sample the water phase at a single sampling site. Participating laboratories were free and encouraged to send all recently available types/designs of passive samplers for deployment that are believed to be suitable for sampling the selected target analytes.

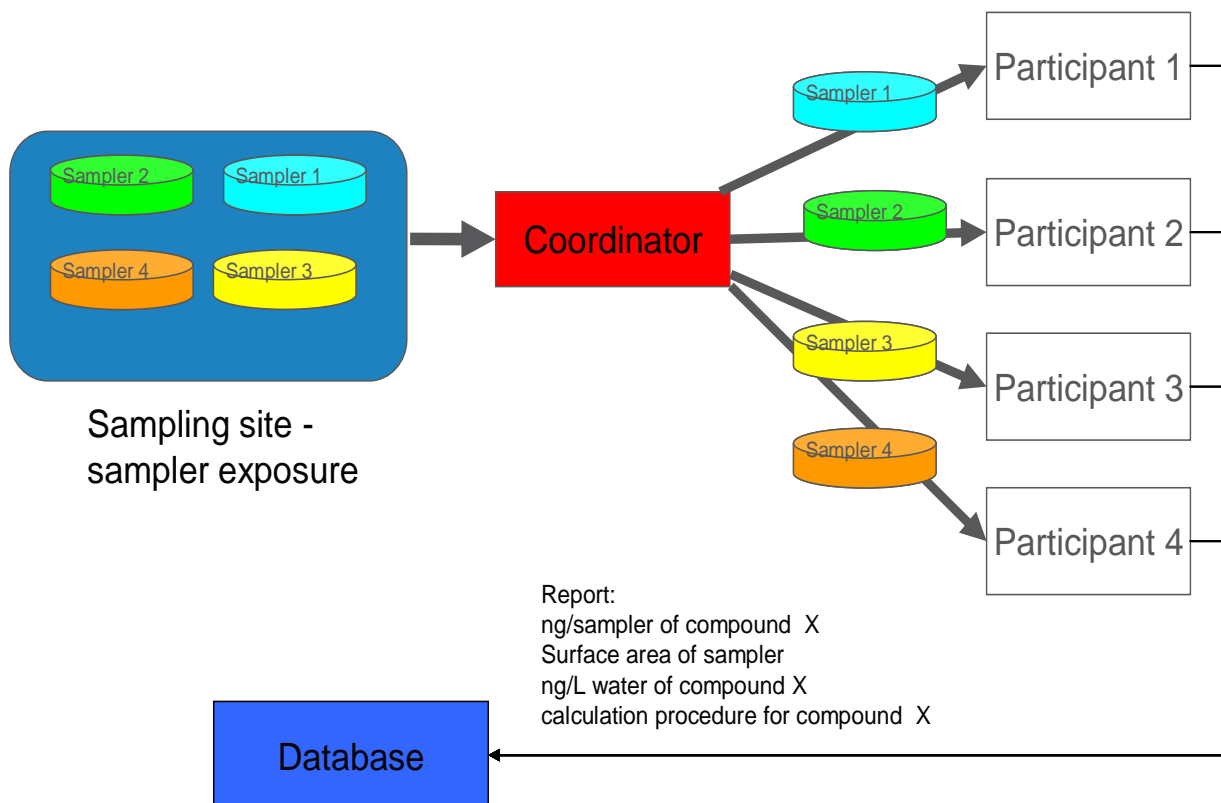


Figure 3B Participant passive samplers. Following exposure samplers were sent to participating laboratories for analysis.

4.3 Composite water sample

The average value of concentration of analytes measured in collected 2 weekly composite samples of water (for all target analytes excepting brominated diphenyl ethers) during sampler exposure provides the comparison with a conventional sampling approach. Uptake of passive samplers is proportional to the dissolved concentration in water and, provided the sampling rate is accurately known, a direct comparison with the water sampling (filtered composite water samples) is possible for polar compounds. This step could not be performed for brominated diphenyl ethers since alternative methods (other than PS) for measurement of their dissolved concentrations in water are not available.

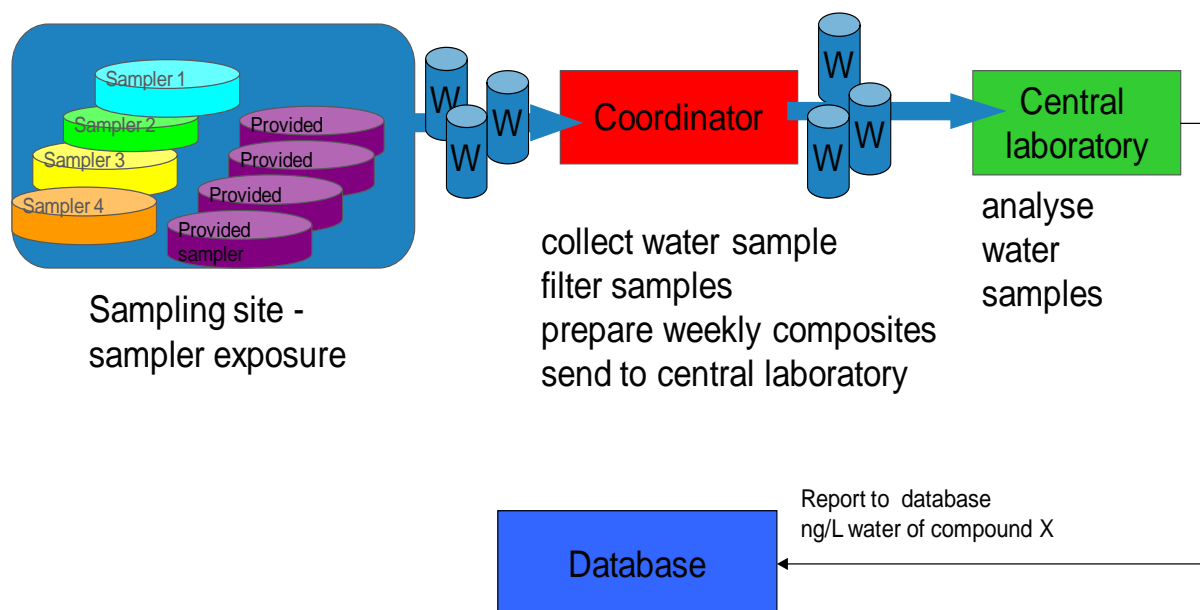


Figure 4 Spot sampling in water. The concentration of analytes measured in 2 weekly composite samples of water during passive sampler deployment provided the comparison with a conventional sampling approach. Spot sampling was not performed for PBDEs.

5. Target compounds

Selection of the target compounds was performed based on results of a questionnaire that was circulated in April 2010 to the participants of the NORMAN expert group meeting in Prague 2009 and laboratories that have experience with application and analysis of passive samplers.

The questionnaire contained a broader list of potentially interesting compounds, which was based on the NORMAN list of the most frequently discussed emerging substances. This has been published also in the NORMAN position paper on PS [11].

The list contained also basic information on

- The potential applicability of passive samplers for the compounds
- Stage of development of passive samplers for the compounds – based on the literature
- Availability of passive sampler calibration data for the compounds
- Whether the substances were detected at the sampling site intended for the inter-laboratory study in previous research and monitoring projects

To simplify selection compounds were highlighted in the questionnaire that fulfilled at least two of the criteria below:

- a) There is published evidence about passive sampler performance in the field
- b) Data from laboratory calibration studies are available
- c) Substance was found at measurable concentration in surface water or wastewater in the area around city of Brno

The correspondents were asked to select from the list substances of interest. The final selection of 29 compounds was based on the response of nine expert laboratories from Europe and one from Australia. The target compounds are listed below.

Many of the selected compounds are regulated as priority substances under the WFD and related Directives on Environmental Quality Standards [2], [3]. Those include atrazine, diuron, PFOS and pentabromodiphenylether. Moreover, diclofenac, 17-alpha-ethynilestradiol and 17-beta-estradiol are compounds from the watch list established in Article 8b of Directive 2013/39/EU.

Table 1 Target analytes : Polar pesticides

	Compound	CAS	Usage
1.	Atrazine	1912-24-9	triazine herbicide
2.	Carbendazim	10605-21-7	benzimidazole fungicide
3.	Desethylatrazine	6190-65-4	triazine metabolite
4.	Desethylterbutylazine	30125-63-4	triazine metabolite
5.	Diuron	330-54-1	phenylurea herbicide
6.	S-metolachlor	87392-12-9	chloroacetanilide herbicides
7.	Terbutylazine	5915-41-3	triazine herbicide

Table 2 Target analytes: Pharmaceuticals

	Compound	CAS	Usage
8.	Alprazolam	28981-97-7	benzodiazepine drug
9.	Atenolol	29122-68-7	beta blocker drug
10.	Carbamazepine	298-46-4	anticonvulsant drug
11.	Diazepam	439-14-5	benzodiazepine drug
12.	Diclofenac	15307-86-5	non-steroidal anti-inflammatory drug
13.	Ibuprofen	15687-27-1	non-steroidal anti-inflammatory drug
14.	Naproxen	22204-53-1	non-steroidal anti-inflammatory drug

Table 3 Target analytes: Steroid hormones

	Compound	CAS	Usage
15.	17-alpha-Estradiol	57-91-0	steroid hormone
16.	17-alpha-Ethinylestradiol	57-63-6	contraceptive
17.	17-beta-Estradiol	50-28-2	steroid hormone
18.	Estriol	50-27-1	steroid hormone
19.	Estrone	53-16-7	steroid hormone

Table 4 Target analytes: Brominated flame retardants

	Compound	CAS	Usage
20.	BDE 28	41318-75-6	Flame retardant
21.	BDE 47	5436-43-1	Flame retardant
22.	BDE 99	60348-60-9	Flame retardant
23.	BDE 100	189084-64-8	Flame retardant
24.	BDE 153	68631-49-2	Flame retardant
25.	BDE 154	207122-15-4	Flame retardant

Table 5 Target analytes: Fluorinated surfactants

	Compound	CAS	Usage
26.	PFOA	335-67-1	fluorosurfactant
27.	PFOS	1763-23-1	fluorosurfactant, fabric protector

Table 6 Target analytes: Bisphenol A and Triclosan

	Compound	CAS	Usage
28.	Bisphenol A	80-05-7	monomer to make plastics
29.	Triclosan	3380-34-5	antibacterial and antifungal agent

6. Steering group

The steering group was established from a group of laboratories with expertise in PS of selected groups of compounds. A meeting of steering group members was held on 24/11/2010 in Bratislava, where the study design and its practical realisation was discussed. Tasks were assigned to members of the steering group. Laboratories and other organisations involved in planning and organisation of the study are listed in Table 7.

Table 7 Steering group of the inter-laboratory study

Role	Organisations and contact persons	Activity
Coordinator	Masaryk university, RECETOX Water Research Institute (VUVH) Branislav Vrana vrana@recetox.muni.cz	study desing, coordination, sampling activities, on-site measurements, preparation of <i>provided samplers</i> , sample distribution
Central laboratory for PBDE	Deltares Foppe Smedes; Foppe.Smedes@deltares.nl	study design, preparation of <i>provided samplers</i> (silicone rubbers)
Central laboratory for pharmaceuticals	ISM-LPTC, University of Bordeaux 1 Hélène Budzinski; h.budzinski@epoc.u-bordeaux1.fr	study design, preparation of QC standards, analysis of water samples
Central laboratory for steroid hormones	Irstea Lyon Marina Coquery, Cecile Miege, Nicolas Morin marina.coquery@irstea.fr	study design, preparation of QC standards, analysis of water samples
Central laboratory for PFOA and PFOS, standard solutions of PBDE	European Commission DG JRC Robert Loos	study design, preparation of QC standards, analysis of water samples

	robert.loos@jrc.ec.europa.eu	
Central laboratory for bisphenol A, triclosan	Environment Agency Wales UK Environment Agency Anthony Gravell David Westwood anthony.gravell@environment-agency.wales.gov.uk	study design, preparation of QC standards, analysis of water samples
Participant interface for results reporting	QUASIMEME Steven Crum Ann-Marie Ryan steven.crum@wur.nl Ann-Marie.Ryan@wur.nl	setup of sharepointsites Introduce the lab specific contact information into the database, help desk facility with respect to data-transfer
Sampling support + Data interpretation	Masaryk university, RECETOX Foppe Smedes Branislav Vrana smedes@recetox.muni.cz vrana@recetox.muni.cz	participant registration, , data assessment data and interpretation, report preparation
Consultant + Screening	Eawag Etienne Vermeirssen Etienne.Vermeirssen@eawag.ch	study design, screening of the sampling site
Sampling support	IPH Ostrava Tomas Ocelka	providing sampling materials
Logistic support + study dissemination	European Commission DG JRC Robert Loos Bernd Gawlik robert.loos@jrc.ec.europa.eu bernd.gawlik@jrc.ec.europa.eu	study design, sampling logistics, host a meeting for the participants to discuss study results

7. Participants

7.1 Registration

The study was open for participants from commercial, academic and regulatory laboratories. Potential participants were informed by e-mail from the NORMAN network to its members. The study was announced on 9.3.2011 with a deadline for participant registration on 31.3.2011. Participants were asked for participation on their own expenses. Registration of participants was done online on a website setup by RECETOX, Masaryk university [24].

The organiser provided participants with detailed information on the study design and time schedule. The exercise manual contained information on important dates for the exercise (deadline to send equipment to the organiser, sampler deployment period, expected date to receive materials for analysis), general information for the participants (samplers to be sent to the organiser, deployment device to be sent to the site,

"NORMAN provided sampler" to be received from the organiser, information on protocol for sampler deployment, requirements for the solvent of the QC check solutions as well as general information on the result reporting and data evaluation and information about registration fees.

Table 8 Self assessed level of expertise in analysis of target compound groups in passive samplers.

Laboratory	Polar pesticides	Pharmaceuticals	Steroid hormones	Fluorinated surfactants	Triclosan	Bisphenol A	Brominated flame retardants
16	A ¹		A	A	C ³	A	A
17	A	A					
18	A						
19	A	B ²	B	B	B	B	B
20			C		B	C	B
21	C			C			C
23	A	A	B	A	A	A	A
25							B
26			C			C	C
29		A		A			A
30	A						A
31		A	A				
32	B	B					
33			A				
36	B	B	B				B
37	B		C	C			B
38							C
39	B	B	B	B		B	
40	A	A					
42	C						
43	B	B	B				A
44	C	C	C	C	C	C	C

Laboratory	Polar pesticides	Pharmaceuticals	Steroid hormones	Fluorinated surfactants	Triclosan	Bisphenol A	Brominated flame retardants
45			B			B	
46		C					
47	B	B			B	B	
48	A	A					
49	B	B	A		A	B	
50	C	C	C		C	C	C
51							
52				A			

¹A - expert laboratory that routinely analyses target compounds in passive samplers

²B - laboratory with some experience with analysis of analytes in passive samplers

³C - laboratory with a limited experience with analysis of target compounds in passive samplers but wants to test the performance of their samplers

Participants had the option to register for individual groups of compounds (4.1-4.6), which means that not all laboratories participated in the exercise for all groups of compounds.

During the registration participants provided following information:

- a) Identification of the participant laboratory
- b) Name and contacts of the corresponding person
- c) Selection of target compound classes and individual compounds
- d) Passive samplers *provided by participants* for analysis of selected target compounds
- e) Statement of ability to analyse their selected analytes in *NORMAN provided samplers*
- f) Statement on level of expertise in analysis of selected analytes in passive samplers (Table 8):

Altogether, 30 laboratories registered for the study, with the following numbers of participants registered to analyse individual contaminant classes:

Polar pesticides	– 19 participants
Pharmaceuticals	– 17 participants
Steroid hormones	– 15 participants
Triclosan	– 8 participants
Bisphenol A	– 11 participants

PFOA, PFOS – 8 participants
 PBDE – 16 participants

Note that despite registration, not all laboratories delivered results for all registered compound classes and several laboratories did not report any data.

7.2 Participating laboratories

For the result presentation anonymous codes from **Lab16** to **Lab51** were attributed to the participants.

Table 9 List of participating laboratories

Institute	Institute address	Country	Participant name
Aix Marseille University Institut des Sciences Moleculaires de Marseille (ISM2) Equipe AD2EM	Europole Environnement Petit Arbois - Bat Villemin - BP80 Aix en Provence 13545	France	Laure Malleret laure.malleret@univ-cezanne.fr
BRGM	3 avenue Claude Guillemin Orleans 45060	France	Catherine Berho c.berho@brgm.fr
Irstea	3 bis quai Chauveau, CP 220 Lyon 69336	France	Cecile Miege cecile.miege@irstea.fr
Cemagref UR REBX	50 avenue de Verdun Cestas 33612	France	Nicolas Mazzella nicolas.mazzella@irstea.fr
Deltares/TNO	PO Box 85467 Utrecht 3508 AL	The Netherlands	Foppe Smedes Henry Beeltje foppe.smedes@deltares.nl
Eawag Swiss Federal Institute of Aquatic Science and Technology,	Überlandstr. 133 Dübendorf 8600	Switzerland	Juliane Hollender Etienne Vermeirssen juliane.hollender@eawag.ch etienne.vermeirssen@eawag.ch
Oekotoxzentrum Eawag-EPFL	Überlandstr. 133 Dübendorf 8600	Switzerland	Nadzeya Homazava nadzeya.homazava@eawag.ch

Institute	Institute address	Country	Participant name
Environment Agency, National Laboratory Service	19 Penyfai Lane, Furnace, Llanelli Carmarthenshire SA15 4EL	Wales	Anthony Gravell anthony.gravell@environment-agency.gov.uk
European Commission, DG Joint Research Centre (JRC)	Unit H01 - Water Resources Unit, Via Enrico Fermi, I-21020 Ispra	Italy	Robert Loos robert.loos@jrc.ec.europa.eu
Institute for Environmental Studies	De Boelelaan 1085 Amsterdam 1081HV	The Netherlands	Petra Booij petra.booij@ivm.vu.nl
Institute of Public Health Ostrava	Partyzánské nám. 7 Ostrava 70200	Czech Republic	Samuel Mach samuel.mach@zu.cz
LABAQUA	C/ Dracma 16-18 Alicante 03114	Spain	Julio Llorca julio.llorca@labaqua.com
Marine Scotland Science	Marine Laboratory, PO Box 101, 375 Victoria Road, Aberdeen AB11 9DB	UK	Craig Robinson craig.robinson@scotland.gsi.gov.uk
Masaryk University RECETOX,	Kamenice 126/3 Brno 62500	Czech Republic	Jiří Kohoutek jiri.kohoutek@recetox.muni.cz
NIVA Norwegian Institute for Water Research	Gaustadalleen 21 Oslo NO-0349	Norway	Ian Allan ian.allan@niva.no
Omegam Laboratoria	HJE Wenckebachweg 120 Amsterdam 1096 AR	The Netherlands	Linda Landwehr L.Landwehr@omegam.nl
Ontario Ministry of Environment - Laboratory Services Branch	125 Resources Road Etobicoke M9P 3V6	Canada	Rita Dawood rita.dawood@ontario.ca
SLU, Dep of Aquatic Sciences and Assessment	P.O Box 7050 Uppsala SE-750 07	Sweden	Christer Jansson Christer.Jansson@slu.se
T. G. Masaryk Water Research Institute	Podbabská 30/2582 Prague 160 00	Czech Republic	Magdalena Kvíčalová magdalena_kvicalova@vuv.cz

Institute	Institute address	Country	Participant name
UFZ- Helmholtz Centre for Environmental Research Department of Ecological Chemistry,	Permoserstrasse 15 Leipzig 04318	Germany	Albrecht Paschke albrecht.paschke@ufz.de
Universita degli Studi di Genova Dipartimento di Chimica e Chimica Industriale	Via Dodecaneso, 31 Genoa 16146	Italy	Emanuele Magi magi@chimica.unige.it
Università di Cagliari Dipartimento di Igiene e Sanita pubblica	Via Porcell, 4 Cagliari 9124	Italy	Marco Schintu schintu@unica.it
University Bordeaux 1, EPOC-LPTC, UMR 5255 CNRS	351 crs de la Liberation Talence 33405	France	Helene Budzinski h.budzinski@epoc.u-bordeaux1.fr
University of Connecticut, Department of Marine Sciences	1080 Shennecossett Rd. Groton, CT 6340	USA	Penny Vlahos penny.vlahos@uconn.edu
University of Portsmouth, School of Biological Sciences	King Henry I Building, King Henry I Street Portsmouth PO1 2DY	United Kingdom	Janine Bruemmer janine.bruemmer@port.ac.uk
University of Queensland Entox	39 Kessels Road Coopers Plains 4108	Australia	Karen Kennedy k.kennedy@uq.edu.au
University of Rhode Island Graduate School of Oceanography	South Ferry Road Narragansett RI 02882	USA	Rainer Lohmann lohmann@gso.uri.edu
University of Winnipeg	515 Portage Ave. Winnipeg, Manitoba R3B2E9	Canada	Charles Wong wong.charles.shiu@alum.mit.edu
Veolia Environnement Recherche et Innovation (site de St Maurice)	Immeuble "Le Dufy" - 1 place de Turenne Saint Maurice Cedex 94417	France	Perrine Wund p.wund@epoc.u-bordeaux1.fr
Waterproof Foundation	Dijkgraaf Poschlaan 6 Edam 1135 ZG	The Netherlands	Mai Thao Nguyen m.nguyen@waterproef.nl

8. Sampling station

8.1 Site description

The exercise was performed at a single sampling site – the discharge of treated wastewater from a large municipal WWTP in Brno-Modřice (capacity cca. 500 000 equivalent inhabitants). The sampling was performed in an effluent basin that is used for measurement of flow and volume of discharged treated wastewater. The basin is cube-shaped with vertical concrete walls. The basin is situated at the end of a straight horizontal wastewater discharge pipeline that feeds into the basin at a depth of 3 m below ground level. The minimum water depth in the basin is 2.35 m. Standard parameters of the discharged treated wastewater that were sampled/measured during the exercise are shown in Section 8.5. The basin is equipped with side walkways which were used for suspension of PS devices during the exercise.

The site was secure so that expensive onsite equipment such as the continuous automatic water sampler could be used. Also, WWTP kindly provided some of the necessary supporting measurements (continuous temperature, discharge, pH). Access to the sampling site was permitted by the WWTP operator. Details of the WWTP facility are given at the website [25].

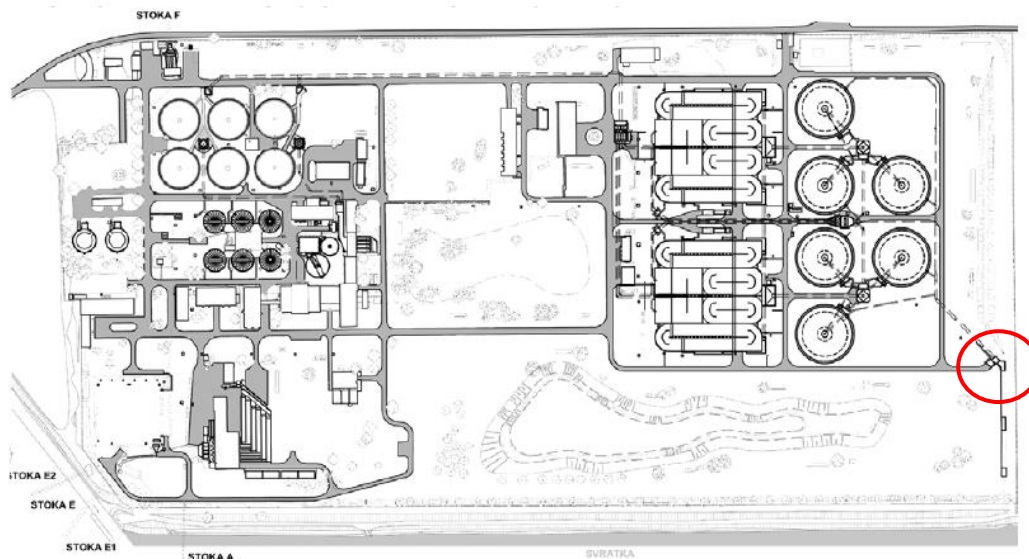


Figure 5. Layout of the WWTP in Brno-Modřice. The sampling site is located at the discharge of treated wastewater and is marked with the red circle.

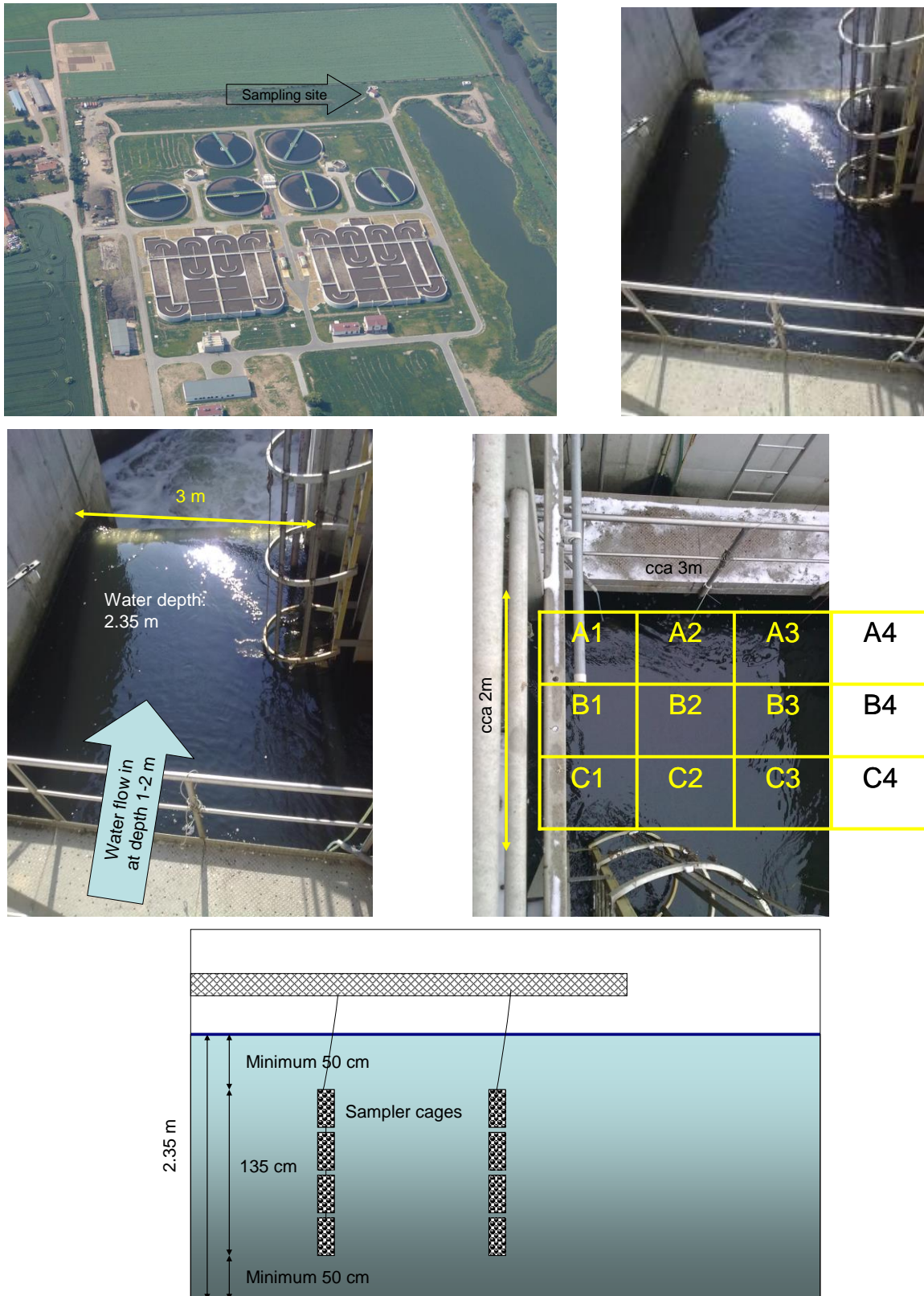


Figure 6. Views of the sampling site; discharge of treated wastewater from the WWTP in Brno-Modřice. A suspended sidewalk above the basin with the discharge pipe allowed a convenient deployment of passive samplers. The yellow rectangles in the middle right picture describe horizontal coordinates of possible positions for sampler deployment. The bottom picture illustrates vertical profile of the basin. Samplers were suspended from the sidewalk on ropes and exposed at water depth 0.5-2 m.

8.2 Initial sampling site characterisation

Preliminary information on emerging organic contaminants present in the treated wastewater at the outflow of the WWTP was available from a study "New procedures for monitoring the impact of urban agglomerations on qualitative parameters of fluvial environment with emphasis on the identification of endocrine substances" (funded by the Czech The Ministry of Education, Youth and Sports)¹ that was performed also at this sampling site, allowed preliminary identification of relevant substances Data from the study was kindly provided by Institute of Public Health Ostrava.

An initial screening campaign at the sampling site was performed from 18th June to 2nd July 2010. Several types of passive samplers were deployed (POCIS, Chemcatcher fitted with SDB/RPS, SDB/XC with and without polyethersulphone membrane, silicone sheets) and analysed in several laboratories. Results from the screening survey are available [26].

Table 10 Compound classes analysed in passive samplers from an initial screening of the sampling site.

Compound class	Sampler	Laboratory
Polar pesticides	POCIS	Irstea Lyon
Polar pesticides, pharmaceuticals	SDB/RPS Empore disk	Eawag
Steroid hormones	POCIS, SDB-XC Empore disk	RECETOX
PBDE	Silicone sheets	RECETOX
Pharmaceuticals	POCIS	University Bordeaux
PFOA, PFOS	POCIS	RECETOX
Triclosan	SPMD	IPH Ostrava
Bisphenol A	Water sample/SBSE	VUVH

Photos of the sampling site, collected during the initial screening campaign, are available (Vrana, 2010a,b).

8.3 Passive sampling homogeneity test

One of the critical issues in preparation of the interlaboratory study was the suitability of the selected sampling site in terms of (1) the presence of target analytes in time, (2) homogeneity of their aqueous concentrations and (3) homogeneity of sampler exposure conditions in the basin (i.e. flow conditions and temperatures).

¹ New procedures for monitoring the impact of urban areas on qualitative parameters of fluvial environment with emphasis on the identification of endocrine substances. Project MŠMT 2B06093, funded by the Czech The Ministry of Education, Youth and Sports.

The issue of homogeneity of exposure conditions, especially the possible effect of flow velocity/turbulence on passive sampler performance has been raised at the steering group meeting on 24th November in Bratislava. To assess this aspect, a test of exposure homogeneity was performed before the actual study.

From 20th December 2010 till 3rd January 2011 (14 days), 5 standard POCIS sampler deployment cages containing 3 POCIS (with Oasis HLB adsorbent and fitted with polyethersulphone membrane) were deployed each at various positions (2 positions and 3 water depths). The aim of the study was to investigate whether the position of cages within the basin had a significant effect on the sampler uptake. Following exposure, sorbent from individual samplers was transferred to SPE cartridges, dried, weighted, eluted and the extracts were analysed for a suite of polar pesticides by LC/MS.

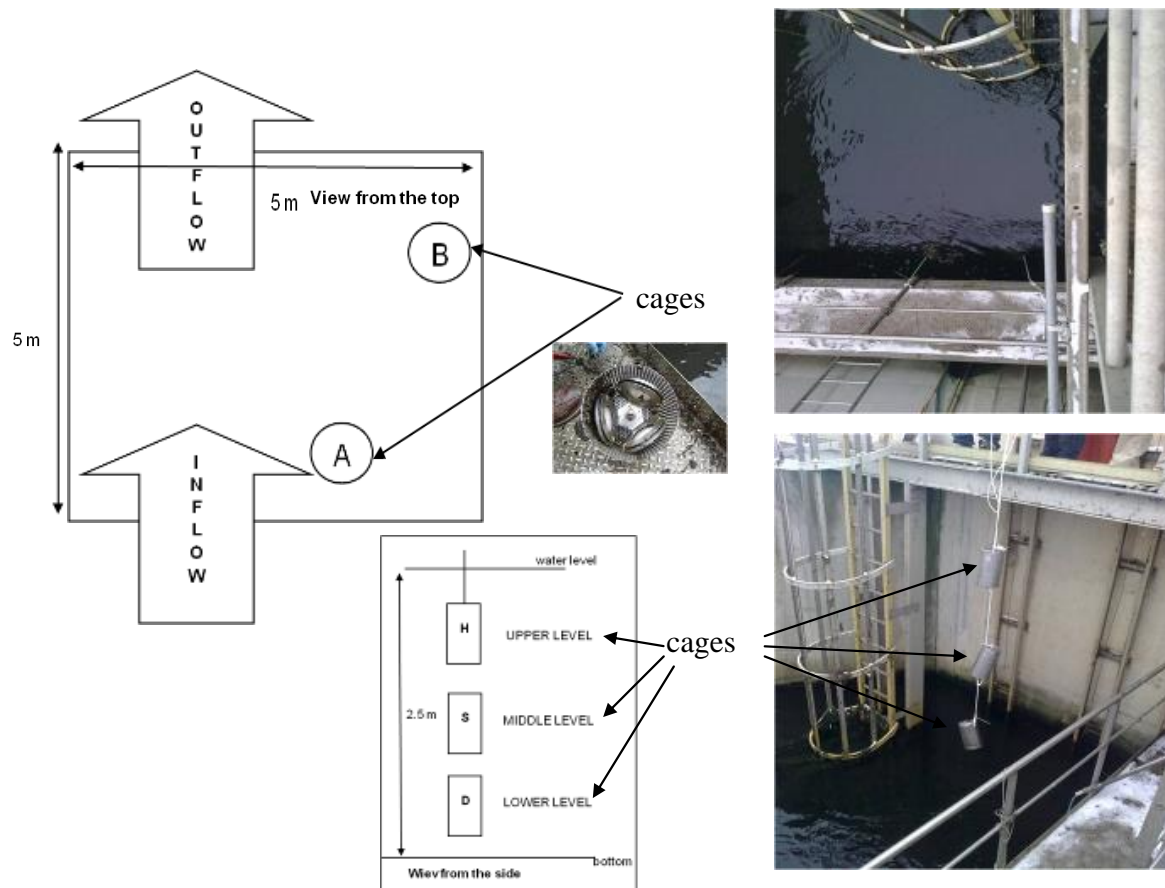


Figure 7 Sampling homogeneity test using POCIS samplers. Five standard POCIS sampler deployment cages containing 3 POCIS (with Oasis HLB adsorbent) each were deployed at various positions (2 positions and 3 depths) in the outflow object of the WWTP in Brno Modřice.

Data for compounds are reported where levels were higher than limit of quantification (LOQ). Blank samplers contained concentrations below method LOQ for all analysed compounds. Graphs in Figure 8 are comparing individual cages for different compounds (ng/sampler).

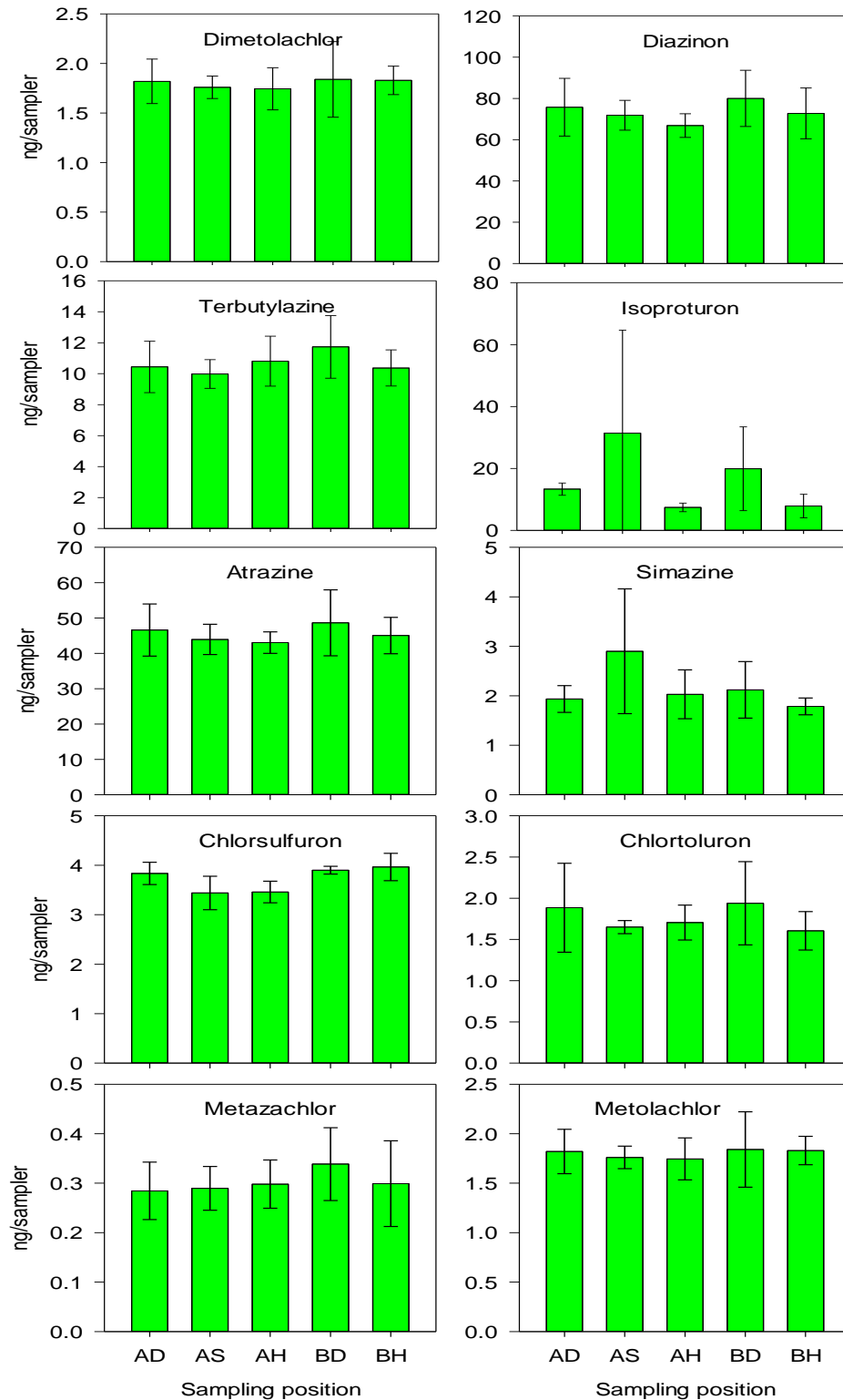


Figure 8 Mean amounts [ng/sampler] (± 1 standard deviation) of pesticides accumulated in triplicate POCIS samplers placed in 5 deployment cages at various positions (2 positions and 3 depths) in the outflow object of the WWTP in Brno Modřice. The various sampling coordinates are outlined in Figure 7 (e.g. AD means horizontal position A and vertical position D).

The results of the homogeneity test were following:

1. Data were normally distributed, with equal variance, with exception of isoproturon. There was a high variability of isoproturon even in parallel samples from the same cage which we cannot explain.
2. The coefficient of variation for the complete dataset for most compounds was less than 20%, with exception of simazine (33%) and isoproturon (>100%). The total coefficient of variation in the final result (CV^2_{total}) is made up of 2 contributions. One is from variation in the composition of the laboratory samples due to the nature of the sorbent material and the sampling procedures used (CV^2_{sample}). The other ($CV^2_{analysis}$) is from the analysis of the samples carried out in the laboratory:

$$CV^2_{total} = CV^2_{sample} + CV^2_{analysis} \quad (\text{Equation 1})$$

The CV of the instrumental analysis of standard solutions of pesticides was ca 5%. The CV of triplicate samples exposed within an individual cage (excluding simazine and isoproturon) was less than 18%. This is a reasonable precision when considering that it includes variability originating from both sampling (within the same cage) and sample analysis.

3. The variability of the amount of analytes in POCIS within individual deployment cages was mostly comparable or even higher than the variability of calculated from the means in the five cages (Table 11).
4. . The test results indicate that if samplers are deployed in the same type of deployment cage, location in the outflow tank within the tested zone did not have an effect on their performance higher than the variance of the analysis of sample replicates in the laboratory. At least not for the compounds under investigation.

Table 11 Comparison of the variability of measured pesticide amount in POCIS within individual deployment cages with the variability of the mean analyte amount determined in the five deployment cages.

Compound	Mean CV within cages	Mean CV between cages
Atrazine	13%	4%
Chlorsulfuron	6%	6%
Diazinon	14%	6%
Simazine	24%	18%
Dimethachlor	8%	10%
Metolachlor	12%	2%
Isoproturon	51%	56%
Metazachlor	21%	6%
Terbutylazine	14%	6%
Chlortoluron	17%	7%

8.4 Sampler exposure

Samplers were exposed in 3 subsequent sampling campaigns. The timeline of the sampler field exposures for the 7 investigated compound groups is shown in Figure 9.

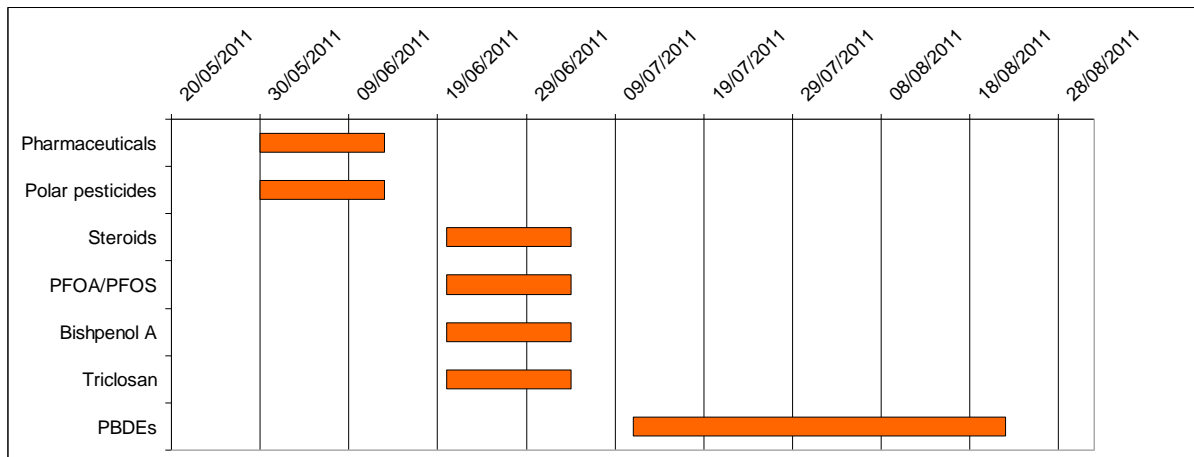


Figure 9 Exposure of samplers for different compound classes.

8.5 Field parameters

Data on several parameters of sampled water were provided by the WWTP operator. Those included water discharge, temperature, suspended solids, pH, conductivity and TOC (Figure 10-15)

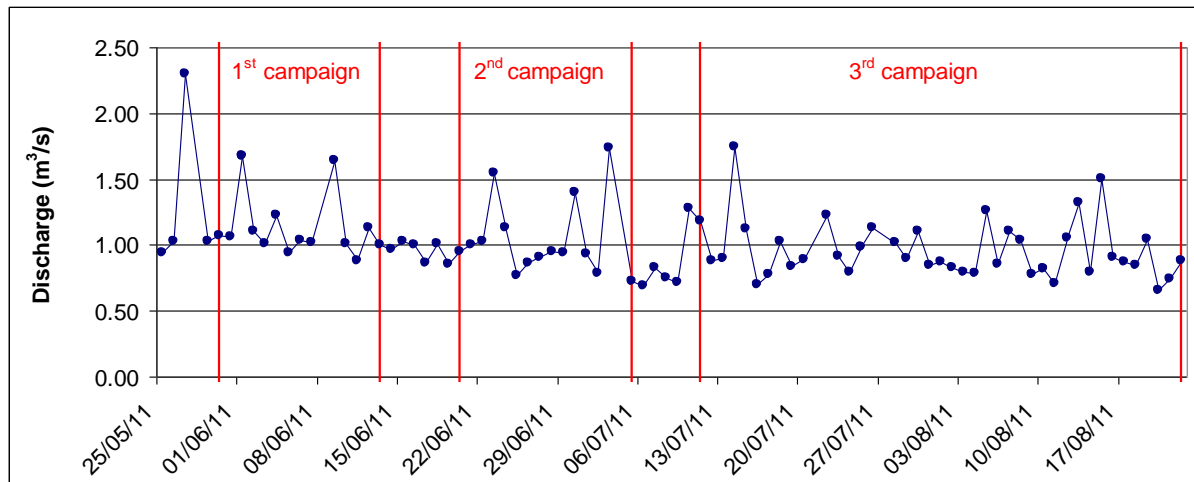


Figure 10 Water discharge.

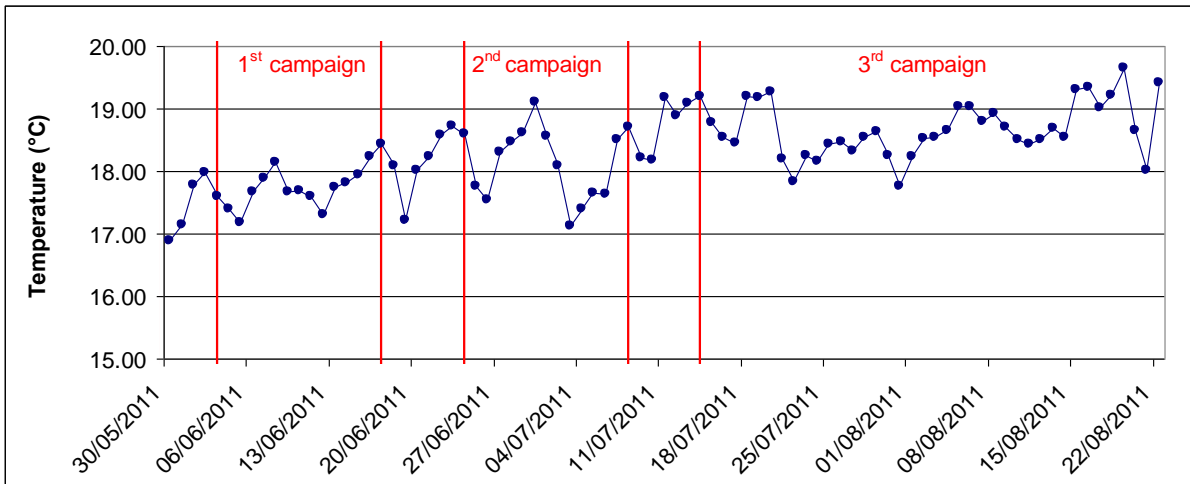


Figure 11 Water temperature.

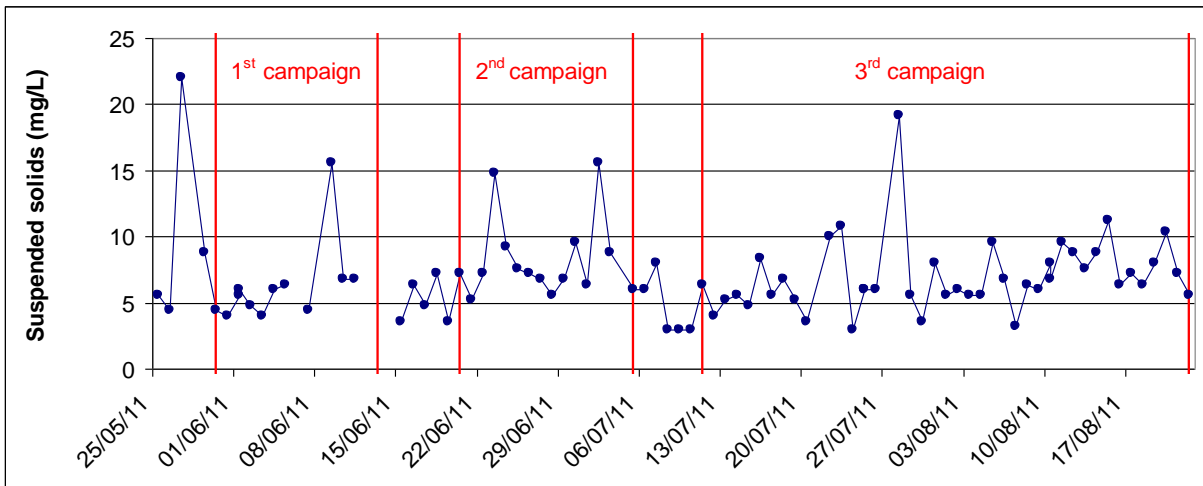


Figure 12 Suspended solids in water samples.

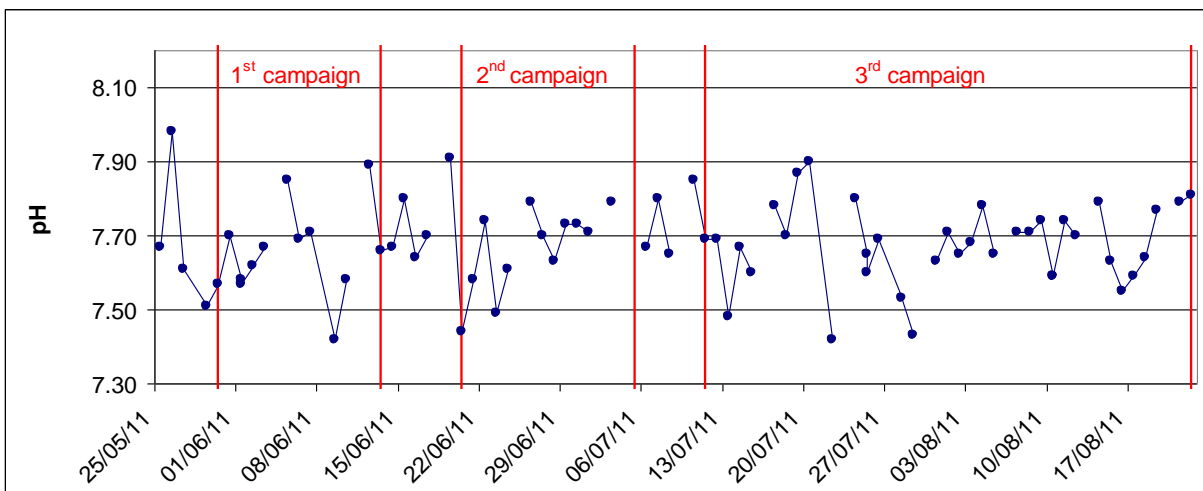


Figure 13 pH in water samples.

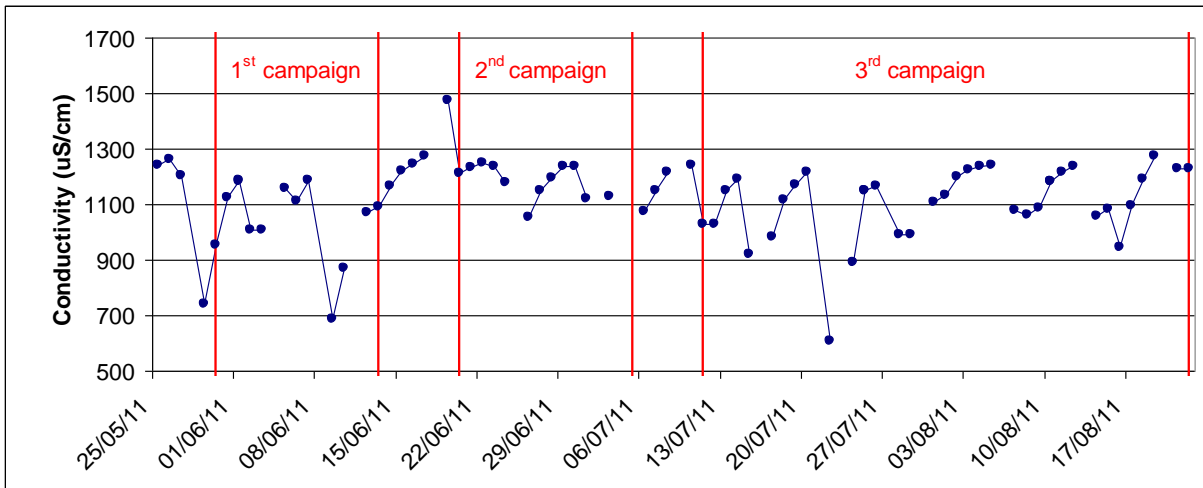


Figure 14 Conductivity in water samples.

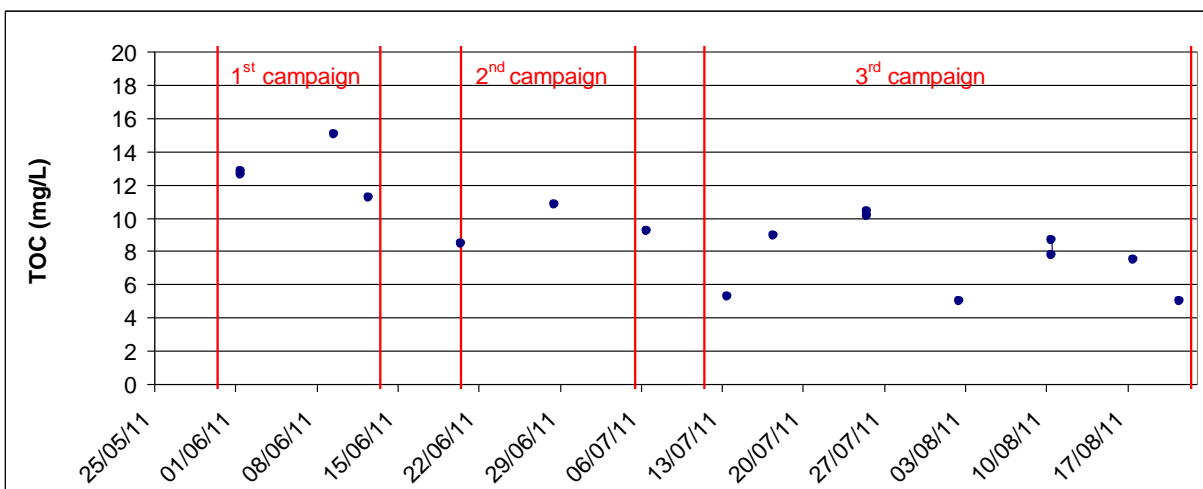


Figure 15 Total organic carbon in water samples.

8.5.1 Current velocities

On 1.6.2011 measurement of local current velocities was performed using a hand held Flow Tracker P3661. Current velocities were measured at several places in the discharge basin at 3 depths (0.1, 0.5 and 1 m) below the water surface. Flow velocities ranged from 2×10^{-4} to 0.36m/s and differences in flow condition were observed in different parts of the system. These may have fluctuated during the sampler exposure, depending on discharge conditions and other effects such as the observed massive growth of green filamentous algae that adhered close to water surface to the ropes with deployed samplers. Samplers were deployed in a way that extreme flow conditions were avoided (e.g. positioning of samplers directly in front of the discharge pipe was avoided). Algae were regularly removed from the ropes and deployment cages. Participants were informed about the coordinates of their sampler in the exposure system and the approximate local flow velocities were provided together with other supporting field parameters. In most cases participants used special deployment devices to buffer potential effects of water currents. Uniform deployment devices were applied for deployment of *provided passive samplers*. Some participants applied various approaches to quantify the potential effect of flow velocity on sampler performance. These included the active pumping of water at a desired flow velocity (CFIS sampler; lab 30); application of passive flow monitors (PFM; labs 19 and 36) [29] or application of performance reference compounds (PRCs). Details can be found in Annexes.

8.6 Water sampling

An automatic water sampler (Bühler 1029, Hach Lange, Germany) collected water samples at the sampling site during entire 14 day passive sampler deployment period (in the first and second sampler deployment period). The sampling was time-proportional, not flow-proportional and followed the schemes in Figure 16 and Figure 17. Every 24 h, the sampler was programmed to collect a total of 2.5 L of water (100 ml water every hour). During collection, the 24-h water sample was evenly distributed to glass cylinders (1 L) inside the apparatus and they were kept at 4°C in the autosampler storage container.

Every 24h the collected water samples from 12x1 L autosampler cylinders were transferred to a single clean 2.5 L amber glass bottle, and this 24-h composite sample was transported on ice to the laboratory.

8.6.1 Preparation of a 7-day composite sample

Immediately after collection of a 24-h composite field sample, the glass bottle containing the 24-h composite sample was transported to laboratory, homogenized (by shaking) and filtered through a Whatman GF/F filter. Aliquots were distributed to storage bottles and stored at 4°C (pesticides, triclosan, bisphenol A, PFOA/PFOS) or frozen to -20°C (pharmaceuticals and steroids).

Every day of a 7-day sampling period, a prescribed aliquot was added to the storage bottles. Seven-day composite samples were obtained every week by applying this procedure. Extra backup field samples were stored at RECETOX until the laboratory analysis was completed. Water samples and blank samples were once per week shipped by a fast courier service from RECETOX to central laboratories for analysis.

8.6.2 Preparation of 7-day composite blank samples

In addition to field samples, blank samples were prepared using aliquots of Milli-Q water filtered daily through Whatman GF/F filter to check for potential contamination during sample treatment. Seven-day composite blank samples were obtained by applying this procedure.

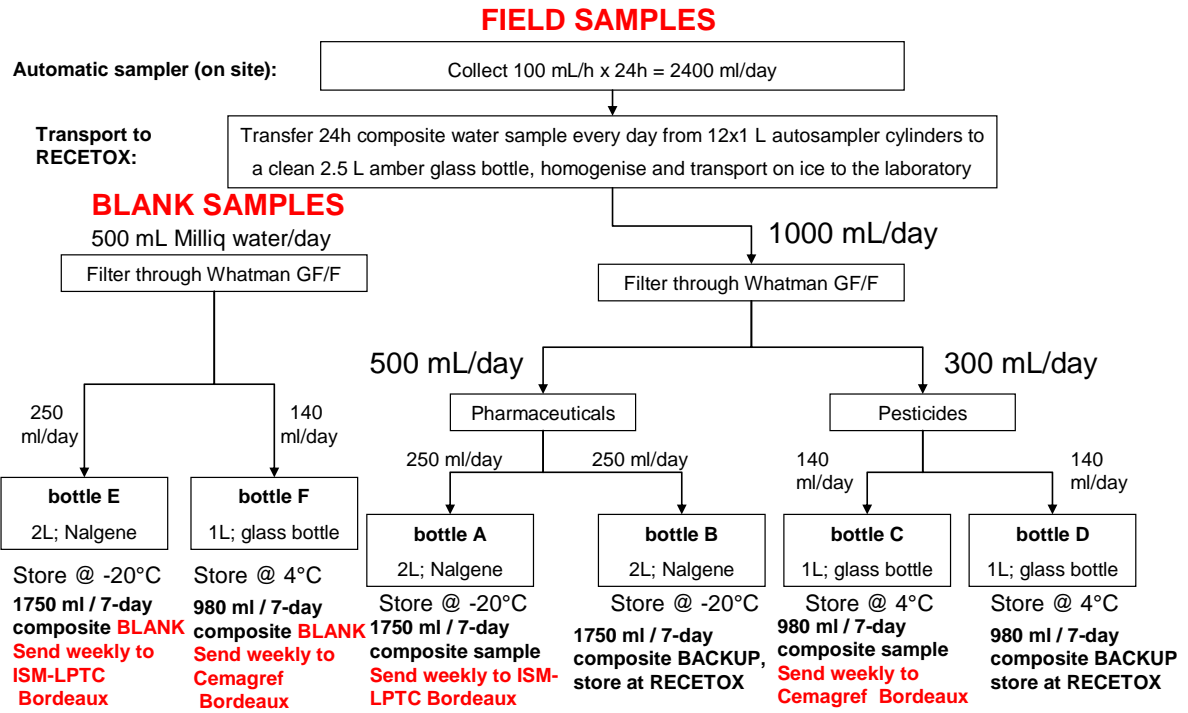


Figure 16 Water sampling scheme for obtaining 7-day composite water samples for analysis of pesticides and pharmaceuticals

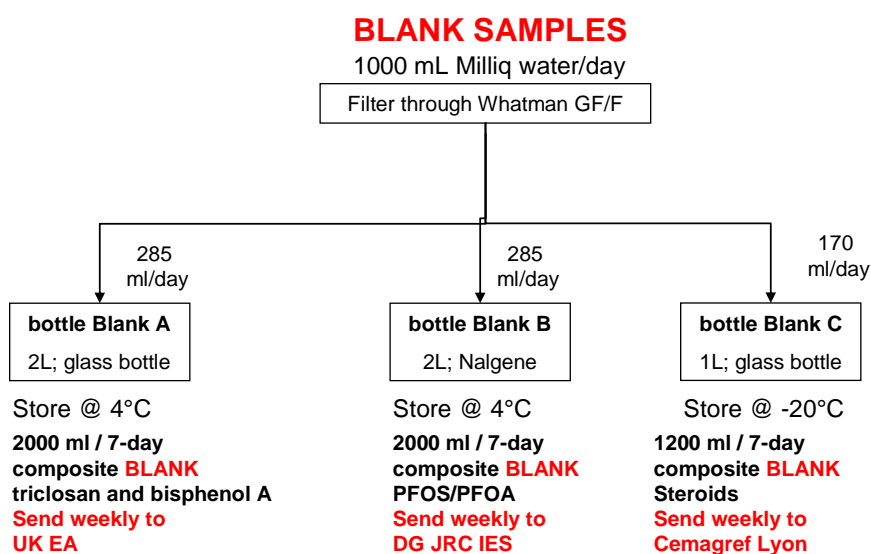
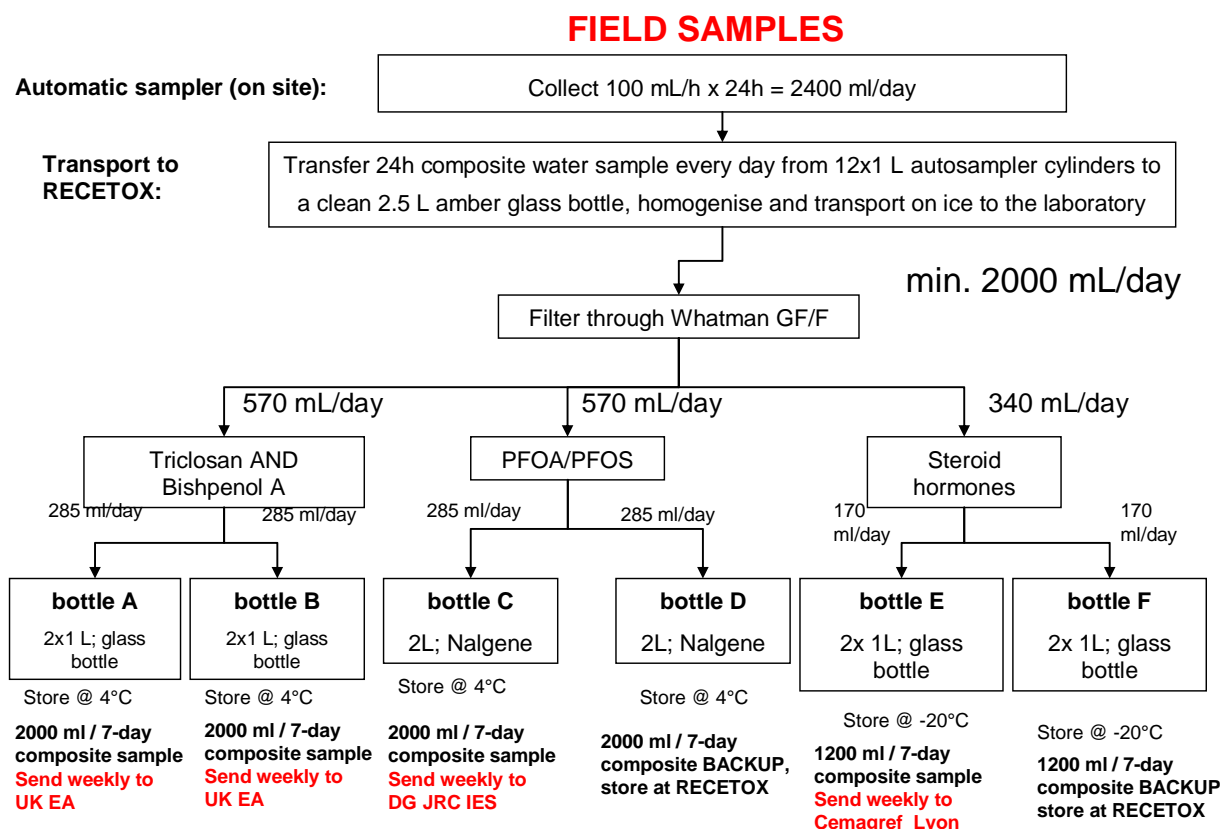


Figure 17 Water sampling scheme for obtaining 7-day composite water samples for analysis of triclosan, bisphenol A, PFOS, PFOA and steroid hormones.

9. Tested materials

9.1 Standard solutions

The standard solution of analytes was prepared by the central laboratories (Table 7), which also performed sample homogeneity tests before distribution to participants. Participants were asked to perform recommended dilution with the appropriate solvents of injection. Participants were asked not to evaporate the standard solutions. A minimum

volume of standard solution was recommended for use for each sample injection. Implementation of gravimetric controls was encouraged. Laboratories were asked to perform 4 replicates of sample injection to the instrumental system. Organisers recommend that the injections of the calibration solution is spread over the analysis sequences so that at least 4 other sample injections are made between individual injections of this solution. Distribution of standard solution to participating laboratories was performed in cooled polystyrene containers together with *provided samplers* by a fast courier service.

9.1.1 Polar pesticides

1 ml of standard solution mixture in amber glass vials with a screw cap, containing 2 µg/mL in acetone of each individual compound, was distributed to participants. Reference concentration of each analyte with associated expanded uncertainty is show in Table 12.

Table 12 Reference concentration of polar pesticides in distributed standard solution, stated by the central laboratory.

CAS	Compound	Standard solution	units	Expanded uncertainty (k=2)	% CV
1912-24-9	Atrazine	1.37	ug/mL	0.29	21%
10605-21-7	Carbendazim	1.85	ug/mL	0.34	18%
6190-65-4	Desethylatrazine	1.88	ug/mL	0.29	15%
30125-63-4	Desethylterbutylazine	2.00	ug/mL	0.22	11%
330-54-1	Diuron	2.76	ug/mL	0.43	16%
87392-12-9	S-metolachlor	1.91	ug/mL	0.17	9%
5915-41-3	Terbutylazine	1.76	ug/mL	0.23	13%

Table 13 Reference concentration of pharmaceuticals in distributed standard solution, stated by the central laboratory.

CAS	Compound	Standard solution	units	Expanded uncertainty (k=2)	% CV
29122-68-7	Atenolol	2.65	ug/mL	0.14	5%
298-46-4	Carbamazepine	2.14	ug/mL	0.13	6%
15307-86-5	Diclofenac	2.79	ug/mL	0.13	5%
15687-27-1	Ibuprofen	3.61	ug/mL	0.12	3%
22204-53-1	Naproxen	2.40	ug/mL	0.13	5%
439-14-5	Diazepam	2.41	ug/mL	0.21	9%
28981-97-7	Alprazolam	3.75	ug/mL	0.62	17%
29122-68-7	Ketoprofen	7.13	ug/mL	0.22	3%

9.1.2 Pharmaceuticals

1 ml of standard solution mixture in amber glass vials with a screw cap, containing 2 µg/mL in acetone of each individual compound, was distributed to participants. The reference concentration of each analyte with associated expanded uncertainty is shown in Table 13.

9.1.3 Steroid hormones

1 ml of standard solution mixture in amber glass vials with a screw cap, containing 20 ng/mL in acetone of each individual compound, was distributed to participants. The reference concentration of each analyte with associated expanded uncertainty is shown in Table 14.

Table 14 Reference concentration of steroid hormones in distributed standard solution, stated by the central laboratory.

CAS	Compound	Standard solution	units	Expanded uncertainty (k=2)	% CV
57-91-0	17-alpha-Estradiol	0.0214	ug/mL	0.0024	11%
57-63-6	17-alpha-Ethinylestradiol	0.0158	ug/mL	0.0012	8%
50-28-2	17-beta-Estradiol	0.0205	ug/mL	0.0029	14%
82115-62-6	Estriol	0.0214	ug/mL	0.0032	15%
50-27-1	Estrone	0.0206	ug/mL	0.0016	8%

9.1.4 Brominated diphenyl ethers - PBDEs

2 mL amber glass ampoules were used for the standard dissolved in cyclohexane. The reference concentration of each analyte with associated expanded uncertainty is shown in Table 15.

Table 15 Reference concentration of PBDEs in distributed standard solution.

CAS	Compound	Standard solution	units	CV Certified by supplier
41318-75-6	BDE 28	20	ng/mL	±10%
5436-43-1	BDE 47	71	ng/mL	±10%
60348-60-9	BDE 99	100	ng/mL	±10%
189084-64-8	BDE 100	20	ng/mL	+10%
68631-49-2	BDE 153	16	ng/mL	±10%
207122-15-4	BDE 154	15	ng/mL	±10%

9.1.5 Fluorinated surfactants

1 ml of standard solution mixture in 2 mL amber glass vials with a screw cap, containing 50 ng/mL in methanol of each individual compound, was distributed to participants. The reference concentration of each analyte with associated expanded uncertainty is shown in Table 16.

Table 16 Reference concentration of fluorinated surfactants in distributed standard solution, stated by the central laboratory.

CAS	Compound	Standard solution	units	Certified by supplier
335-67-1	PFOA	0.048	ug/mL	±10%
1763-23-1	PFOS	0.050	ug/mL	±10%

9.1.6 Bisphenol A and Triclosan

1 ml of standard solution of each compound in amber glass vials with a screw cap, containing cca. 100 ng/mL in acetone was distributed to participants. The reference concentration of each analyte with associated expanded uncertainty is shown in Table 17.

Table 17 Reference concentration of bisphenol A and triclosan in distributed standard solutions, stated by the central laboratory.

CAS	Compound	Standard solution	units	Expanded uncertainty (k=2)	% CV
80-05-7	Bisphenol A	0.110	ug/mL	0.0035	3%
3380-34-5	Triclosan	0.108	ug/mL	0.0030	3%

9.2 Provided samplers

Variability in analytical results increases when samples contain natural matrix, such as co-extracted organic macromolecular material. The analysis of the *provided samplers* (3 replicates + field blank) by participating laboratories allowed an inter-calibration of the analysis of passive samplers and an estimate to be made of the contribution of the analytical (sampler extraction + analysis) component to total variability of PS process.

The samplers to be "*provided samplers*", were exposed to water at the sampling site together with *participant samplers*. Following exposure, each sampler was labelled with a number that enabled to identify exposure conditions including location in the exposure system.

9.2.1 POCIS - provided samplers for polar compounds

The *provided sampler* applied for pesticides, pharmaceuticals, steroid hormones, fluorinated surfactants, bisphenol A and triclosan was a POCIS sampler with a standard configuration (200 mg of OASIS HLB sorbent fitted with polyethersulphone membrane with 0.1 µm pore size and 45.8 cm² surface area), prepared by the central laboratory (

Table 7). For the study with pesticides the adsorbent was spiked with app. 4 µg/g of D5-desisopropylatrazine (D5-DIA) before sampler assembly.

Following exposure, adsorbent material was separated from each sampler by the study organiser in the laboratory, filled into an empty SPE cartridge, dried and the sorbent mass was recorded. Samplers were randomised before distribution to participants and each individual POCIS from the triplicate analysed by each laboratory originated from a different location in the sampled object. Each participant laboratory received sorbent material from 3 replicate samplers + 1 field blank. SPE cartridges with adsorbent were distributed to study participants by courier in cooled containers.

Participants were asked to report results in ng/g of sorbent. For calculation of this concentration the mass of sorbent written on the SPE cartridge was applicable. In case of pesticide analysis, participants were also asked to report PRC data (DIA-d5) in ng/g. In this case the true concentration of DIA-d5 was not considered important but the ratio between the amount in exposed and unexposed sampler, i.e. sample and field blank.

Participants were also asked to report an estimation of the freely dissolved concentration in the water phase (C_w) in ng/L. The procedure to calculate this concentration was not prescribed and participants were asked to use methods that they routinely apply for evaluation of data from POCIS or use relevant up-to-date information from scientific literature. For the calculation of procedure applied, participants were asked to give details including references to calibration data (sampling rates and distribution coefficients) in the reporting form. The reported information is given in Annex I.

9.2.2 Silicone rubbers - provided samplers for PBDEs

The *provided sampler* applied for PBDEs was made of Altesil[®] silicone rubber. Each sampler consisted of 3 sheets (90 x 55 x 0.5 mm) with approximate mass of 8.91 g. The exact dry weight of each sampler was determined by participants after extraction. The samplers were spiked with PRCs (D10-biphenyl, PCBs: CB001, CB002, CB003, CB010, CB014, CB021, CB030, CB050, CB055, CB078, CB104, CB145, CB204) during preparation. "*Provided samplers*" were exposed to water at the sampling site for 42 days from 11.7.-22.8., together with *participant samplers*. Samplers were randomised before distribution to participants and each sampler consisted of 3 sheets randomly taken from a different location in the sampled object.

Each participant laboratory received from the organiser *provided samplers*; 3 replicate field exposed samplers + 1 field blank + 1 field blank spiked by a uniform concentration of BDEs.

Participants were asked to report results in absolute ng/sampler. Participants were also asked to report PRC data. The true concentration of PRCs was not relevant but the ratio between the amount in exposed and unexposed sampler, i.e. sample and field blank. A qualitative standard was supplied to help participants setting up the instrumental method. PRC data were reported in amount/sampler

Participants were also asked to report an estimation of the freely dissolved concentration in the water phase pg/L. The procedure to calculate this concentration was not prescribed and participants were asked to use methods that they routinely apply for evaluation of data from silicone rubber samplers or use relevant up-to-date information from scientific literature. For the calculation procedure applied, participants were asked to give details including references to calibration data (sampling rates and distribution coefficients) in the reporting form.

9.3 Participant samplers

Participants were encouraged to deploy passive samplers (3 replicates and one field blank) that they usually apply in sampling of target compounds. *Participant samplers* were exposed to water at the sampling site together with *provided samplers* according to time schedule given in 8.4. Following exposure, each sampler was handled and stored

according to participant instructions and sent to participant laboratory by courier in cooled containers.

In the reporting form participants described sampler specification, transport and storage, field deployment and recovery, and aspects of analytical and data evaluation (especially calculation of water concentration). Laboratories were asked to use their validated routine methods and procedures to analyse samplers. They were asked not to correct data for blanks except for the calculation of freely dissolved concentrations. For estimation of the freely dissolved concentration in the water phase, laboratories were asked to give details including references to applied procedures and calibration data (sampling rates and partition coefficients) in the report form. Analytes were reported as ng/sampler; ng/cm² of sampler surface area; ng/g of sampler sorbent phase; and finally an estimation of the freely dissolved concentration in the water phase (ng/L or pg/L).

9.4 Spot samples

Despite the lack of an external reference value, water concentrations derived from passive samplers can be compared to an alternative method, which is based on analysis of weekly composite water samples, with exception of PBDEs. In contrast to passive samplers, water samples were analysed only by a single expert laboratory (Table 7). The procedure of collection and preparation of composite water samples is described in 8.6

10. Data evaluation approach

Participant data were log₂ transformed for statistical treatment, assuming a log-normal distribution. For data presentation in graphs, results were back-transformed to original values. Box-and-whisker plots, bar graphs and biplot graphs were used to display participant data. The graphs have equal design for all compound classes and are described just once this chapter not to repeat unnecessary text.

10.1 Box-and-whisker plots

Each of the following chapters discussing the results of the individual analyte groups starts with a general view on the **overall variability of all data** (no outliers rejected) in the form of box-and-whisker plots. The box in the plot comprises the data between the 25th and the 75th percentile with the median of the data shown by the horizontal line inside the box. The ends of the whiskers represent the 10th and the 90th percentile. The plots have a logarithmic scale to show upward and downward variation with equal weight. For all compounds, groups of four graphs were made showing:

1. The results obtained from the analyses of standard solution with the crosses showing the concentration declared as reference value by the central laboratory. The uncertainty ($k=2$) is superimposed on the graph as a blue line error bar.
2. The data obtained from analyses of the *provided sampler* (NPS) expressed as uptake per unit of surface. For NPS uptake is assumed to be integrative and thus proportional to the surface area.
3. Aqueous phase concentrations derived from the *participant`s samplers*. The results from spot samples are drawn as blue crosses and the limit of quantification as a red cross.
4. Ratios between aqueous concentrations derived from *provided sampler* and *participant`s sampler*.

10.2 Bar graphs

Bar graphs were used for comparison of results obtained by individual participating laboratories. Three bar charts that compare results obtained by individual laboratories are shown for every compound. These represent 3 matrices analysed: the standard solution, the *provided sampler* (NPS, expressed as uptake per unit of sampler surface

area) and the *participant Sampler* (PPS, expressed as calculated water concentration), respectively. Since results of the latter two sample types could be linked neither to a standard nor to and an externally assigned value, a comparison was only made among the participating laboratories, showing the deviation of their own result from the median of all reported data.

The number on the x-axis identifies the laboratory. In contrast to a traditional proficiency testing scheme approach, results obtained by laboratories are not ranked from the lowest to the highest value, but the position of data by a particular laboratory on the x-axis of the bar graph is kept fixed. This allows an easy comparison of results obtained by the laboratory for a particular compound across different matrices (standard solution, *provided sampler*, *participant sampler*).

Before plotting, identifying outliers, and calculation of the standard deviations the data were log transformed (base 2). Log base of 2 was selected since such scale allows a good orientation in the data – one tick increase on the y-axis represents a factor 2 increase in the displayed value that was back transformed to a regular number. Data on the y-axis is always centred to the median of all participant's data. The bars represent the mean values of the replicate (4 for the analysis of standards and 3 for the analysis of samplers) determinations in a particular matrix by an individual laboratory. Consequently, the length of the bar represents the deviation of the laboratory's mean result from the median. The median is selected is because a standard or externally assigned "reference" value was not available and a comparison was only made between the participating laboratories.

The repeatability (within laboratory variability) of participant data is indicated by error bars. The error bars are calculated from replicate determinations and represent ± 2 times the standard deviation.

High outliers were identified as values larger than the sum of the 75% percentile and 1.5 times the inner quartile range (the inner quartile range is the 75th minus the 25th percentile). Values lower than the 25th percentile subtracted by 1.5 times the inner quartile range are also marked as outliers. Outliers are coloured orange in the bar charts.

The reproducibility (between laboratory variability) of data is displayed as horizontal dashed lines above and below the median line, which represent ± 2 times the standard deviation, after excluding outlier values.

In the graph showing results of the standard solution analysis, reference values of concentrations (determined by central laboratories) are shown in the bar chart as a blue horizontal line. The dotted blue horizontal lines cover the interval of reference value \pm declared expanded uncertainty with the coverage factor $k=2$.

With exception of PBDEs, central laboratories measured concentration of analytes in 2 weekly composite samples of water (water samples). The mean of the 2 composite samples is displayed as a blue dotted horizontal line. In addition, the limit of detection in water samples is displayed as a red horizontal line.

Statistical data are displayed left of the bar graphs. These include the median (*Median*), standard deviation (s)², geometric mean (*Geomean*), number of data points (n) of all participant data and the number of outlier values (*Outliers*), and a standard deviation of data excluding those outlier values (*s excl. outl*), respectively. For the standard solution, the reference value of the concentration (*Refvalue*) and associated expanded combined uncertainty with coverage factor 2 (*Exp. unc.*) are displayed. Next to the participant

² Errata: In statistical data that are displayed left of the bar graphs showing results for the analysis of the standard solution, (s) values shown below the lines (*Median*) show the relative standard deviation. The value of standard deviation can be obtained by multiplying this value with the value of (*Median*).

sampler bar graph (showing calculated water concentration), analysis results are shown of the two 7-day composite water samples (*water samples; Period 1 and Period 2*) and the spot sample detection limit (*LOD*), respectively.

Meaning of various objects and symbols in the graph is shown in Figure 18.

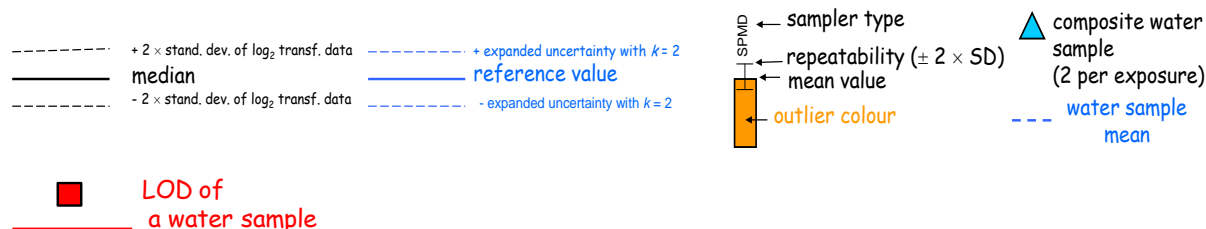


Figure 18 Explanation of objects and symbols in bar graphs that display results of analysis of standard solution, provided and participant sampler by participating laboratories.

10.3 Biplot graphs

A scatter biplot graphical method (sometimes referred to as “Youden plot”) was applied for analysis of inter-laboratory data, where laboratories have analysed the compounds of interest in 2 samples (the *participant sampler* and the *provided sampler*). The plot visualises the between-laboratory variability along the diagonal line and deviations from the line indicate differences within laboratory or, only for the left plot, differences in uptake rate between *provided* and *participant sampler* (possible if types were different). In other words, points that lie near the equality line (the 45 degrees line), but far from each other, indicate systematic error. Points that lie far from the equality line indicate random error or differences between *provided* and *participant sampler* (only left biplot).

Most of the laboratories that participated in the exercise analysed the target compounds in 2 types of samplers: the *participant sampler* and the *provided sampler*. Data obtained by these two methods can be directly compared, assuming that certain simplifying criteria are fulfilled.

1. The samplers differed in the surface area and the mass of sorbent material applied. In most cases the sampler uptake capacity was high and an integrative uptake over the 2 weeks of exposure can be assumed. This implies that the mass of analyte found in the sampler depends solely on the sampling rate and not on the sampler uptake capacity. In other words, sampling is considered to be integrative and the samplers far from the thermodynamic equilibrium with the sampled water.
2. The sampling rate is a product of mass transfer coefficient and the active sampler surface area. In most samplers applied the main barrier to mass transfer is the water boundary layer and similar mass transfer coefficients are expected.

Thus, it is reasonable to directly compare surface specific uptake (ng/cm^2) in two different samplers analysed by the same laboratory. Furthermore, water concentration calculated from analyte uptake in different samplers should ideally result in the same value.

The axes in the biplot are drawn on the same log 2 scale: one unit on the x-axis (ng/cm^2 or ng/L) has the same length as one unit on the y-axis. Each point in the biplot corresponds to the results of one laboratory and is defined by the *provided sampler* data on the horizontal axis and the *participant sampler* data on the vertical axis, respectively. In addition, analyte concentrations determined in 2 weekly composite water samples by central laboratories are shown on the biplot as blue triangles and the limit of quantification in spot water samples is plotted as a red square. A one to one reference

line (the 45 degrees line) is drawn to show the equality of the 2 values. Labels of points identify the type of *participant passive sampler* according to Table 18 unless the participant sampler had the same design as the sampler provided by the organiser (POCIS for polar compounds or silicone rubber for PBDEs, respectively). In such case the points are not labelled.

10.4 Expression of data variability as coefficient of variation

Variability of participant data at different procedural levels is expressed as coefficient of variation (CV). CV was estimated from standard deviations of \log_2 transformed data according to the properties of the log-normal distribution [30].

$$CV = \ln 2 s_{\log 2} \quad (\text{Equation 2})$$

Where $s_{\log 2}$ is the standard deviation of $\log 2$ transformed data without outliers.

Within laboratory variability (repeatability) was determined from replicate determinations of analytes in different matrices analysed: standard solution ($n = 4$), participant sampler ($n = 3$), *provided sampler* ($n = 3$) and associated water concentration estimates ($n = 3$).

Between laboratory variability was determined from standard deviations of the mean of replicate values reported by laboratories. Outlier values were identified according to the procedure described in 10.2 and were excluded from the calculation of reported coefficients of variation.

Variability (CVs) of reported results for individual compounds at different procedure levels is presented in bar graphs (see e.g. Figure 27). The procedure levels include the analysis of standard solution, the "*participant sampler*" (PPS) and the *provided sampler* (NPS), respectively. For passive sampler results the variability is shown as that of the surface specific uptake (ng/cm^2) as well as that of the reported water concentration (ng/L), respectively.

Note that the calculated CV of surface specific uptake results (ng/cm^2) from participant sampler (PPS) may be an overestimation since the uptake per surface unit may differ between sampler types and the reported CV has not been corrected for those systematic differences.

Summary tables that report the variability range at different procedure levels for the compound groups (i.e. polar pesticides, pharmaceuticals etc.) are also provided (see e.g. Table 19).

10.5 Contribution of the calculation procedure to data variability

Besides sampling and analytical variability, the calculation of water concentration C_w from PS data contributes to the result uncertainty. In general, passive samplers for compounds under investigation in this study are considered to be integrative during the entire sampling period and linear uptake of compounds is assumed. In most cases participants applied a simple linear uptake model to calculate C_w :

$$C_w = \frac{N_{PS}}{R_S t} \quad \text{Equation 3}$$

Where N_{PS} is the amount analysed on the sampler, R_S is the sampling rate and t the deployment time. For this model, neglecting the error in t , the combined coefficient of variation can be expressed from the law of error propagation as:

$$CV_{C_w} = \sqrt{CV_{N_{PS}}^2 + CV_{R_S}^2} \quad \text{Equation 4}$$

where individual terms express coefficients of variation of the water concentration estimate (CV_{C_w}), of the analyte amount accumulated by the *provided sampler* ($CV_{N_{PS}}$) and of the sampling rate applied in calculation (CV_{R_S}), respectively. The rearranged

equation provides a formula to calculate the coefficient of variation of the sampling rates applied in calculation:

$$CV_{R_s} = \sqrt{CV_{C_w}^2 - CV_{N_{PS}}^2} \quad \text{Equation 5}$$

10.6 Sampler designs employed by participating laboratories

A wide range of passive sampler designs has been applied by the participants. Table 18 lists the main categories of sampler design which were applied and their abbreviations that are used to label them in the graphs. The details of sampling methods applied and associated aspect of sample storage, transport, extraction and instrumental analysis can be found in Annexes II, IV, VI, VIII, X, XII, XIV.

Table 18. A brief description and abbreviations of various passive sampler designs applied in the interlaboratory study

Sampler	Abbreviation
POCIS pharmaceutical version	POCIS
Empore Disk	ED
POCIS, pesticide version	POCIP
Chemcatcher (3rd generation) polar configuration	CCPOL
silicone rubber material	SR
Empore SDB-RPS with PES-Membrane (0.1µm)	EDPES
CFIS (Continuous Flow Integrative Sampler)	CFIS
BAKERBOND® Speedisk	SPEED
Polyoxymethylene sheet	POM
Modified POCIS	POCIM
standard SPMD (length 1m)	SPMD
Low density polyethylene	LDPE
membrane enclosed silicone collector (MESCO)	MESCO
non-polar Chemcatcher (3rd generation)	CCNP

11. Results

11.1 Polar pesticides

Up to 19 laboratories participated in the exercise, but the numbers varied depending on target analytes and matrices analysed. One of the laboratories (Lab 50) did not provide own samplers for the exercise and only reported results for the standard solution and the *provided sampler* using 2 different analytical methods.

Overall data variability is shown in box-and-whisker plots in Figure 19. Results for individual compounds and laboratories are displayed in bar graphs in Figure 20-26. The explanation of data projection applied is described in chapter 10.

11.1.1 Overall data variability

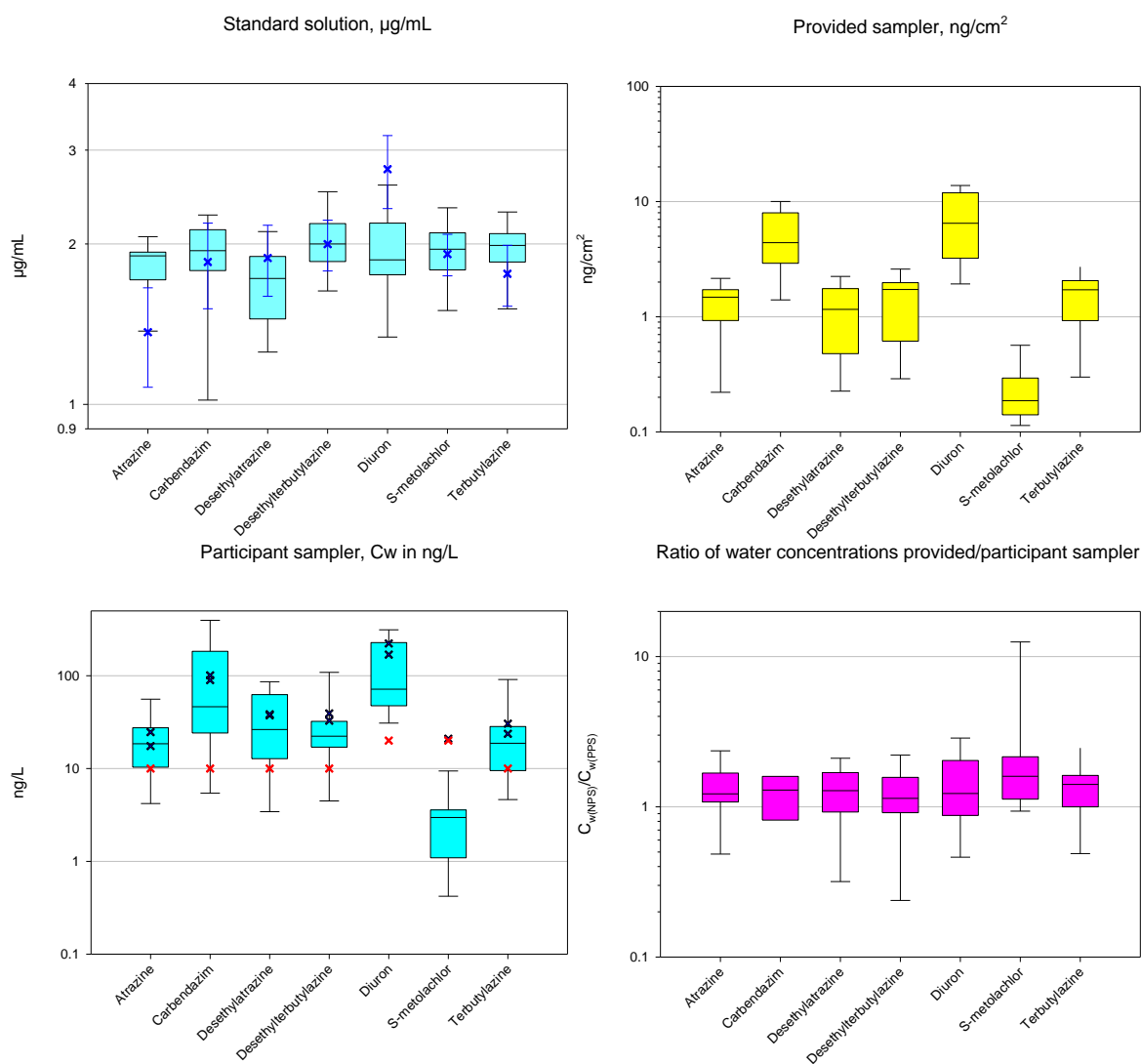


Figure 19 Concentrations of polar pesticides in various analysed matrixes: standard solution (top left), provided sampler (top right), water concentration estimated from the participant sampler (bottom left) and the ratio of water concentrations determined in provided and participant passive sampler (bottom right), respectively. Further graph explanation is given in 10.1.

11.1.2 Results by laboratories – polar pesticides

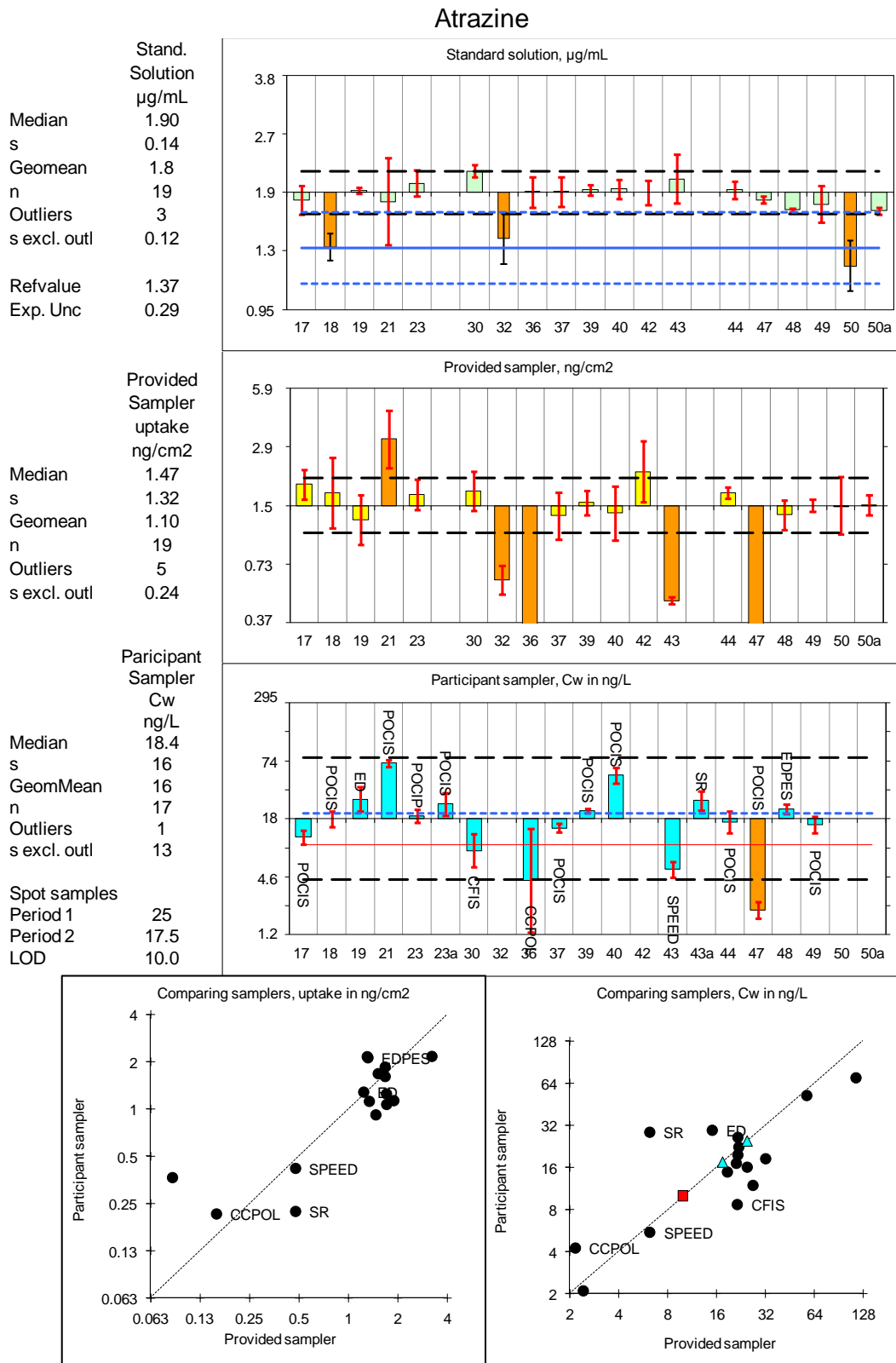


Figure 20 Results of analysis of atrazine Graph explanation is given in 10.2.and 10.3

Carbendazim

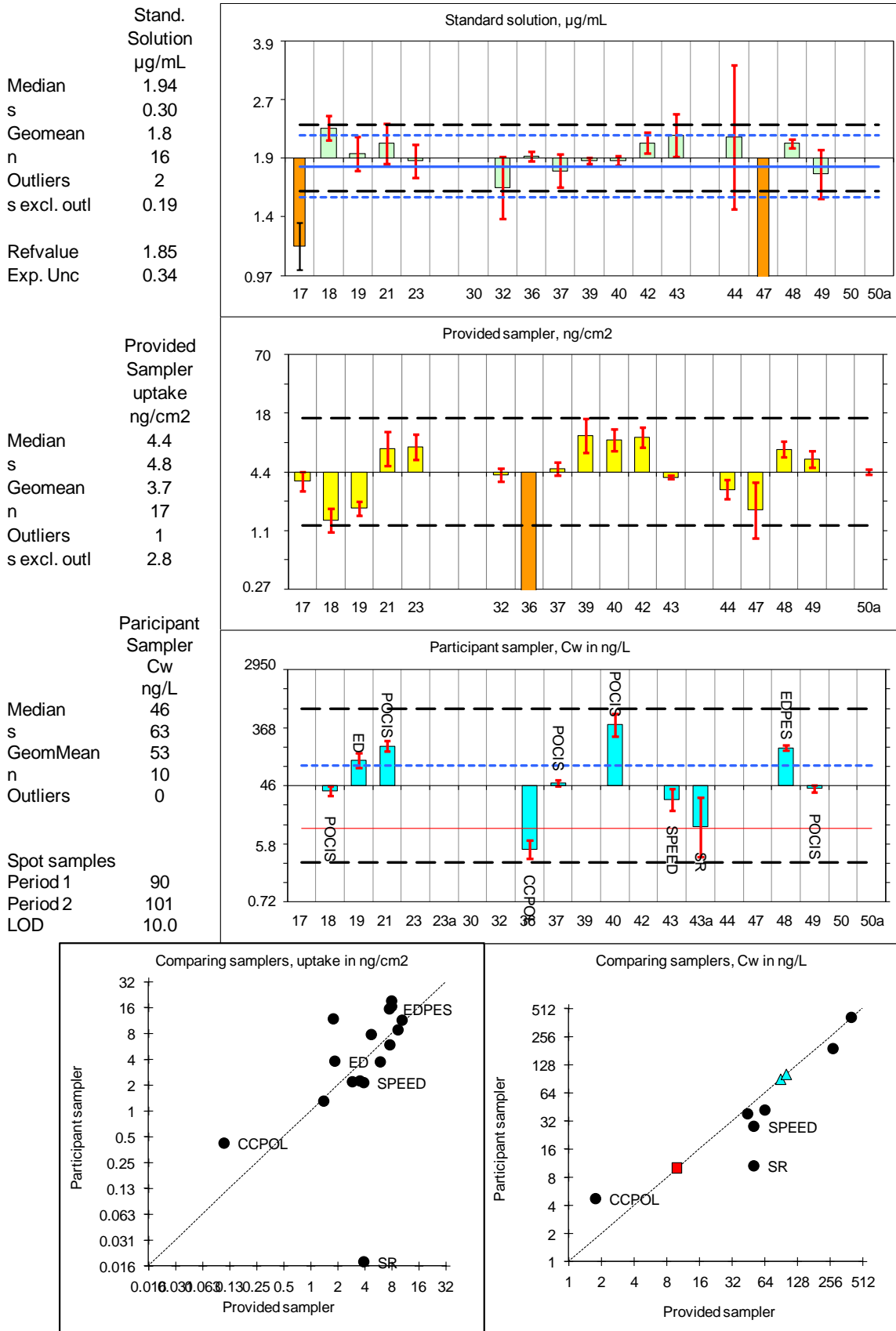


Figure 21 Results of analysis of carbendazime. Graph explanation is given in 10.2 and 10.3

Desethylatrazine

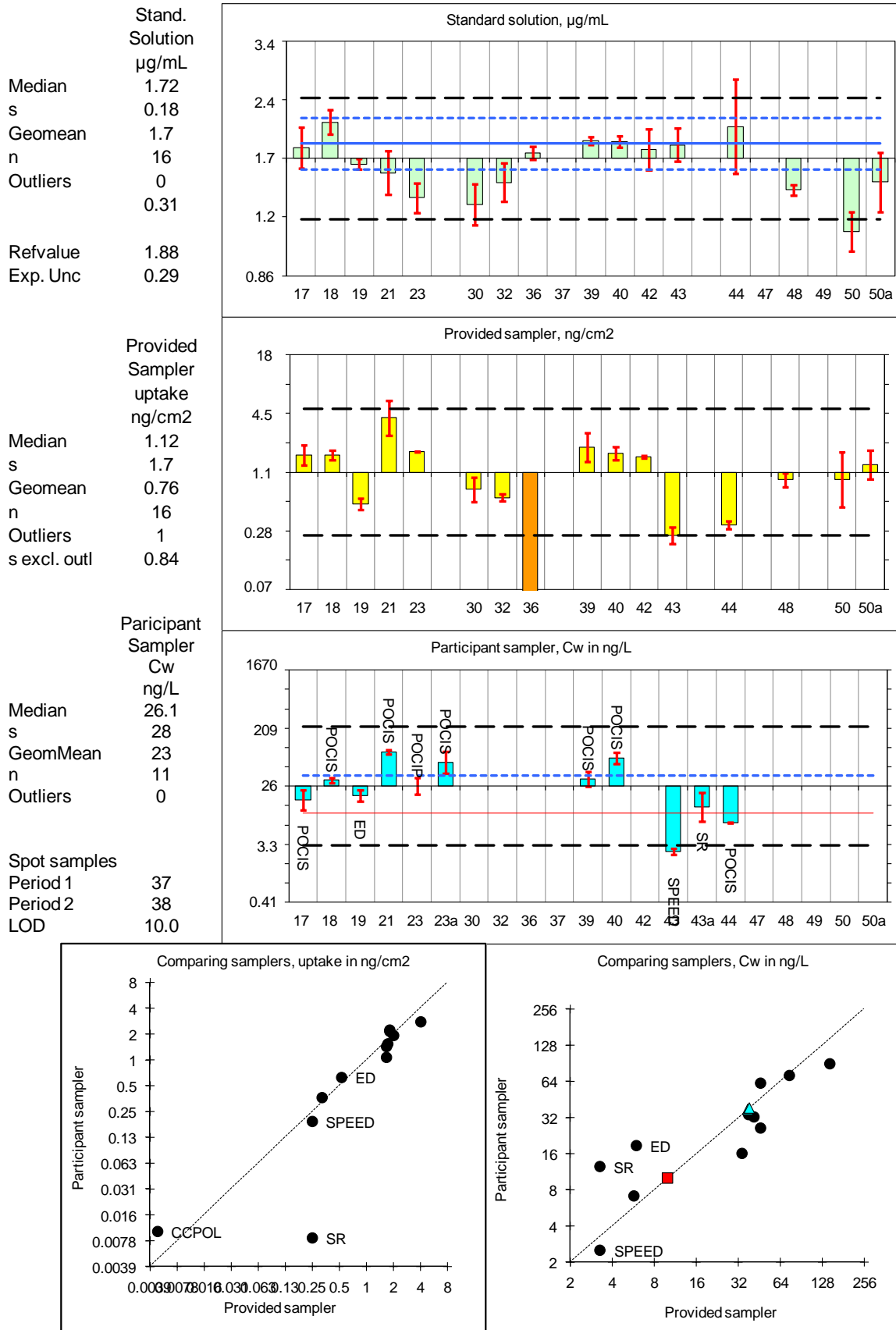


Figure 22 Results of analysis of desethylatrazine. Graph explanation is given in 10.2.and 10.3

Desethylterbutylazine

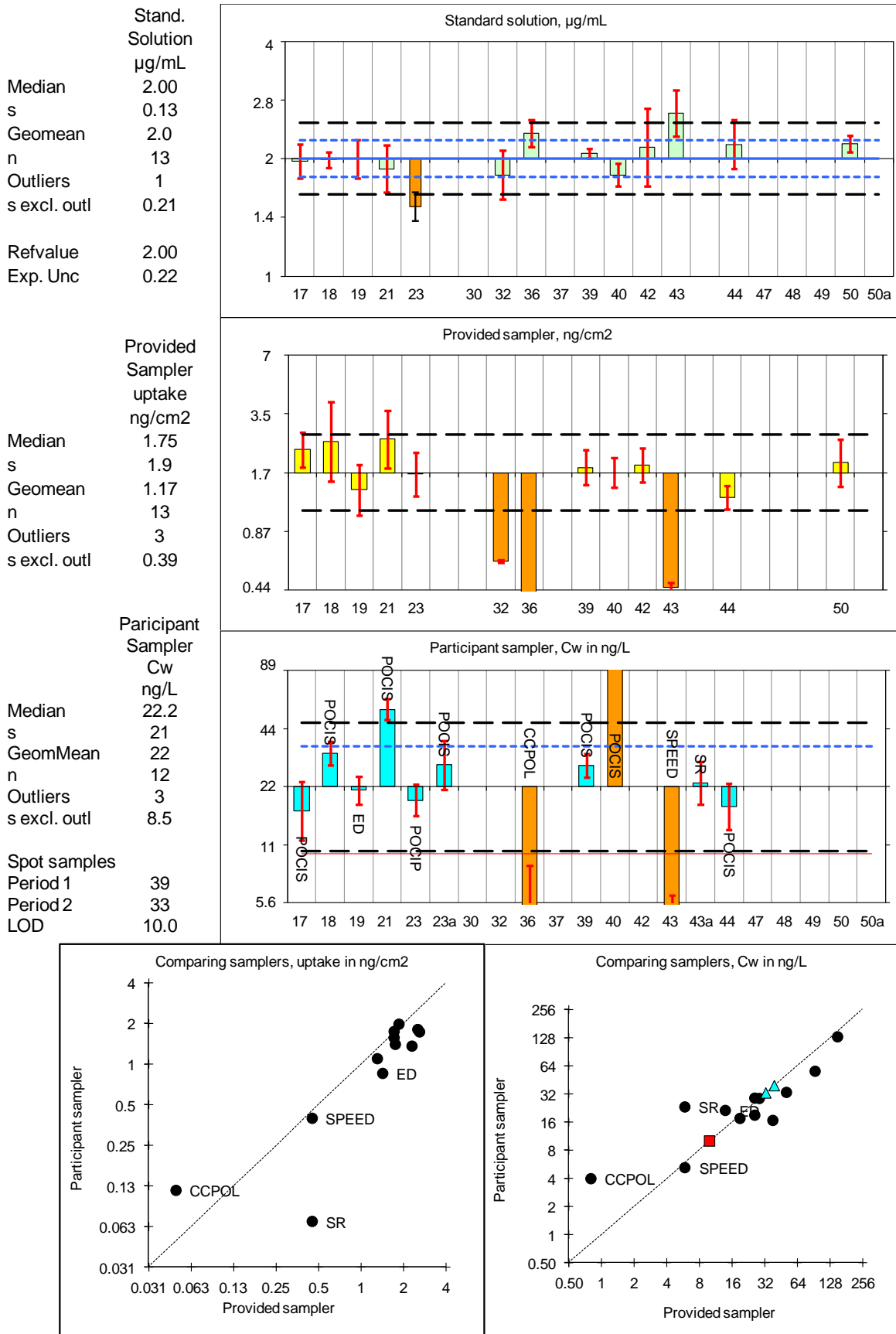


Figure 23 Results of analysis of desethylterbutylazine. Graph explanation is given in 10.2 and 10.3

Diuron

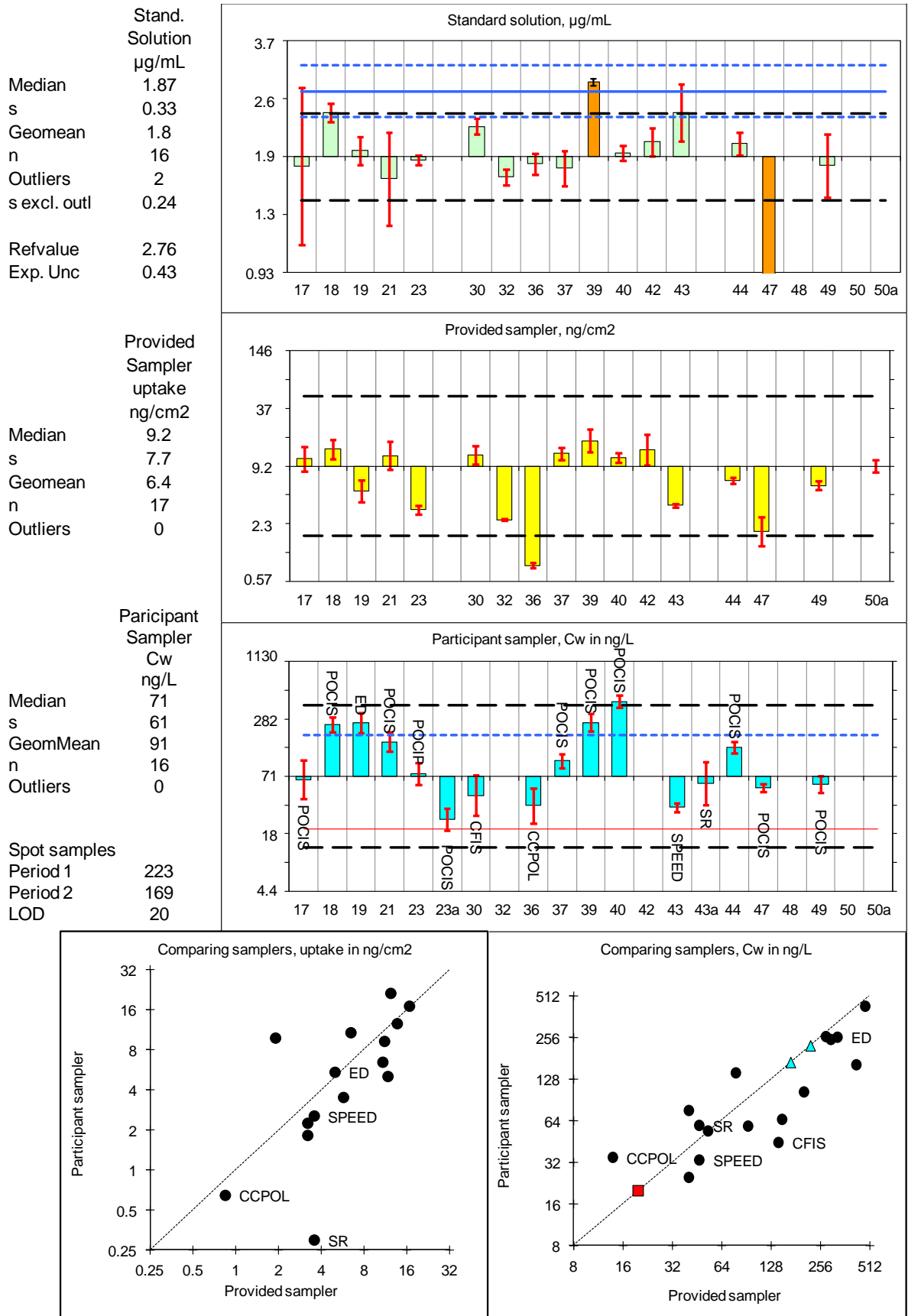


Figure 24 Results of analysis of diuron. Graph explanation is given in 10.2. and 10.3

S-metolachlor

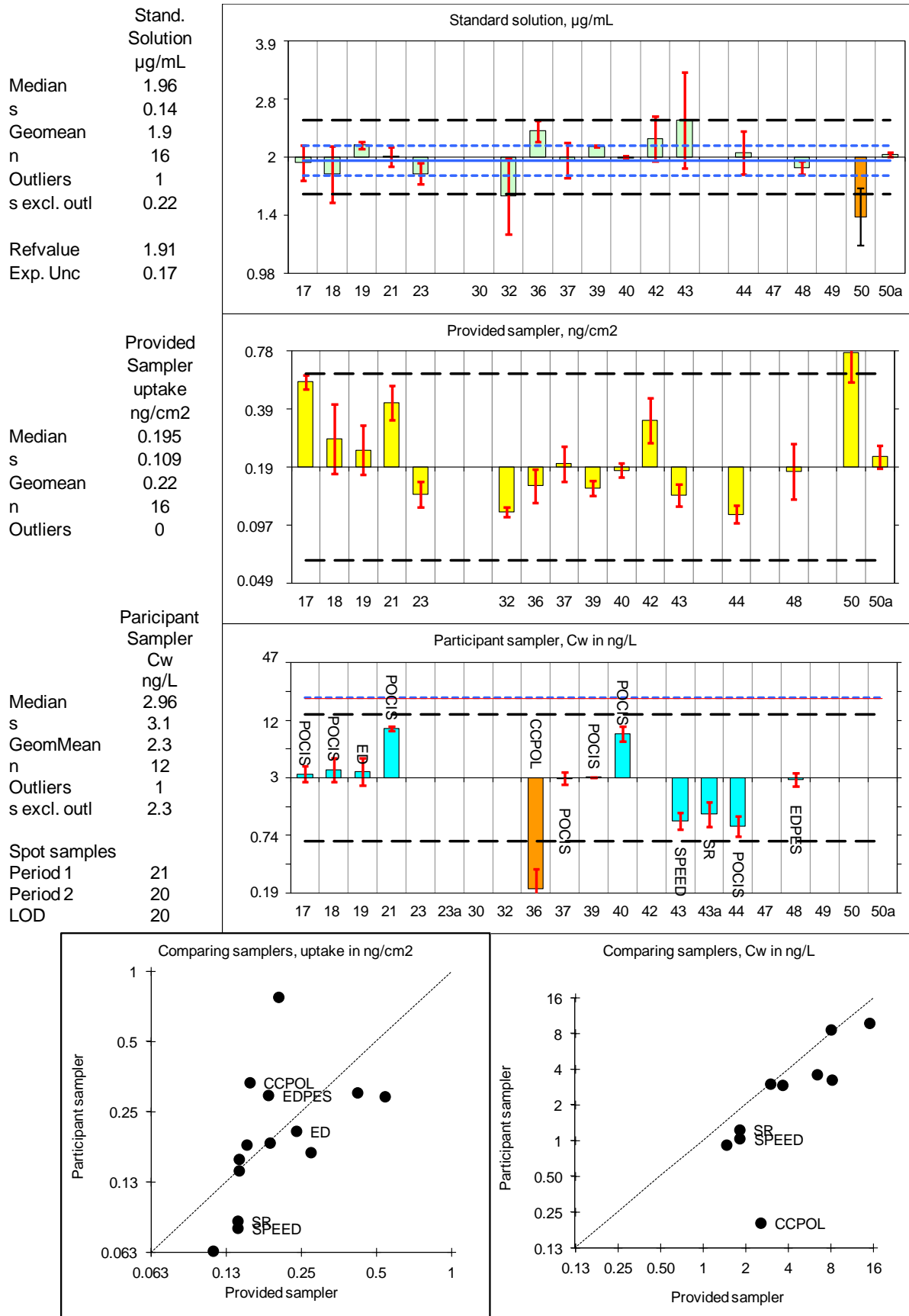


Figure 25 Results of analysis of S-metolachlor. Graph explanation is given in 10.2.and 10.3

Terbutylazine

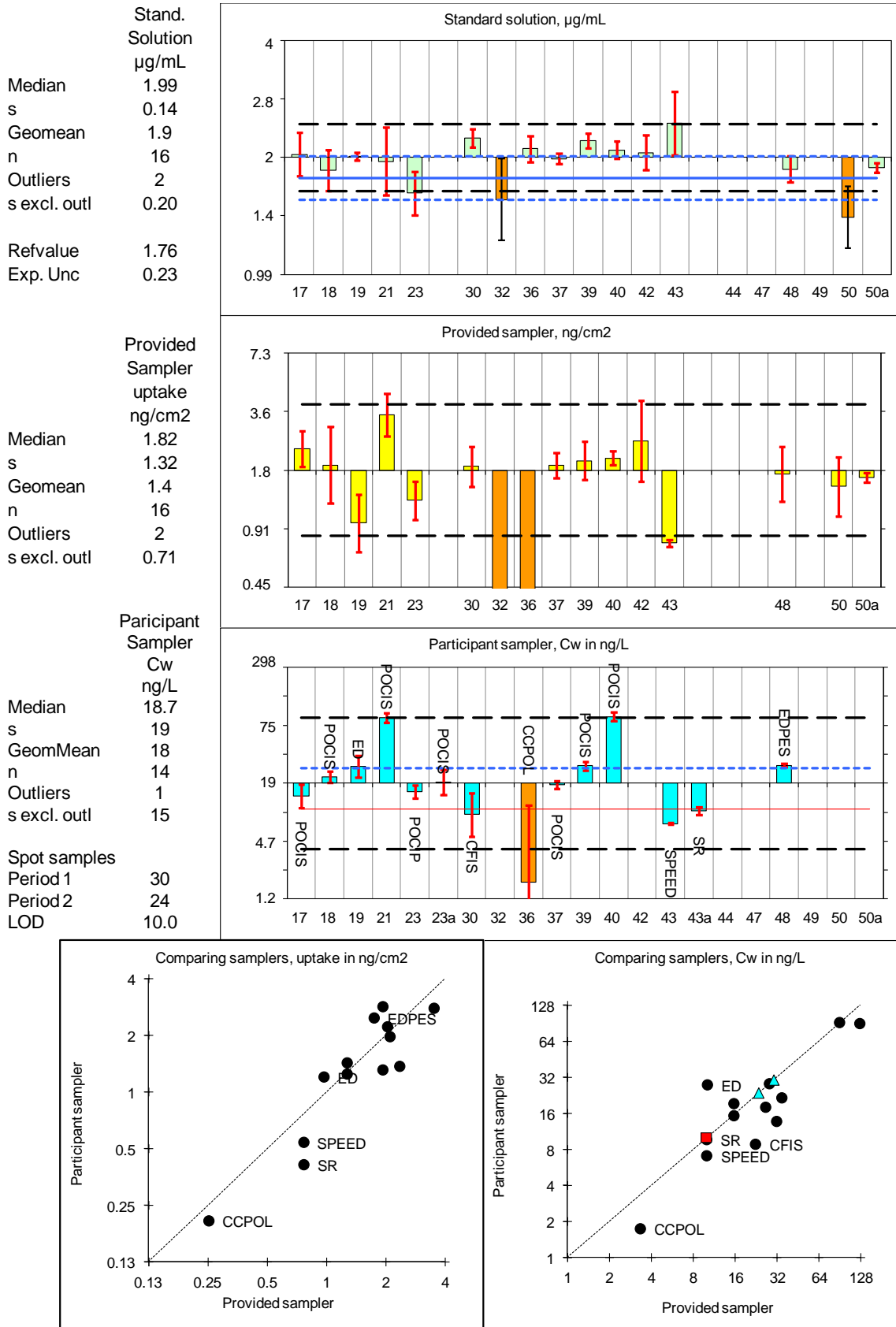


Figure 26. Results of analysis of terbutylazine. Graph explanation is given in 10.2 and 10.3

11.1.3 Sample variability

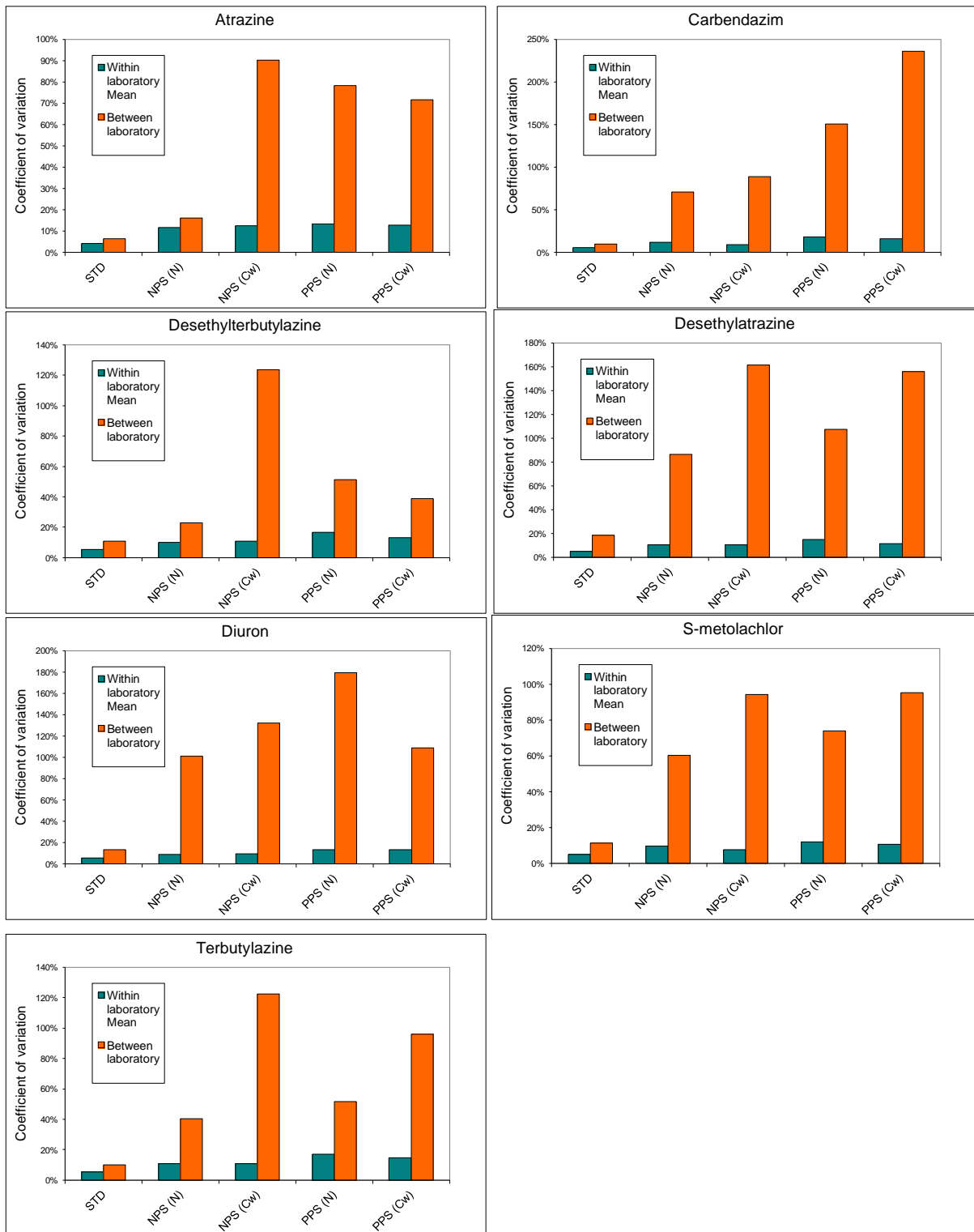


Figure 27 Variability of reported pesticide results at different procedure levels. Coefficients of variation for individual compounds are shown. NPS – provided passive sampler; PPS – participant passive sampler. (N) – amount; (Cw) – water concentration. See also 10.4.

Table 19. Variability range at different procedure levels Polar pesticides.

		Coefficient of variation (%)			
Variability:		Within laboratory		Between laboratory	
Matrix analysed:		Min.	Max.	Min.	Max.
Standard solution		4%	6%	6%	18%
<i>Provided sampler</i>	NPS amount (ng/cm ²)	9%	12%	16%	101%
	NPS water concentration	8%	13%	89%	161%
<i>Participant sampler</i>	PPS amount (ng/cm ²)	12%	18%	51%	179%
	PPS water concentration	11%	16%	39%	236%

See 10.4 for further explanation

11.1.4 Standard solution

A good within laboratory variability of analysis of individual compounds in pesticide standard solution was observed with the mean CV from 4 to 6% (Figure 24-26, Table 19). The between laboratory variability was satisfactory, too, ranging between 6 and 18%. With exception of atrazine and diuron the reference concentration of pesticides was within the range comprised by the participant results (median \pm 2 standard deviations excluding outliers) and vice versa, the median and geometric mean of participant results were within the uncertainty range stated by the central laboratory. For atrazine and diuron in standard solution there was a significant difference between median of participant results and the reference value stated by the central laboratory. An error in preparation of standard solution or a stability issue are 2 possible reasons of the observed bias.

Also for these two compounds, (atrazine, terbutylazine,) participants with outlier results showed also the highest within laboratory variability, which indicates that the instrumental methods were not under control.

11.1.5 Provided sampler

11.1.6 Field blanks

Concentrations of polar pesticides in field blank samplers was low, always <10% of the concentration found in exposed samplers and in most cases close to method detection limits (Table 20).

11.1.7 Sampling variability

An excellent within laboratory variability of analysis of polar pesticides in *provided sampler* (ng/cm²) was observed with the mean CV between 9 and 12% for sampler uptake and between 8 and 13% for the water concentration estimate, respectively (Table 19).

The between laboratory variability (excluding outliers) for sampler uptake (ng/cm²) was higher, ranging from 16 to 101% for different compounds. A higher (81 to 161%)

variability (1.3-5.6 times higher) was observed for the derived water concentration estimate.

The between laboratory variation of the analysis of individual compounds was 2-7 times larger for the *provided samplers* than the standard solution.

11.1.8 Contribution of the calculation procedure to data variability

Contribution of the applied calculation procedure of C_w from the amount on the sampler, to the overall coefficient of variation in C_w was estimated using the approach described in 10.5. Table 21 shows that for atrazine, desethylterbutylazine and terbutylazine, the variability of applied calculation procedure and sampler calibration procedure is the main factor causing the elevated between laboratory variability in C_w estimates from *provided sampler* data. For the remaining compounds the analytical variability was too high to distinguish the contribution of the applied calculation procedure from the overall variability of C_w estimates.

Table 20. Concentrations of polar pesticides in field blank sampler (ng/sampler) provided by the organizer .

Laboratory	Terbutylazine	Desethyl-atrazine	Desethyl terbutylazine	Atrazine	Carben-dazim	S-Metolachlor	Diuron
17	<2.80	<2.80	<2.80	<2.80	<2.80	<2.80	<2.8
18							
19							
21							
23							
23a							
30	<0.12	<0.12		<0.12			<0.12
32							
36	1.09	0.57	0.03	1.57	0.07	0.21	0.96
37							
39	0.92					0.42	
40	0.54					0.07	
42	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20
43	<2.00	<2.00	<2.00	<2.00	<2.00	<2.00	<2.00
43a	<2.00	<2.00	<2.00	<2.00	<2.00	<2.00	<2.00
44		0.11	0.02	0.04	0.37	0.05	0.05
47				0.01	0.02		0.70

Table 20 (continued) Concentrations of polar pesticides in field blank sampler (ng/sampler) provided by the organizer .

Laboratory	Terbutylazine	Desethylatrazine	Desethylterbutylazine	Atrazine	Carbendazim	S-Metolachlor	Diuron
48	<4.00	<4.00		<3.00	<1.00	<1.60	
49				0.00	0.00		3.62
50							
50a	0.05	0.40		0.02		0.05	

*Empty fields indicate cases where participants did not report a value.

Table 21. Estimated CV(R_s) for C_w calculation for *provided sampler*; Polar Pesticides

Compound	CV(N_{NPS}) (%)	CV(C_w;NPS) (%)	CV(R_s) (%)
Atrazine	16	90	88
Carbendazim	68	96	67
Desethylatrazine	82	138	111
Desethylterbutylazine	23	110	108
Diuron	94	125	82
S-metolachlor	59	93	72
Terbutylazine	40	124	118

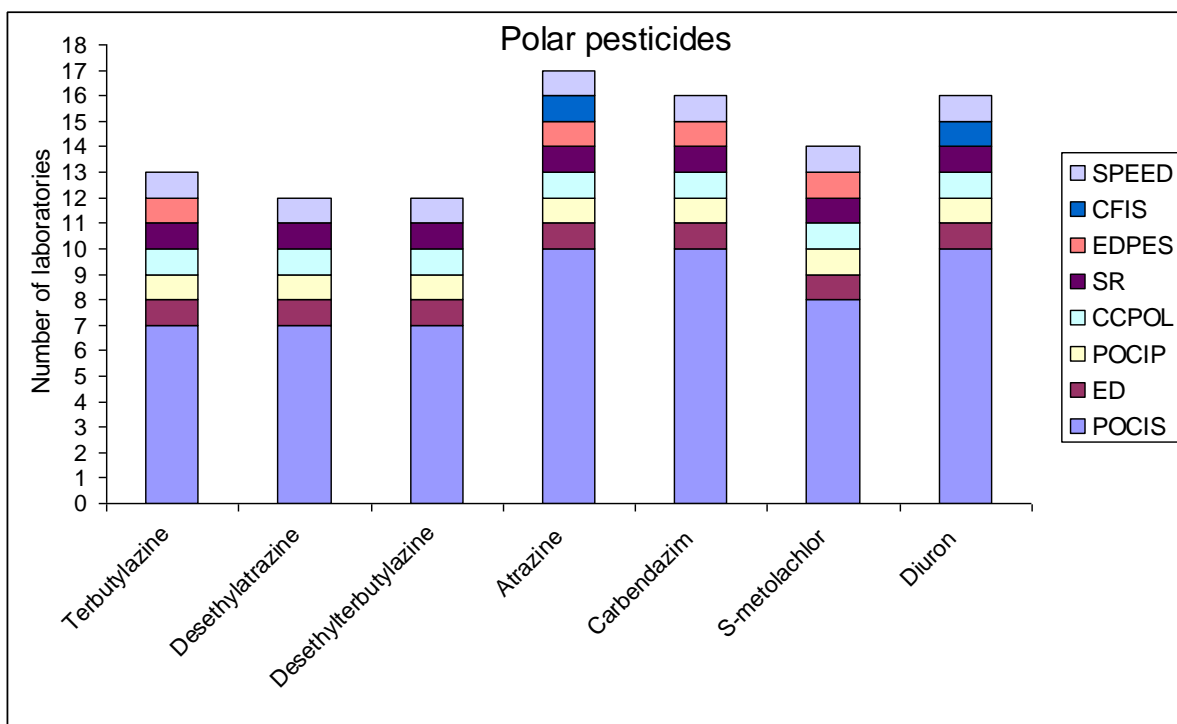


Figure 28 Various categories of participant passive samplers applied in analysis of polar pesticides. Sampler was counted only when a particular compound was measured above the method LOQ. A brief description of sampler category (shown as abbreviation in the legend) is given in Table 18.

11.1.9 Participant samplers

Figure 28 shows the different types of samplers successfully employed (above method LOQ) for polar pesticide sampling. The most frequent design of sampler applied in the study corresponded with the standard configuration of the POCIS with OASIS HLB adsorbent and fitted with polyethersulphone membrane. The same design was also applied in the *provided passive sampler*. Other types of samplers applied included Empore disks, the “pesticide” version of POCIS, the polar version of Chemcatcher, silicone rubber sheets, Empore disks fitted with a polyethersulphone membrane and Speeddisks. Details on samplers applied by participants and their processing are also given in Annex II.

11.1.10 Field blanks

Concentrations of polar pesticides in field blank samplers was low, always <10% of the concentration found in field exposed samplers (with exception of desethylatrazine in lab 36 and lab 43; desethylterbutylazine, atrazine and carbendazime in lab 43; S-metolachlor in labs 17, 36, 43 and 48) and close to method detection limits.

11.1.11 Sampling variability

Also in *participant samplers* a good within laboratory variability of analysis of polar pesticides (ng/cm²) was observed with the mean CV between 12 and 18% for sampler uptake and between 11 and 16% for the related water concentration estimate, respectively (Table 19).

The between laboratory variability (excluding outliers) for sampler uptake (ng/cm²) was higher, ranging from 51 to 179% for different compounds³. Even higher (39 to 236%) variability was observed for the water concentration estimate.

With exception of carbendazim, the between laboratory variability of water concentration estimate derived from participant passive samplers was lower than that derived from *provided sampler*. This may reflect that participating laboratories had more experience in use and data interpretation of samplers they normally apply in their research.

Table 22. Concentrations of polar pesticides in field blank participant sampler (ng/sampler)*.

Laboratory	Sampler type	Terbutylazine	Desethylatrazine	Desethylterbutylazine	Atrazine	Carbendazim	S-Metolachlor	Diuron
17	POCIS	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0
18	POCIS							
19	ED						0.12	
21	POCIS							
23	POCIP							
23a	POCIS							
30	CFIS	<1.0			1.0			<1.0
36	CCPOL	0.05	0.19	0.04	0.14	0.15	4.7	0.07
37	POCIS							
39	POCIS	1.0					0.37	
40	POCIS	0.36				0.24	0.13	
43	SPEED	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0
43a	SR	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0
44	POCIS		0.06	0.07	0.06	0.28	0.03	0.19
47	POCIS				0.20	0.77		0.74
48	EDPES	<4.0	<4.0		<3.0	<1.0	<1.6	
49	POCIS							<0.02

*Empty fields indicate cases where participants did not report any value.

Individual laboratories found in most cases well comparable results (close to equality) for participant and *provided sampler* (when both were POCIS) for uptake per surface area

³ Note that uptake per surface unit may differ between sampler types and the CV is not corrected for that systematic differences.

(left-hand biplots), as well as the resulting water concentration (C_w , right-hand biplot) (Figure 20-26). In several cases points far from the equality line for uptake (left biplot) can be explained from a significantly different working principle in comparison to the *provided samplers*, e.g. silicone rubber that often attained equilibrium during exposure. After transferring to C_w the data are much closer (right biplot).

11.1.12 Water samples

Results of water sample analysis are given in Table 23. Pesticide concentrations in water, reported from spot samples, were above the method limit of quantification, with exception of S-metolachlor. A comparison of these concentrations with water concentration estimates from passive samplers is displayed in bottom bar charts and right hand biplot charts in Figure 20-26. The concentration of pesticides in composite spot samples was always within the range comprised by the water concentration estimates from passive sampler results (median \pm 2 standard deviations excluding outliers).

Table 23 Concentrations of polar pesticides in weekly composite water samples

Sample/Compound	Filtration blank (30.5.-5.6.)	Filtration blank (6.6.-13.6.)	Weekly composite (30.5.-5.6.)	Weekly composite (6.6.-13.6.)	Units
Atrazine	<10	<10	25	17	ng/L
Carbendazim	<10	<10	90	100	ng/L
Desethylatrazine	<10	<10	37	38	ng/L
Desethylterbutylazine	<10	<10	39	33	ng/L
Diuron	<20	<20	220	170	ng/L
S-metolachlor	<20	<20	21	<20	ng/L
Terbutylazine	<10	<10	30	24	ng/L

11.1.13 Conclusions for polar pesticides

1. An acceptable within laboratory variability was observed for standard solution of polar pesticides showing that calibration of instrumental methods was not expected to cause excessive variability in reported data.
2. A very low (<12%) within laboratory variability was observed for the *provided samplers* which basically evidenced that the sampling process and samplers position caused little variation; i.e. confirming the investigations reported in section 8.3 .
3. Consequently, the high between laboratory variability is dominantly connected to laboratory born analytical differences.
4. Both the analysis and the procedure for calculation of C_w are a large source of between laboratory variability and both need improvement..
5. Within laboratory differences between *provided* and *participant samplers* were small when that was expected based on similarity of the sampler design.
6. The water concentrations obtained by PS and spot sampling do not disagree, however, the variability of reported results is high.

11.2 Pharmaceuticals

Up to 17 laboratories participated in the exercise, but the numbers varied depending on target analytes and matrices analysed. Results for individual compounds are displayed in Figure 30-37. The explanation of data projection applied is described in chapter 10.

11.2.1 Overall data variability

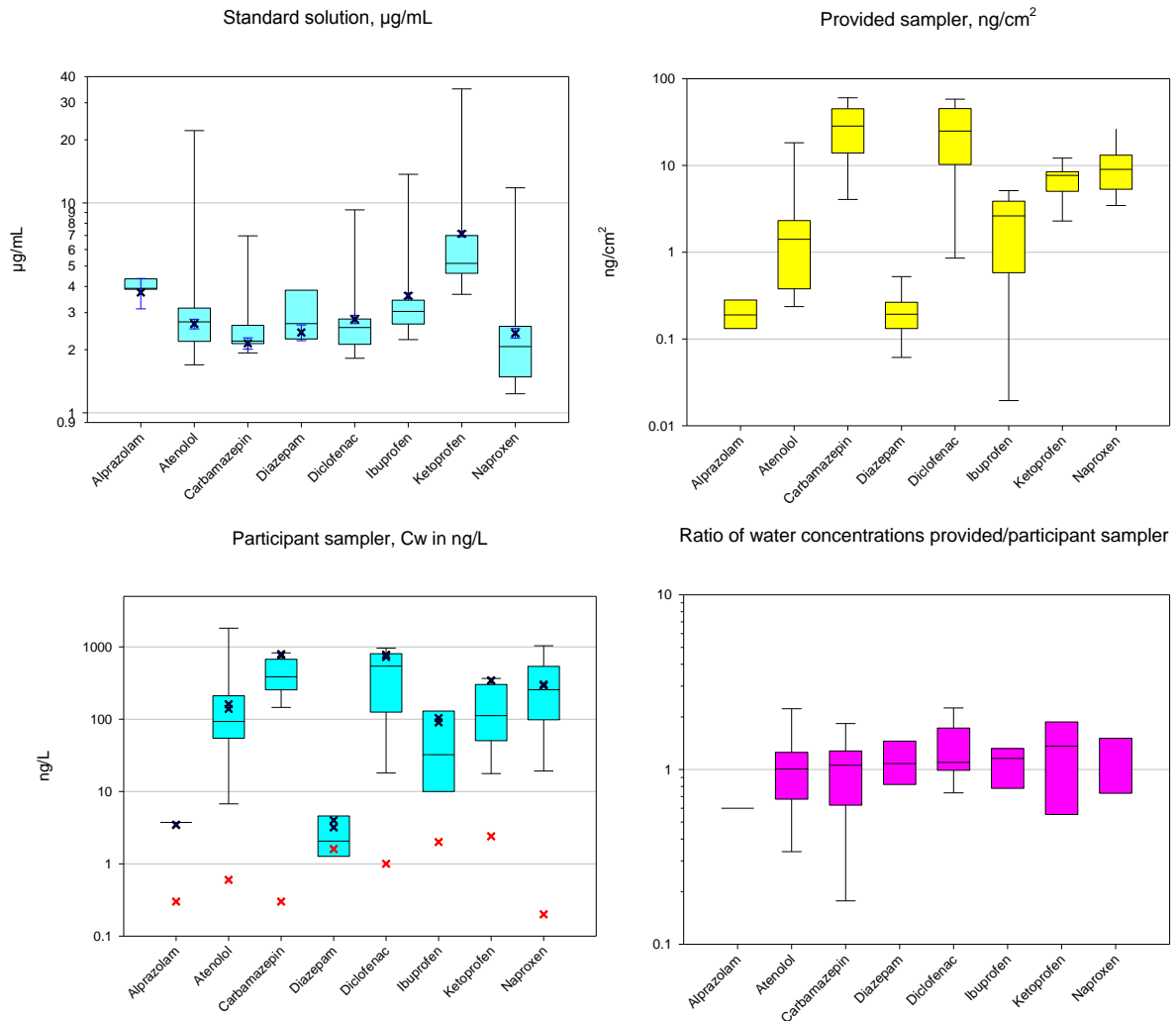


Figure 29 Concentrations of pharmaceuticals in various analysed matrixes: standard solution (top left), provided sampler (top right), water concentration estimated from the participant sampler (bottom left) and the ratio of water concentrations determined in provided and participant passive sampler (bottom right), respectively. For explanation of symbols see legend to Figure 19.

11.2.2 Results by laboratories - pharmaceuticals

Alprazolam

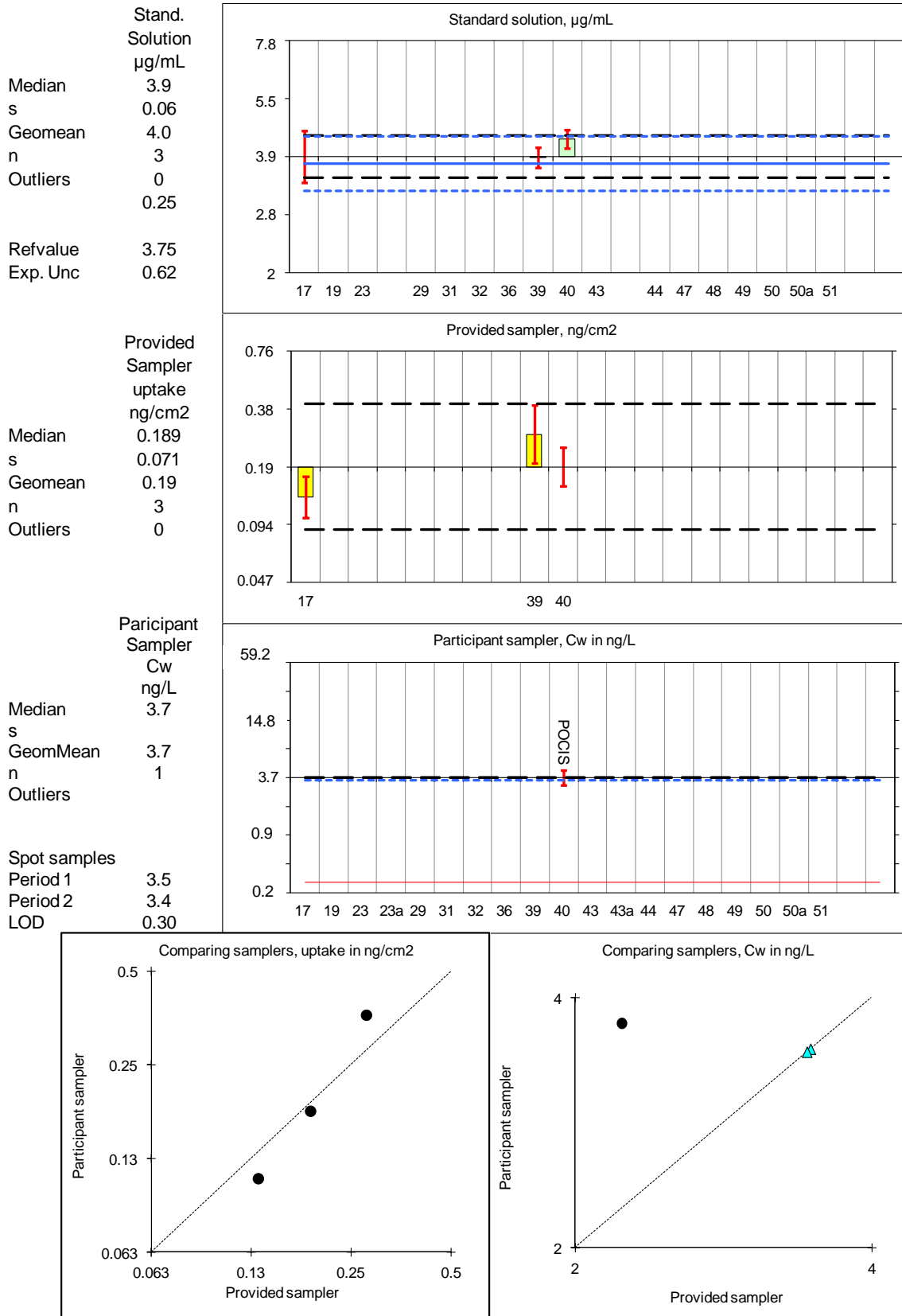


Figure 30 Results of analysis of alprazolam. Graph explanation is given in 10.2 and 10.3

Atenolol

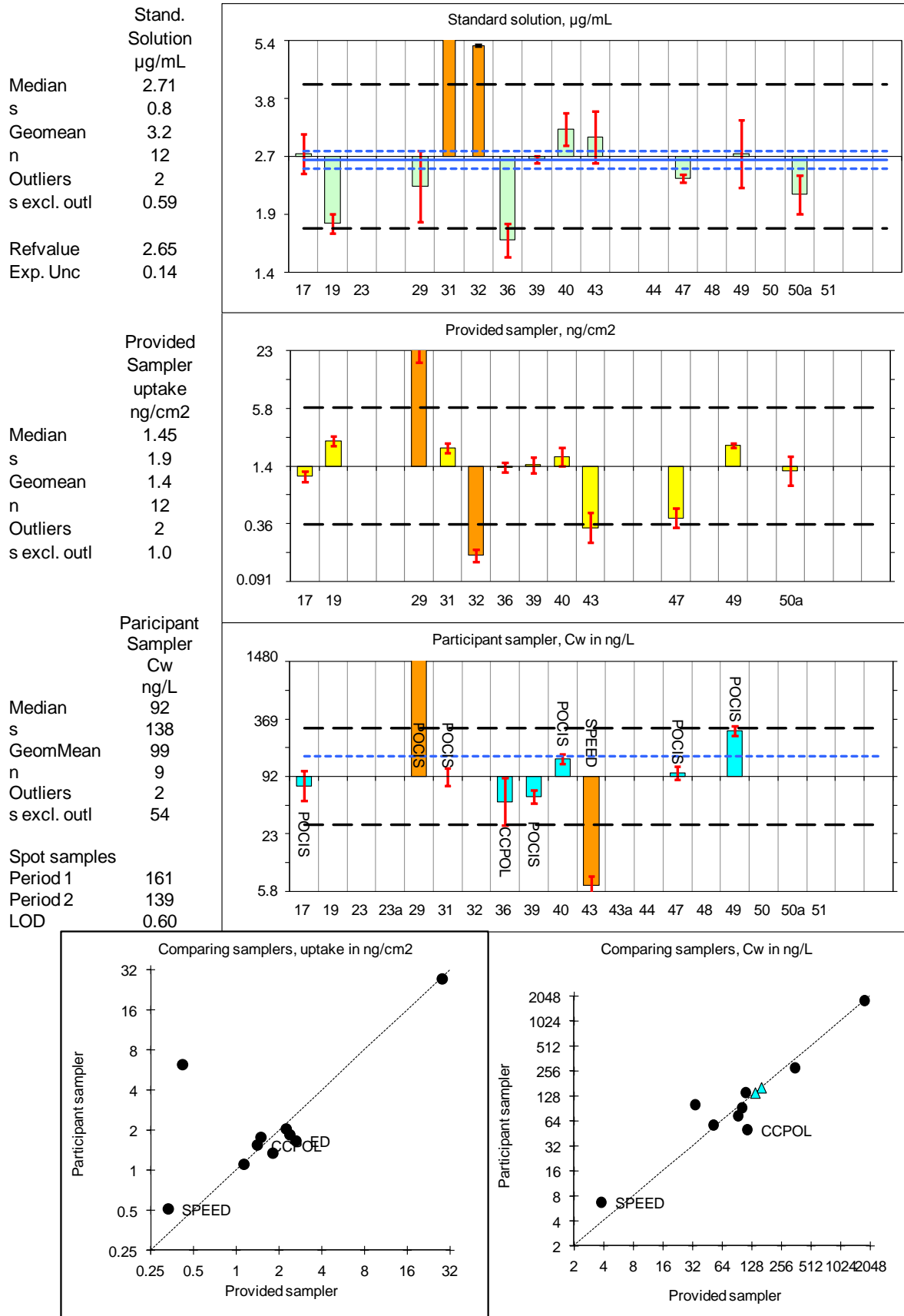


Figure 31 Results of analysis of atenolol. Graph explanation is given in 10.2 and 10.3

Carbamazepine

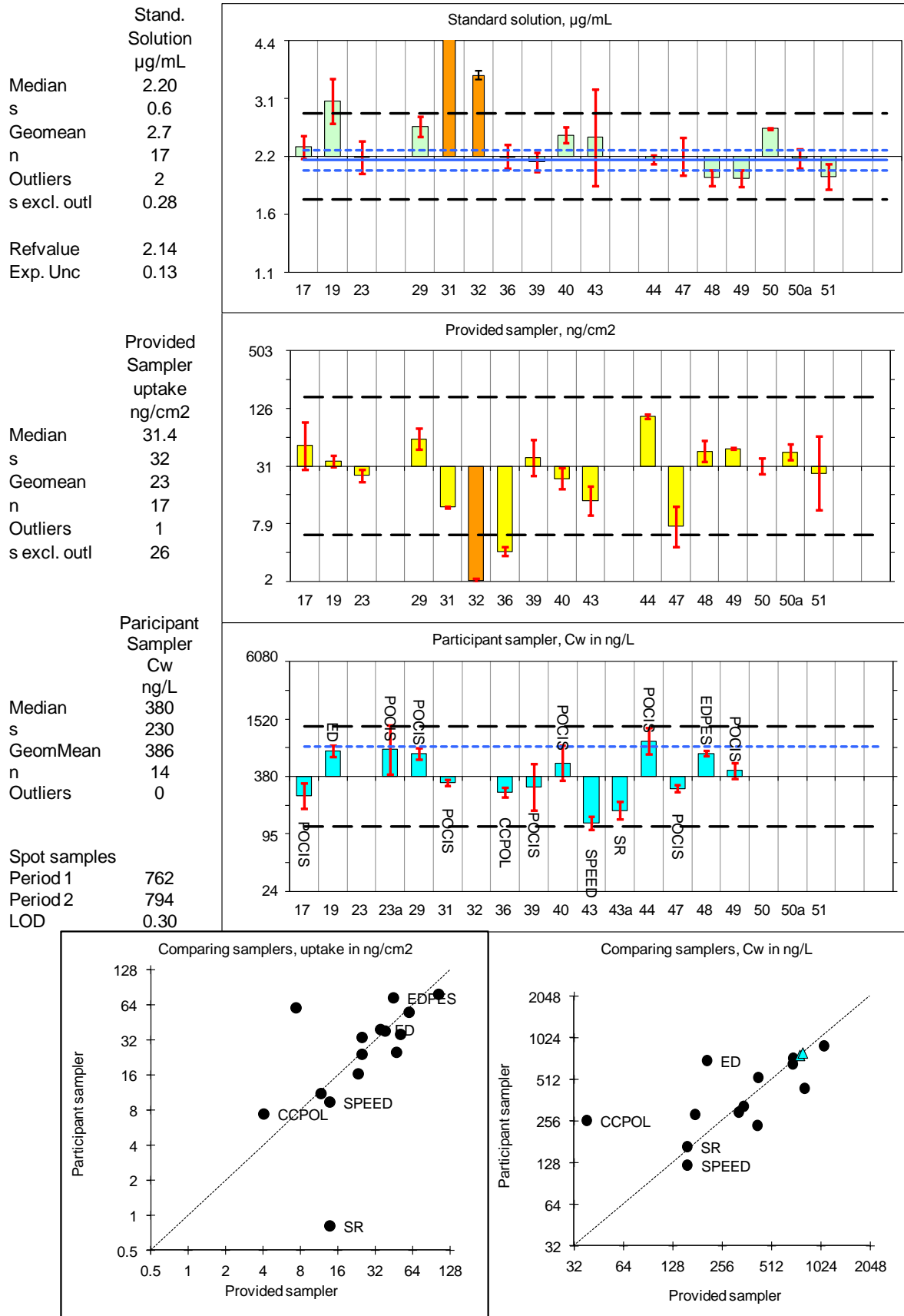


Figure 32 Results of analysis of carbamazepine. Graph explanation is given in 10.2.and 10.3

Diazepam

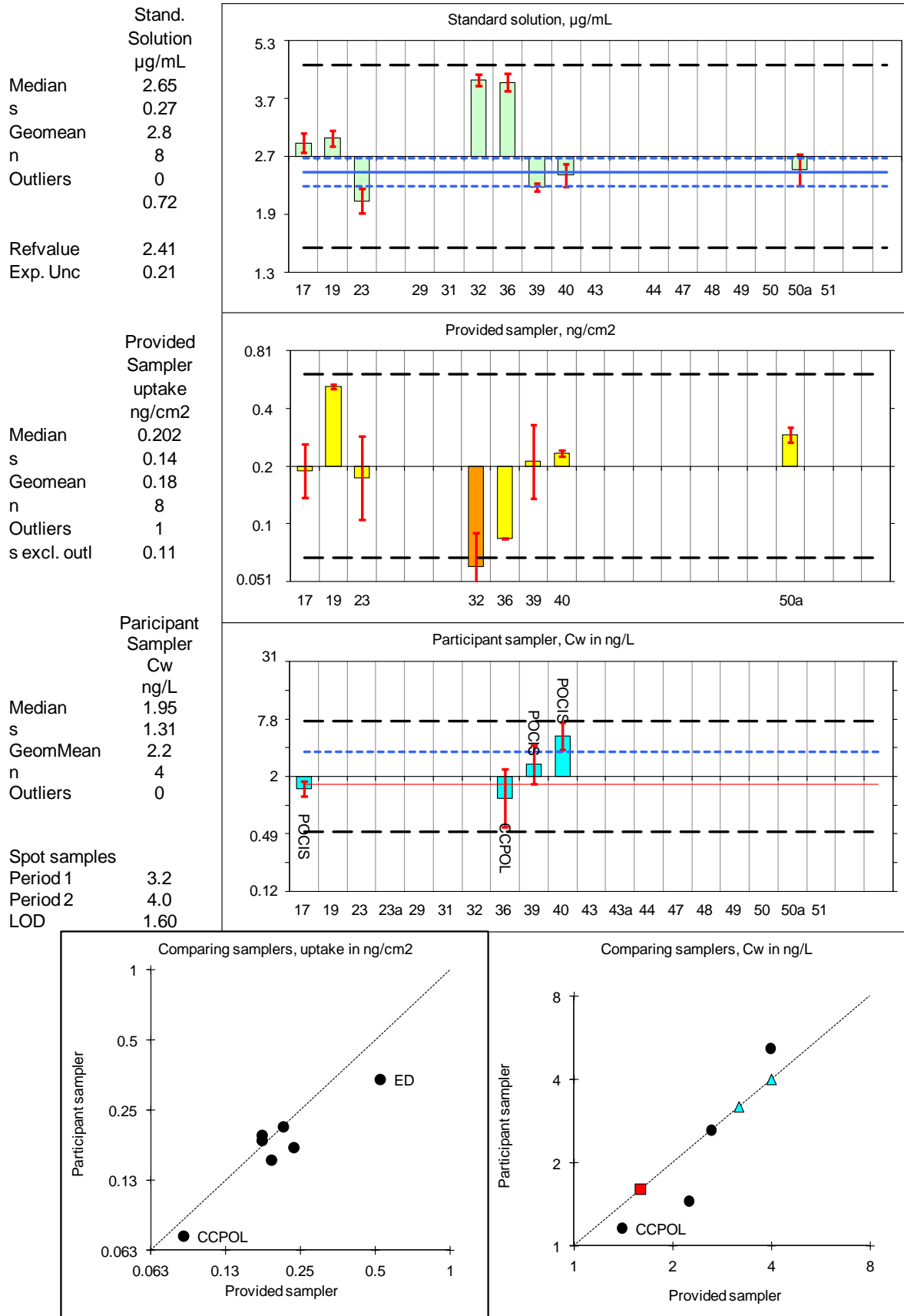


Figure 33 Results of analysis of diazepam. Graph explanation is given in 10.2.and 10.3

Diclofenac

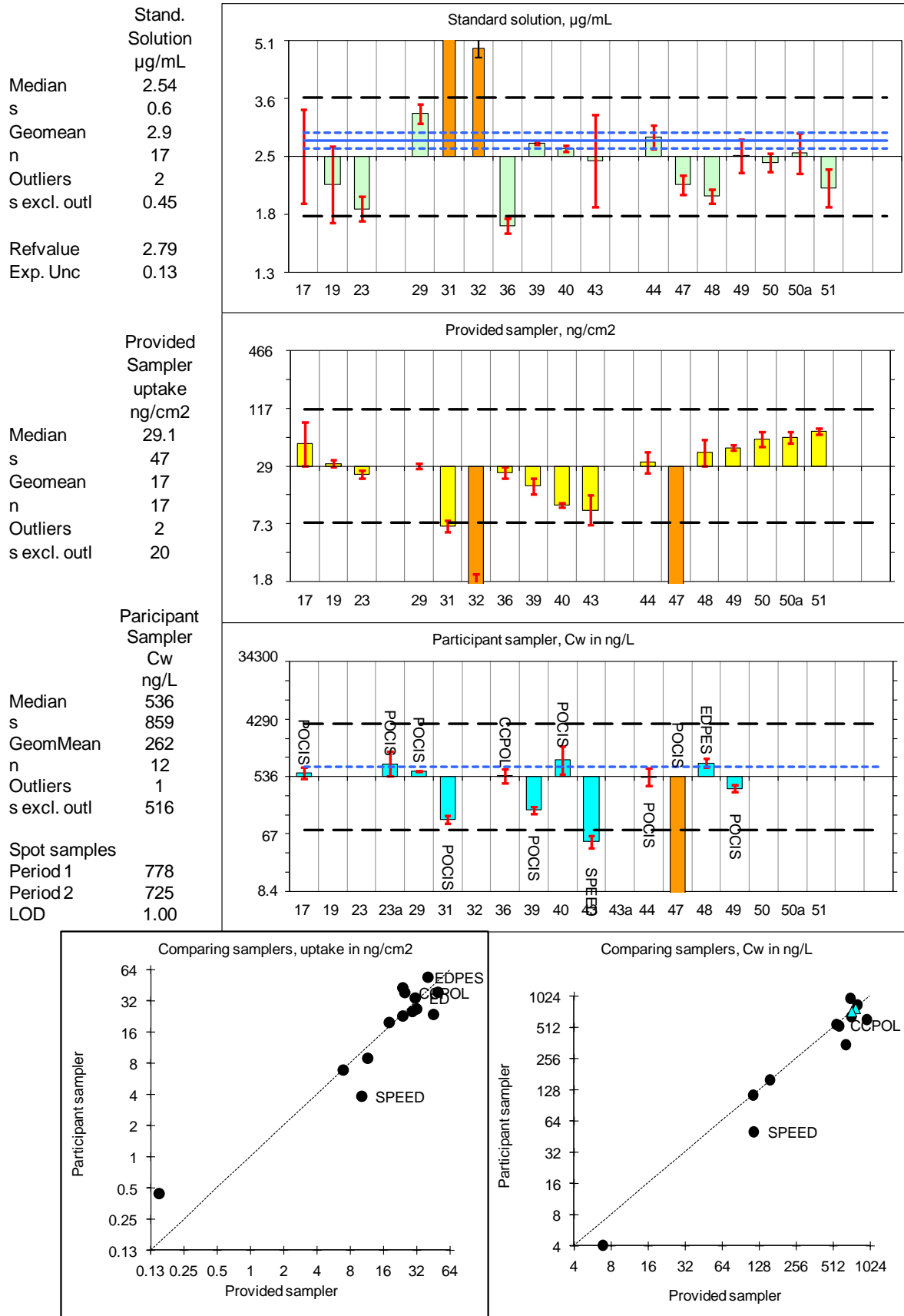


Figure 34 Results of analysis of diclofenac. Graph explanation is given in 10.2.and 10.3

Ibuprofen

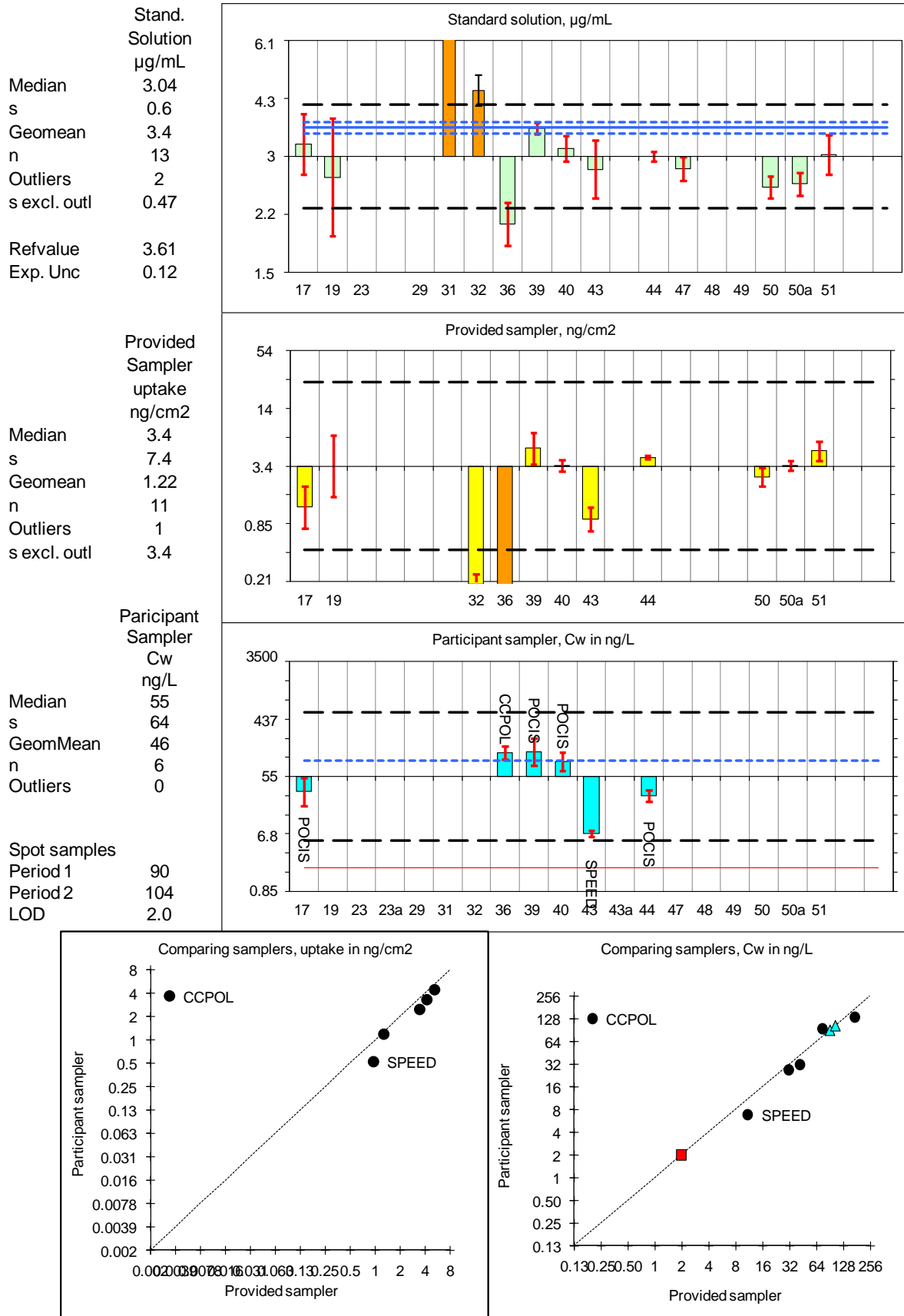


Figure 35 Results of analysis of ibuprofen. Graph explanation is given in 10.2.and 10.3.

Ketoprofen

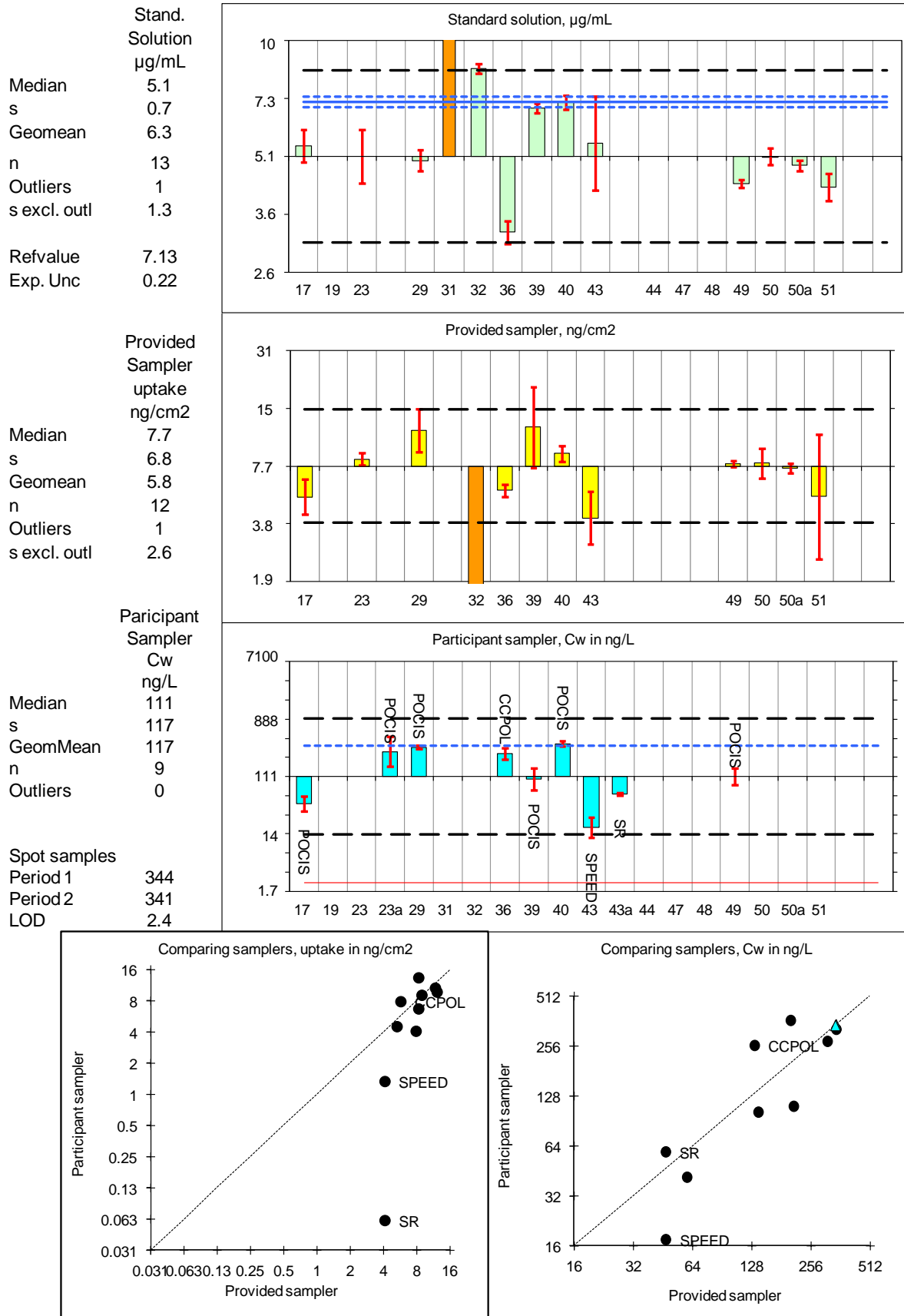


Figure 36 Results of analysis of ketoprofen. Graph explanation is given in 10.2. and 10.3.

Naproxen

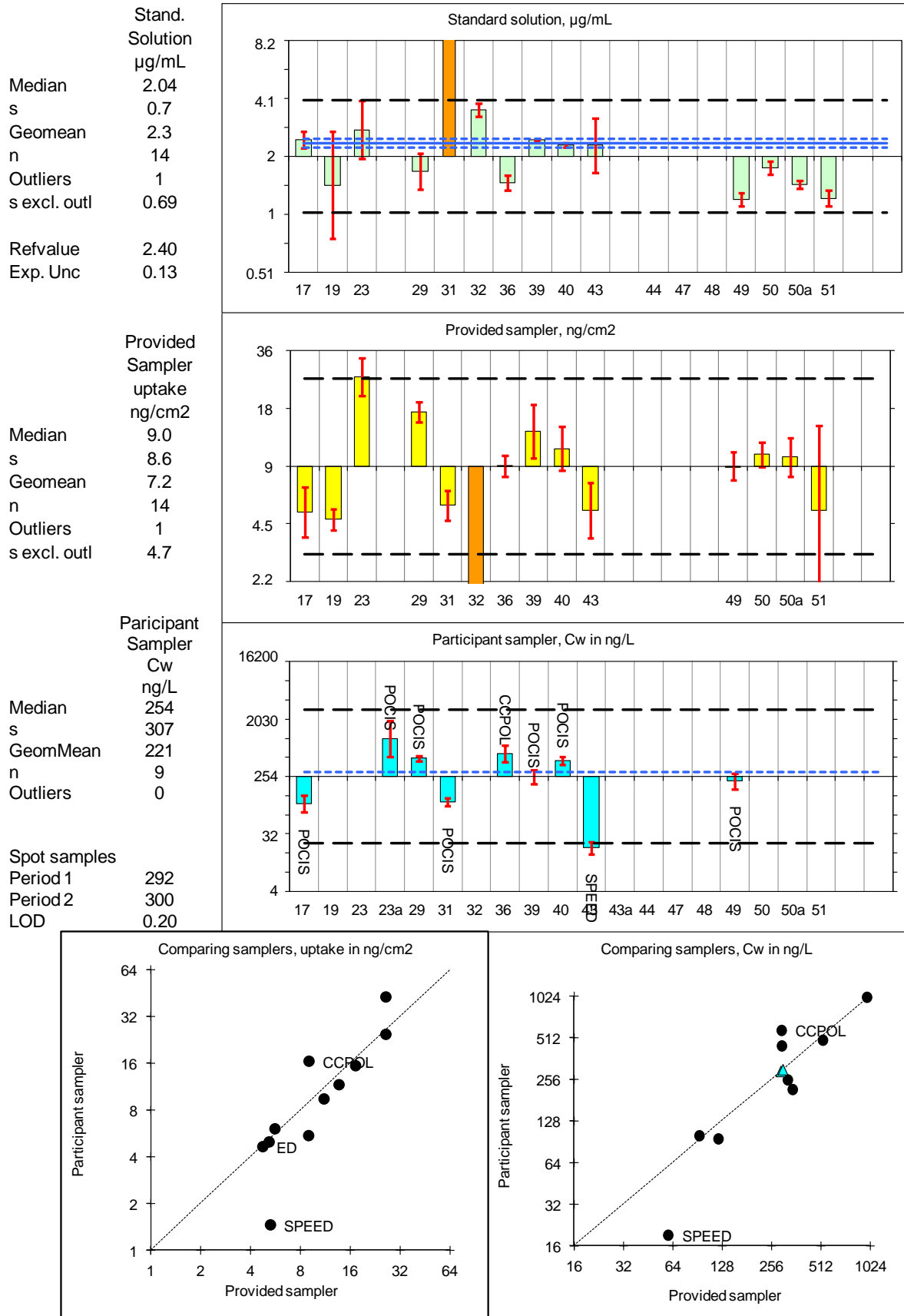


Figure 37 Results of analysis of naproxen. Graph explanation is given in 10.2.and 10.3.

11.2.3 Sample variability

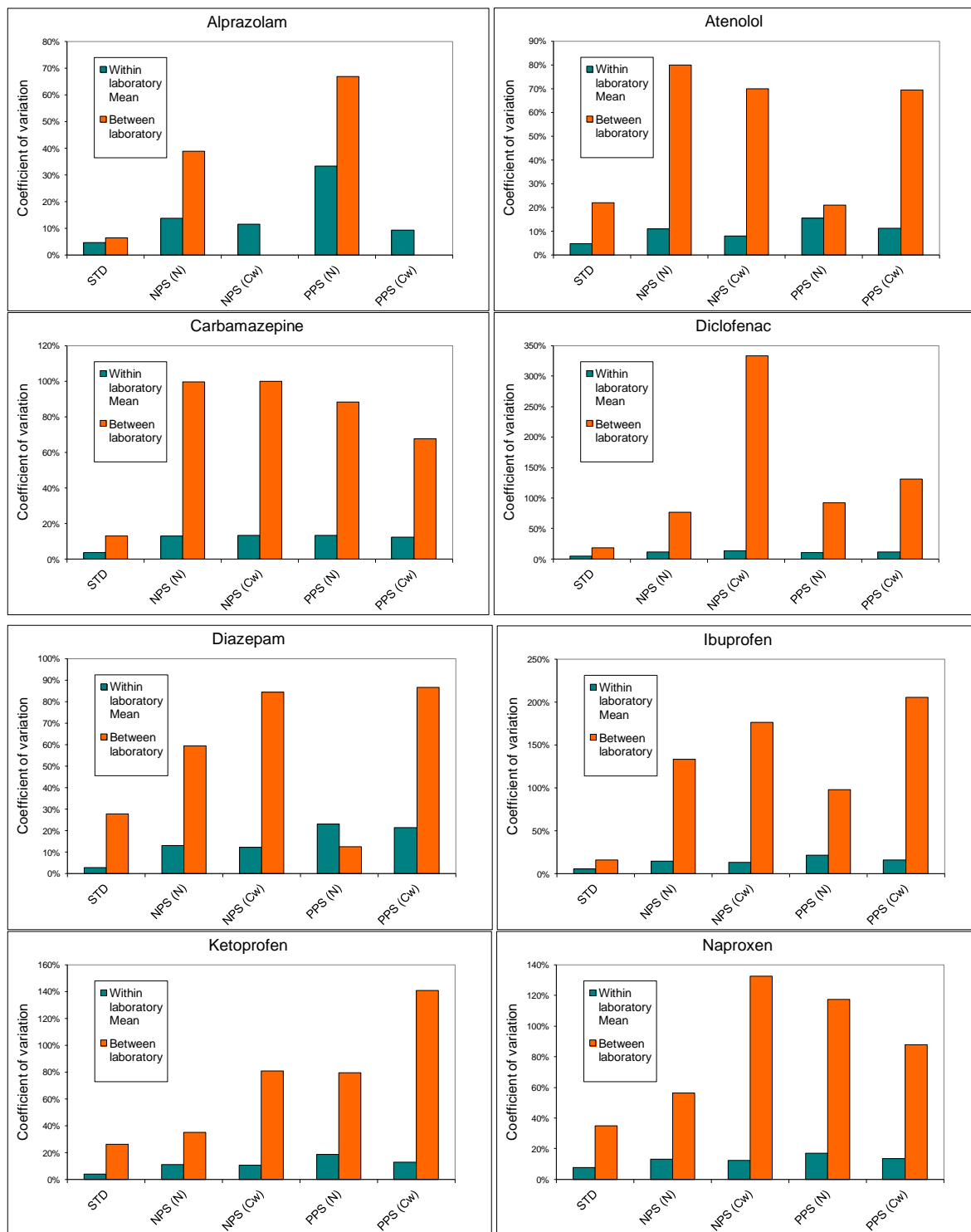


Figure 38 Variability of reported pharmaceutical results at different procedure levels. Results are the coefficients of variation for individual compounds. NPS – provided passive sampler; PPS – participant passive sampler. (N) – amount; (C_w) – water concentration.

Table 24 Variability range at different procedure levels for pharmaceuticals.

Pharmaceuticals					
		Coefficient of variation (%)			
Variability:		Within laboratory		Between laboratory	
Matrix analysed:		Min.	Max.	Min.	Max.
Standard solution		3%	8%	6%	35%
<i>Provided sampler</i>	NPS amount (ng/cm ²)	11%	14%	35%	133%
	NPS water concentration	8%	13%	70%	333%
<i>Participant sampler</i>	PPS amount (ng/cm ²)	10%	33%	13%	117%
	PPS water concentration	9%	21%	68%	205%

11.2.4 Standard solution

Results provided by participating laboratories for the standard solution are shown in the top bar charts in Figure 30-37. The range of variability of reported results is given in Table 24. Variability observed for individual compounds is also shown in Figure 38.

A good within laboratory variability of analysis of individual compounds in pharmaceutical standard solution was observed with the mean CV from 3 to 8% (Table 24). The between laboratory variability (excluding outliers) ranged between 6 and 35% and averaging around 20%. Also because this rather high variability the reference concentration of pharmaceuticals was in all cases within the range comprised by the participant results (median \pm 2 standard deviations excluding outliers). For diclofenac, ibuprofen, naproxen and ketoprofen, the median and geometric mean of participant results were outside the uncertainty range stated by the central laboratory. Laboratory 31 reported outlier results for all analysed compounds, which indicates a systematic error, possibly related to sample dilution or calculation.

11.2.5 Provided sampler

The results provided by participating laboratories compared to the median are shown in the middle bar charts in Figure 30-37.

11.2.6 Field blanks

Concentrations of polar pesticides in field blank samplers was low, in most cases less than 10% of the concentration found in field exposed samplers (exceptions are alprazolam in lab 17, atenolol in lab 43, diazepam in lab 17 and ibuprofen in lab 47) and close to method detection limits (Table 25).

11.2.7 Sampling variability

An excellent within laboratory variability of analysis of pharmaceuticals in *provided sampler* (ng/cm²) was observed with the mean CV between 11 and 14% for sampler uptake and between 8 and 13% for the water concentration estimate, respectively (Table 24).

The between laboratory variability (excluding outliers) for sampler uptake (ng/cm²) was higher, ranging from 35 to 133% for different compounds. Even higher (70 to 333%) variability (up to 4.3 times higher) was observed for the water concentration estimate.

Analysis of individual compounds in *provided sampler* was affected by between laboratory variation 1.3 to 9 times larger than the analysis of standard solution.

Participants can check whether results reported by their laboratory are comparable (within the study variability) with results provided by the other laboratories (Figure 30-Figure 37). Participants also may check whether a bias in instrument calibration (outlier result in analysis of standard solution) may have contributed to the bias of *provided sampler* data reported by this laboratory. For example, for atenolol, carbamazepine and diclofenac results by laboratory 32 were evaluated as outliers for analysis of standard solution and the *provided sampler*, respectively.

11.2.8 Contribution of the calculation procedure to data variability

Coefficient of variation of the applied calculation procedure was estimated using the approach described in 10.5. For atenolol and carbamazepine the contribution of uncertainty in calculation procedure to the overall uncertainty of water concentration procedure was minor. For the remaining compounds the variability of the applied calculation procedure and the sampler calibration procedure were the main factors causing the elevated between laboratory variability of water concentration estimate from *provided sampler* data.

Table 25 Concentrations of pharmaceuticals in field blank sampler (ng/sampler) provided by the organizer¹.

Labo- ratory	Alpra- zolam	Ateno- lol	Carba- mazepi ne	Diaze- pam	Diclo- fenac	Ibu- profen	Keto- profen	Napro- xen
17	<5.2	<5.2	<5.2	<5.2	<5.2	<5.2	<5.2	<5.2
19								
23			0.80	<0.17	2.4		1.8	15
23a			0.80	<0.17	2.4		1.8	15
29		<1.2	<3.2		<3.2		<1.2	<3.2
31		4.8	5.2		2.9			3.0
32								
36		0.86	1.3	0.03	0.09		2.8	
39		0.08	2.9		2.2			0.68
40								
43		<4.0	<4.0		<4.0	<4.0	<4.0	<4.0
43a		<4.0	<4.0		<4.0	<4.0	<4.0	<4.0
44			0.10		2.7	0.62		

Table 25 (continued) Concentrations of pharmaceuticals in field blank sampler (ng/sampler) provided by the organizer¹.

Labo- ratory	Alpra- zolam	Ateno- lol	Carba- mazepine	Diaze- pam	Diclo- fenac	Ibu- profen	Keto- profen	Napro- xen
47		1.1	<0.02		<0.02	<2.0		
48			<1.6		<3.0			
49		<2.5	<0.002		19		<0.01	<0.04
50			0.75		1.9	0.48	1.5	1.4
50a		0.04	0.21				0.43	
51								

¹Empty fields indicate cases where participants did not report any value.

Table 26. Estimated CV(R_s) for C_w calculation for *provided sampler*; pharmaceuticals.

Compound	CV(N _{NPS}) (%)	CV(C _{w;NPS}) (%)	CV(R _s) (%)
Alprazolam	38	not estimated	not estimated
Atenolol	76	73	not estimated
Carbamazepine	93	100	37
Diazepam	58	88	66
Diclofenac	74	256	245
Ibuprofen	119	171	123
Ketoprofen	35	73	64
Naproxen	55	112	97

11.2.9 Participant sampler

Figure 39 shows the different sampler types successfully (above method LOQ) applied by participants in sampling of pharmaceuticals. As for pesticides, the most frequently applied design of sampler applied in the study corresponded with the standard configuration of the POCIS with OASIS HLB adsorbent and fitted with polyethersulphone membranes. The same design was also applied in the *provided passive sampler*. Other types of samplers applied included Empore disks, the "pesticide" version of POCIS, the polar version of Chemcatcher, silicone rubber sheets, Empore disks fitted with a polyethersulphone membrane and Speeddisks. Details on samplers applied by participants and their processing are given also in Annex IV.

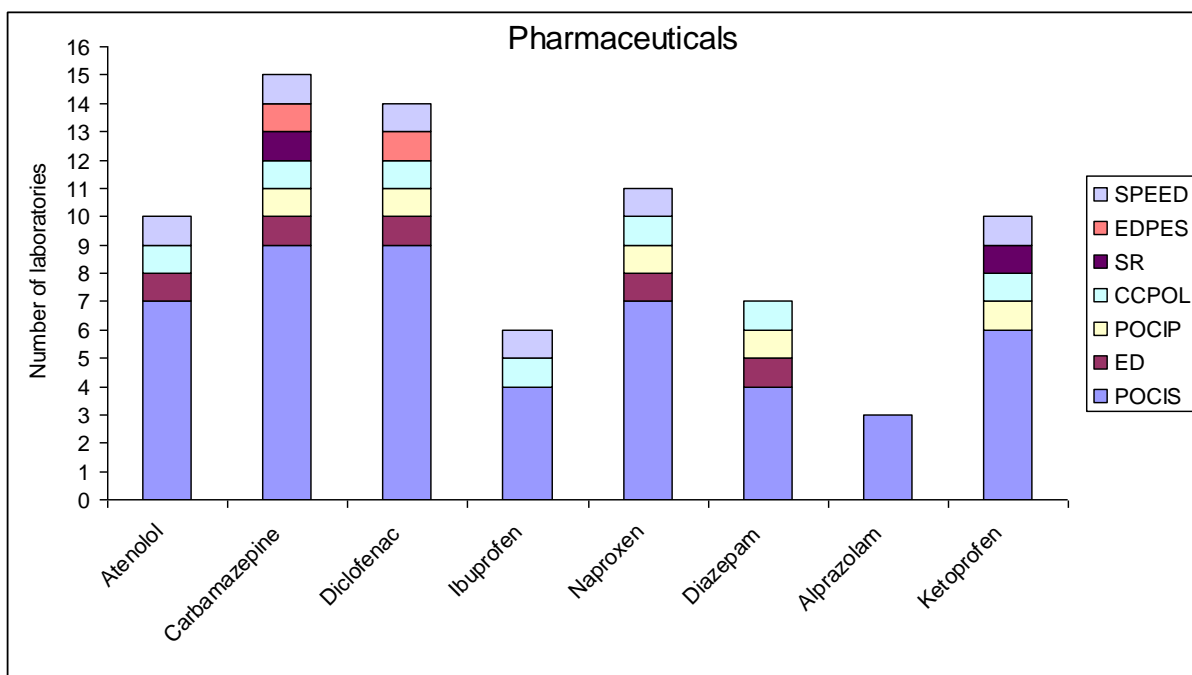


Figure 39 Various categories of participant passive samplers applied in analysis of pharmaceuticals. A sampler was counted only when a particular compound was measured above method LOQ. A brief description of sampler category (shown as abbreviation in the legend) is given in Table 18.

The results provided by participating laboratories compared to the median are shown in the bottom bar charts in Figure 30-37.

11.2.10 Field blanks

Concentrations of pharmaceuticals in field blank samplers were low, always <10% of the concentration found in field exposed samplers and close to method detection limits (Table 27).

11.2.11 Sample variability

A good within laboratory variability of analysis of pharmaceuticals in *participant samplers* (ng/cm²) was observed with the mean CV between 10 and 33% for sampler uptake and between 9 and 21% for the related water concentration estimate, respectively (Table 24).

The between laboratory variability (excluding outliers) for sampler uptake (ng/cm²) was higher, ranging from 13 to 117% for different compounds. Even higher (68 to 205%) variability was observed for the water concentration estimate.

In most cases the between laboratory variability of water concentration estimate derived from participant passive samplers was comparable to that derived from *provided samplers*.

Individual laboratories found in most cases well comparable results (close to equality) for *participant* and *provided sampler* for uptake per surface area (left-hand biplots), as well as the resulting water concentration (C_w , right-hand biplot) (Figure 30-Figure 37). Points that lie near the equality line but far from the median values indicate a large systematic error introduced by the laboratory. Points far from the equality line for uptake are mostly data from samplers that significantly differ from *provided samplers* in terms of their working principle (e.g. silicone rubber).

Table 27. Concentrations of polar pharmaceuticals in field blank participant sampler (ng/sampler)*.

Laboratory	Sampler	Alprazolam	Atenolol	Carbamazepine	Diazepam	Diclofenac	Ibuprofen	Ketoprofen	Naproxen
17	POCIS	<6	<6	<6	<6	<6	<6	<6	<6
19	ED								
23	POCIP								
23a	POCIS								
29	POCIS		<1	<3		<3		<1	<3
31	POCIS		4.6	1.9		1.9			1.0
36	CCPOL		0.2	0.7	0.01	1.0		10.1	
39	POCIS								
40	POCIS			0.2		0.3		3.1	0.1
43	SPEED	<5	<5	<5	<5	<5	<5	<5	<5
43a	SR			<5				5.0	
44	POCIS			0.6		4.2	4.4		
47	POCIS		1.8	<0.1		0.2	<10		
48	EDPES			<1.6		<3			
49	POCIS		<2.5					<0.01	<0.04

11.2.12 Water samples

Results of water sample analysis are given in Table 28. Pharmaceutical concentrations in water, reported from spot samples by the expert laboratory, were above the method limit of quantification. However, concentrations of diazepam and alprazolam were close to the limit of quantification. A comparison of these concentrations with water concentration estimates from passive samplers is displayed in the bottom bar charts and right hand biplot charts in Figure 30-37. The concentration of pharmaceuticals in composite spot samples was always within the range comprised by the water concentration estimates from passive sampler results (median \pm 2 standard deviations excluding outliers).

Table 28 Concentrations of pharmaceuticals in weekly composite water samples, analysed by a central laboratory

Sample/Compound	Filtration blank (30.5.-5.6.)	Filtration blank (6.6.-13.6.)	Weekly composite (30.5.-5.6.)	Weekly composite (6.6.-13.6.)	units
Alprazolam	<0.3	<0.3	3.5	3.4	ng/L
Atenolol	<0.6	<0.6	160	140	ng/L
Carbamazepine	<0.3	<0.3	760	800	ng/L
Diazepam	<1.6	<1.6	3.2	4.0	ng/L
Diclofenac	<1.0	<1.0	780	720	ng/L
Ibuprofen	<2.0	<2.0	90	100	ng/L
Ketoprofen	<2.4	<2.4	340	340	ng/L
Naproxen	<0.2	<0.2	290	300	ng/L

11.2.13 Conclusions for pharmaceuticals

1. An acceptable within laboratory variability was observed for standard solution of pharmaceuticals but the 20% average between laboratory variability is considered high for the analysis of a standard
2. Sampling with *provided samplers* was homogeneous as can be concluded from the very low within laboratory variability of analysis of *provided samplers*.
3. The higher between laboratory variability in water concentration estimates in comparison to sampler uptake per surface area can be attributed to errors introduced by different approaches in the translation of uptake data to water concentrations. For atenolol and carbamazepine the contribution of uncertainty in calculation procedure to the overall uncertainty of water concentration procedure was minor. For the remaining pharmaceutical compounds the variability of applied calculation procedure and/or calibration parameters was the main factor causing the elevated between laboratory variability of water concentration estimate from *provided sampler* data.
4. Similar results for different passive samplers analysed within individual laboratories indicate that the PS process is not causing excessive variability.
5. There was no significant difference between the water concentrations measured by PS and the spot sampling method, however, the PS method precision is low and needs to be improved.
6. The much (up to 13x) higher between laboratory variability of water concentration estimate in comparison to within laboratory precision is likely related to systematic error in results of individual laboratories, which in turn can be related to difficulties with analysis in the complex matrix of the field exposed passive sampler.

11.3 Steroid hormones

Up to 13 laboratories participated in the exercise, but the numbers varied depending on target analytes and matrices analysed. Results for individual compounds are displayed in Figure 41-45. The explanation of data projection applied is described in chapter 10.

11.3.1 Overall data variability

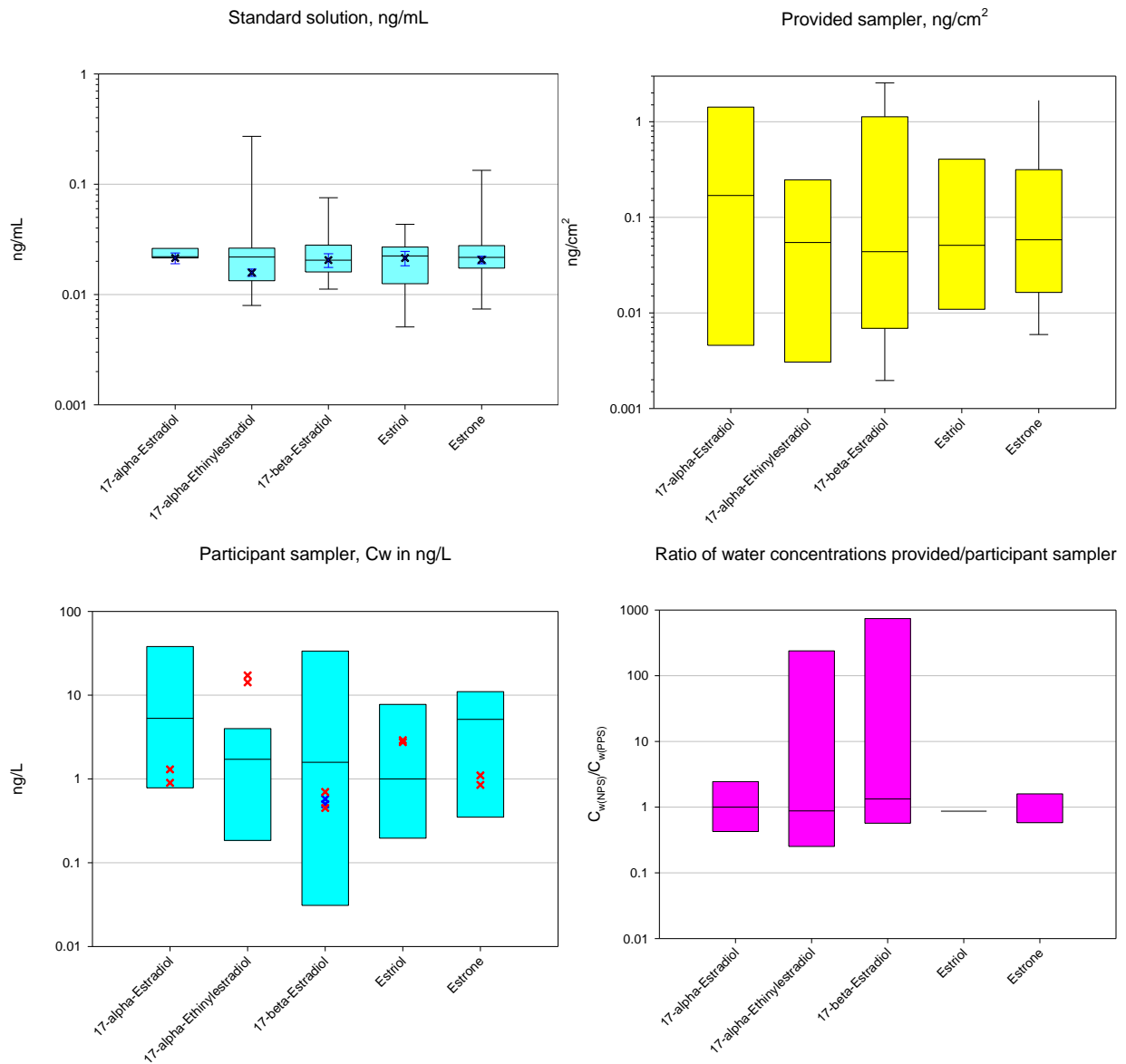


Figure 40 Concentrations of steroids in various analysed matrixes: standard solution (top left), provided sampler (top right), water concentration estimated from the participant sampler (bottom left) and the ratio of water concentrations determined in provided and participant passive sampler (bottom right), respectively. For explanation of symbols see legend to Figure 19.

11.3.2 Results by laboratories – steroid hormones

17-alpha-Estradiol

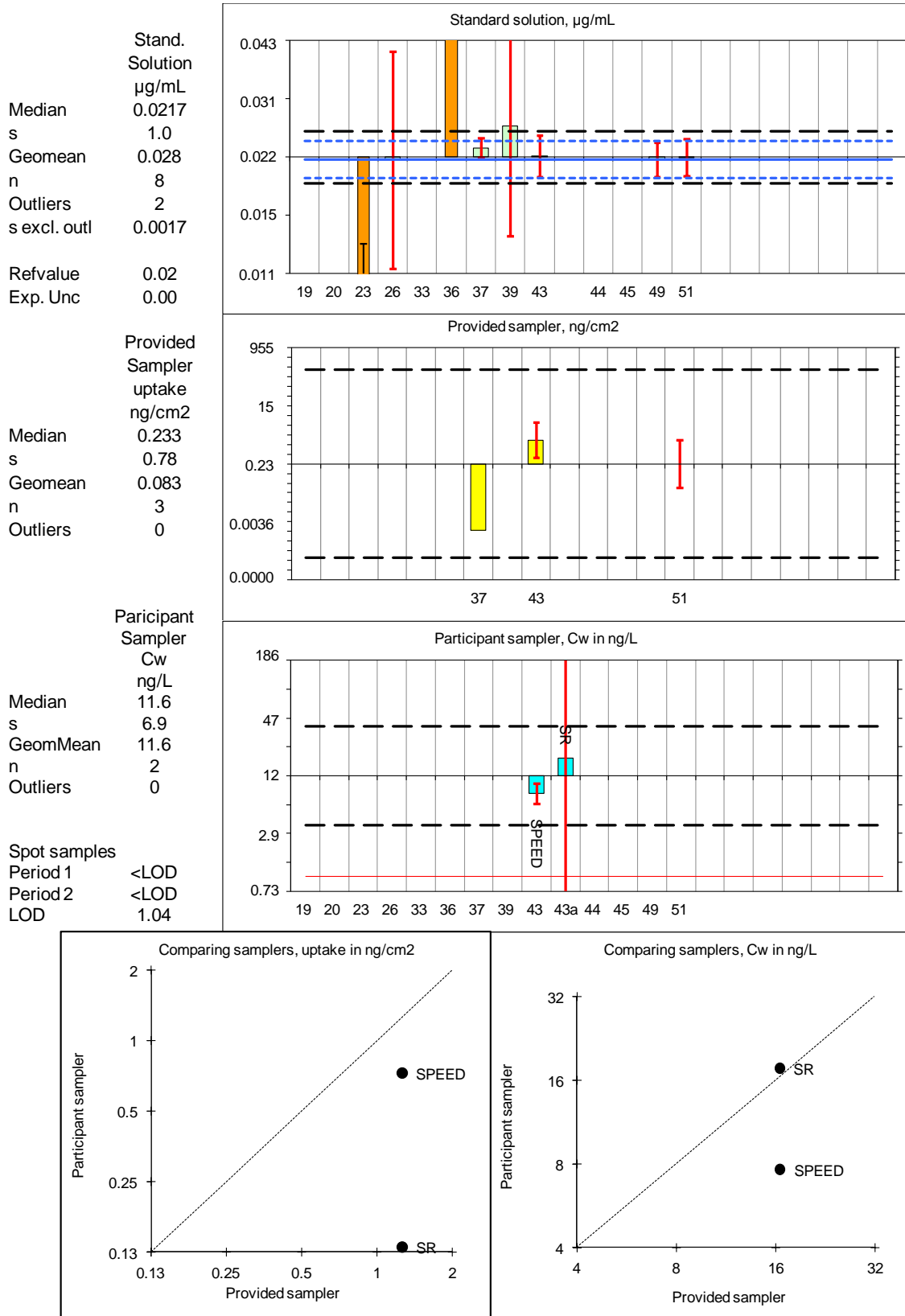


Figure 41 Results of analysis of 17-alpha-estradiol. Graph explanation is given in 10.2.and 10.3.

17-alpha-Ethinylestradiol

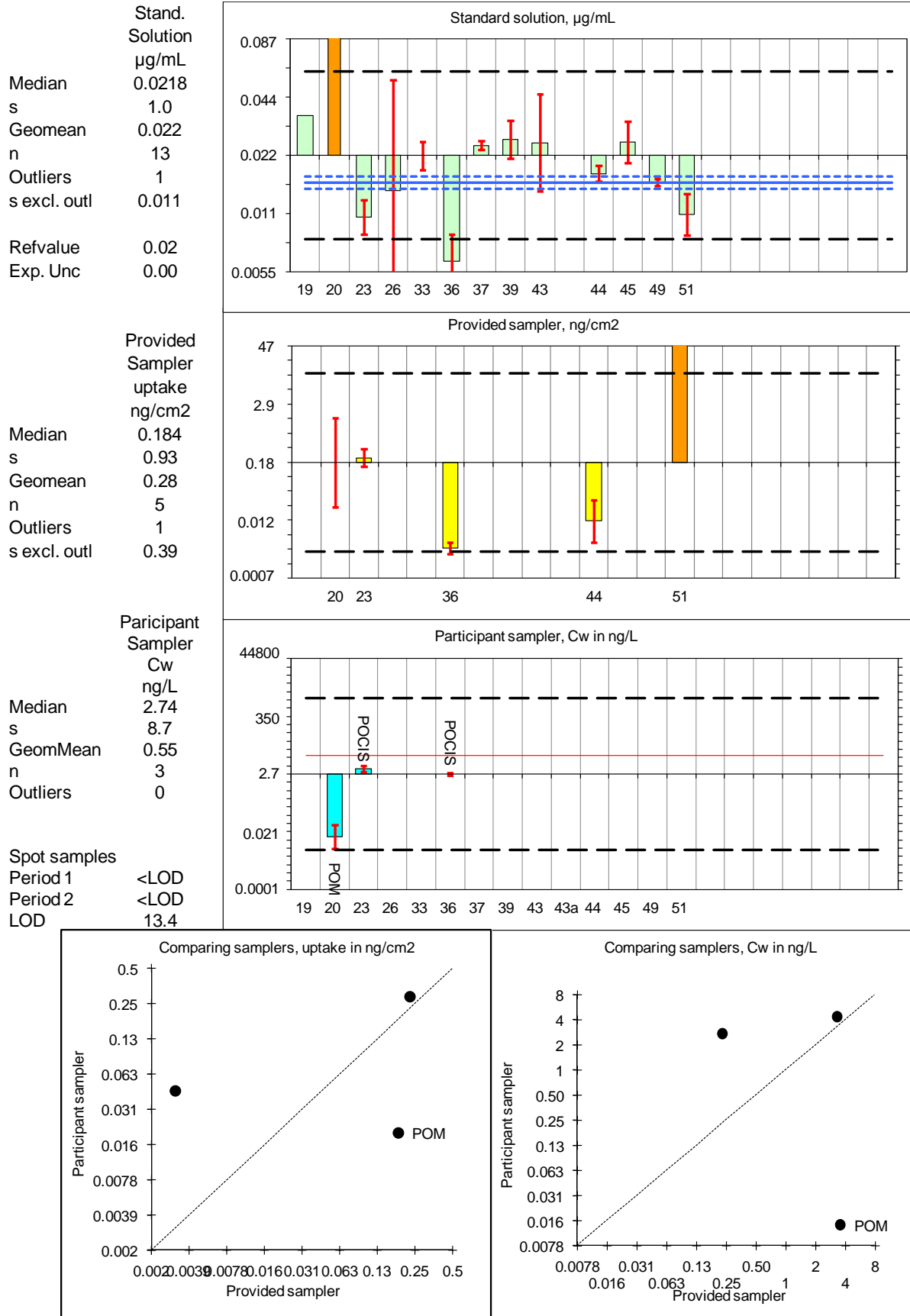


Figure 42 Results of analysis of 17-alpha-ethinylestradiol. Graph explanation is given in 10.2. and 10.3.

17-beta-Estradiol

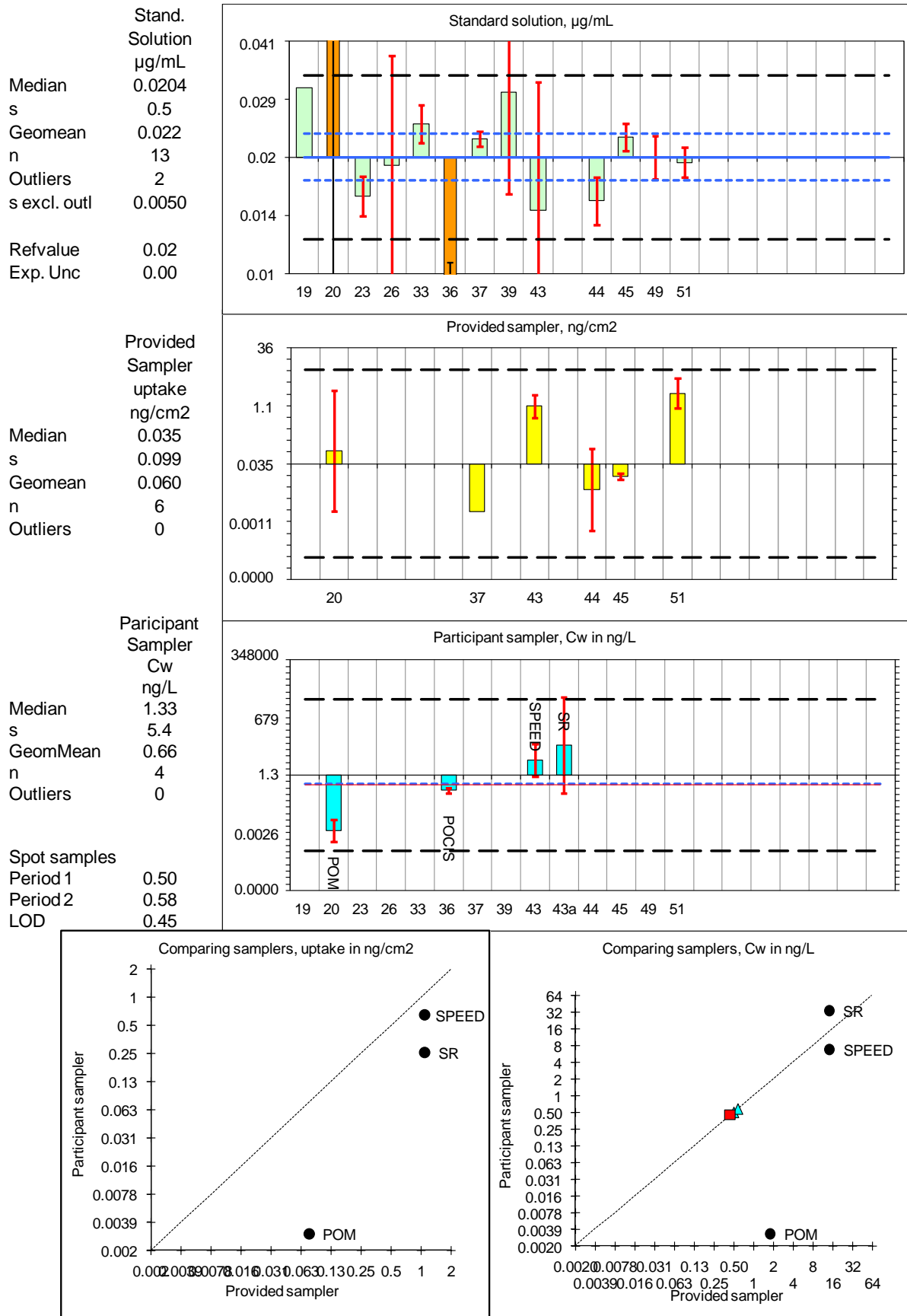


Figure 43 Results of analysis of 17-beta-estradiol. Graph explanation is given in 10.2. and 10.3.

Estriol

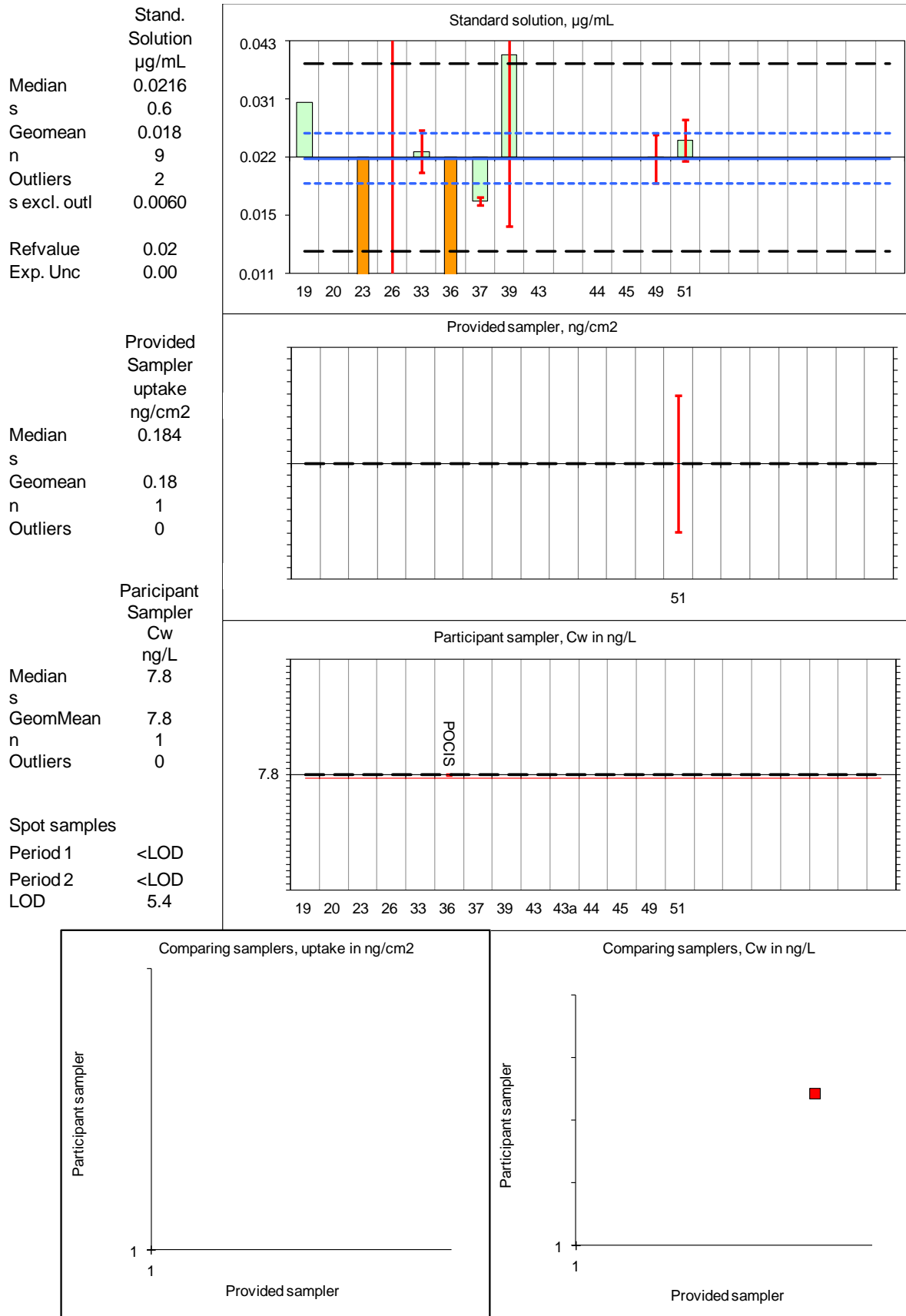


Figure 44 Results of analysis of estriol. Graph explanation is given in 10.2.and 10.3.

Estrone

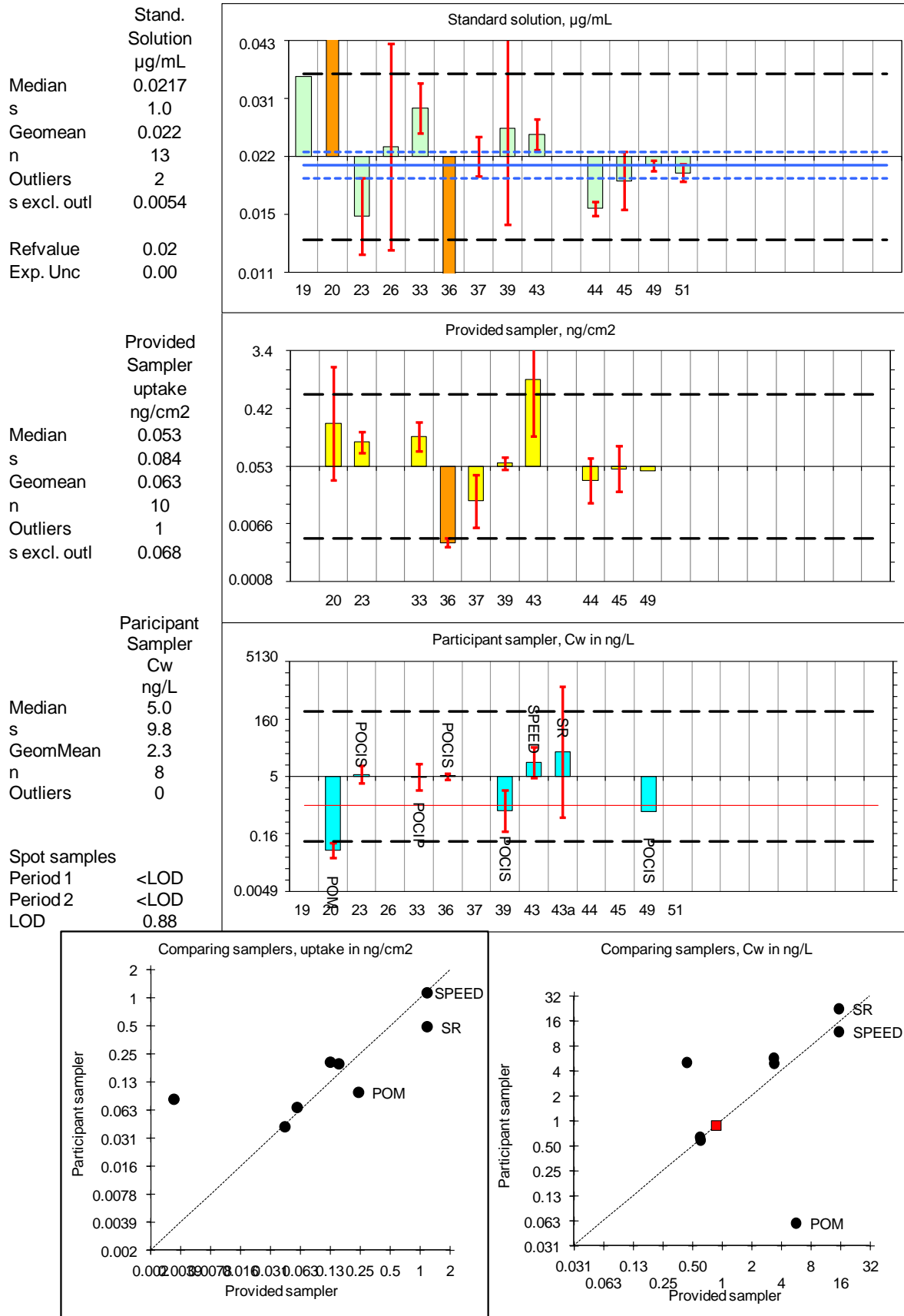


Figure 45 Results of analysis of estrone. Graph explanation is given in 10.2.and 10.3.

11.3.3 Sample variability

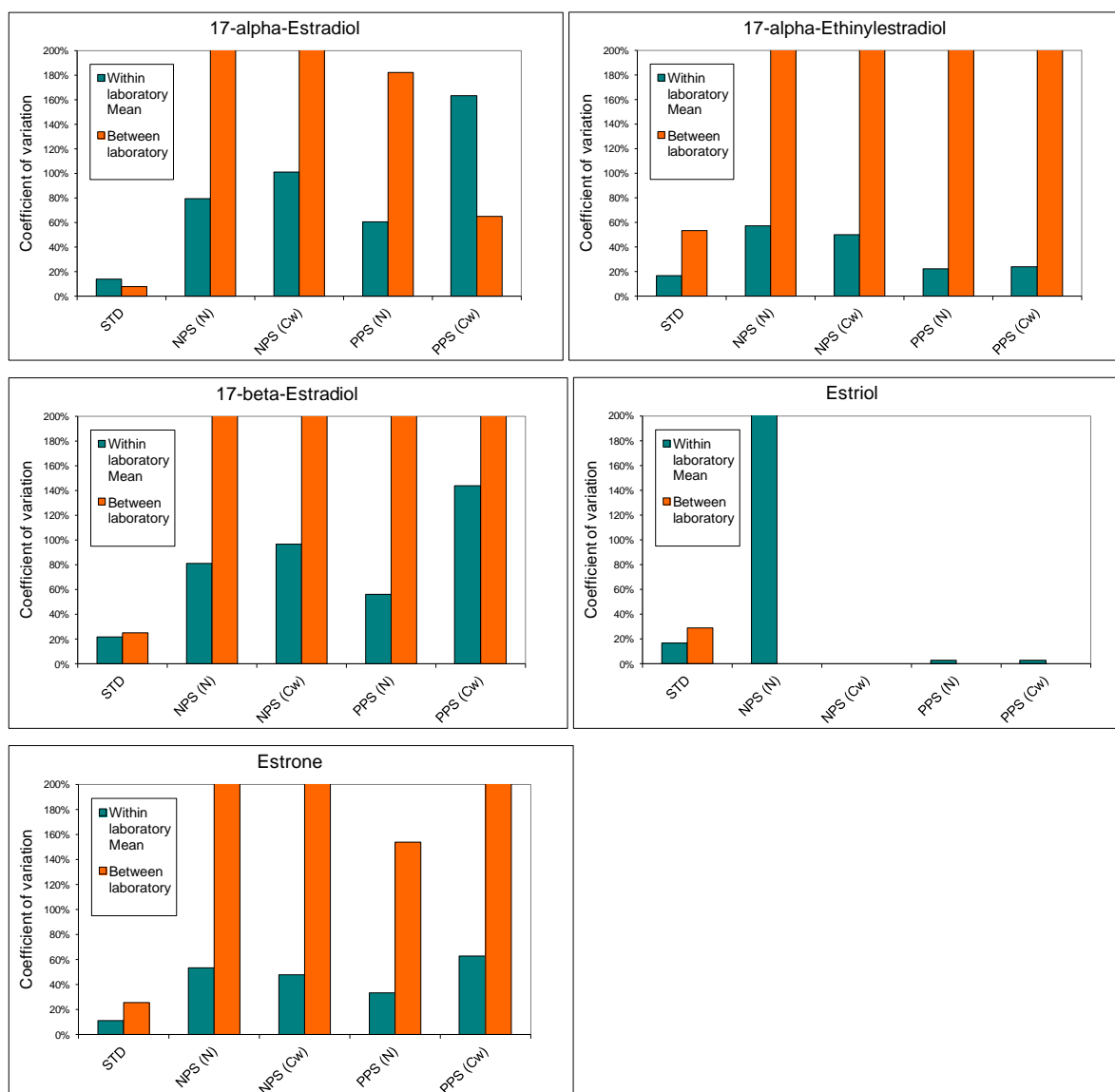


Figure 46 Variability of reported steroid hormone results at different procedure levels. Results are the coefficients of variation for individual compounds. NPS – provided passive sampler; PPS – participant passive sampler. (N) – amount; (C_w) – water concentration.

11.3.4 Standard solution

Results provided by participating laboratories for the standard solution are shown in the top bar charts in Figure 41-45. The range of variability of reported results is given in Table 29. Variability observed for individual compounds is also shown in Figure 46.

A good within laboratory variability of analysis of individual compounds in steroid standard solution was observed with the mean CV from 11 to 22% (Table 29). The between laboratory variability (excluding outliers) was satisfactory, too, ranging between 8 and 53%. In all cases the reference concentration of steroids was within the range comprised by the participant results (median ± 2 standard deviations excluding outliers) and with exception of 17-alpha-Ethinylestradiol the median and geometric mean of participant results were within the uncertainty range stated by the central laboratory. Outlier results were reported by laboratories 20, 23 and 36.

Table 29 Variability range at different procedure levels for steroid hormones.

Steroid hormones					
		Coefficient of variation (%)			
Variability:		Within laboratory		Between laboratory	
Matrix analysed:		Min.	Max.	Min.	Max.
	Standard solution	11%	22%	8%	53%
<i>Provided sampler</i>	NPS amount (ng/cm ²)	53%	>300%	208%	>300%
	NPS water concentration	48%	101%	251%	>300%
<i>Participant sampler</i>	PPS amount (ng/cm ²)	3%	60%	154%	>300%
	PPS water concentration	3%	163%	65%	>300%

11.3.5 Provided sampler

The results provided by participating laboratories are shown in the middle bar charts in Figure 41-45.

The analysis of steroid hormones in *provided passive samplers* proved challenging since the exposure concentrations of target compounds in water were very low (Table 33). This is reflected by the fact that from 13 laboratories that provided results for standard solution, less than a half was able to measure steroids (with exception of estrone) above their method limits of quantification in *provided samplers*.

11.3.6 Field blanks

Concentrations of steroids in field blank samplers was low, in most cases less than 10% of the concentration found in field exposed samplers and close to method detection limits (Table 30).

11.3.7 Sample variability

An elevated within laboratory variability of analysis of steroid hormones in *provided samplers* (ng/cm²) was observed with the mean CV higher than 53% for sampler uptake and between 48 and 101% for the water concentration estimate, respectively (Table 29). This reflects well the fact that measurement uncertainty increases when concentrations are close to the method detection limit.

The between laboratory variability (excluding outliers) for sampler uptake (ng/cm²) as well as related water concentration estimate (ng/L) was very high (higher than 200%). The high variability is likely because the concentrations in *provided samplers* were close to participant method LOQs. Method precision dramatically decreases as the concentration approaches LOQ. Furthermore, analysis of steroids in complex environmental matrixes seems to be challenging for the participating laboratories [31].

11.3.8 Contribution of the calculation procedure to data variability

For steroids the contribution of uncertainty in calculation procedure to the overall uncertainty of water concentration was minor in comparison to the uncertainty of sampling and analysis.

Table 30. Concentrations of steroids in field blank sampler (ng/sampler) provided by the organiser. *Empty fields indicate cases where participants did not report any value.

11.3.9

Laboratory	17-alpha-Estradiol	17-alpha-Ethinylestradiol	17-beta-Estradiol	Estriol	Estrone
19					
20		1.35	0.98		0.37
23	<0.10	<0.08	<0.10	<0.08	<0.08
26					
33					
36					
37					
39					
43	9.17		5.12		8.37
43a	9.17		5.12		8.37
44		0.03	0.03		0.03
45		<0.05	0.008		
49	<0.25	<2.5	<0.13	<0.5	<0.13
51					

Table 31. Estimated CV(R_s) for C_w calculation for *provided sampler*; steroids.

Compound	CV(N _{NPS}) (%)	CV(C _{w;NPS}) (%)	CV(R _s) (%)
17-alpha-Estradiol	1428	1043	not estimated
17-alpha-Ethinylestradiol	413	289	not estimated
17-beta-Estradiol	830	387	not estimated
Estriol	not estimated	not estimated	not estimated
Estrone	169	170	23

11.3.10 Participant sampler

Figure 47 shows the different types of samplers that were successfully (above method LOQ) applied by participants in sampling of steroids. The most frequently applied design of sampler applied in the study corresponded with the standard configurations of the POCIS (pharmaceutical or pesticide version). Other types of samplers applied included silicone rubber and polyoxymethylene. Details on other samplers applied by participants and their processing are given in Annex VI. The results provided by participating laboratories are shown in the bottom bar charts in Figure 41-45.

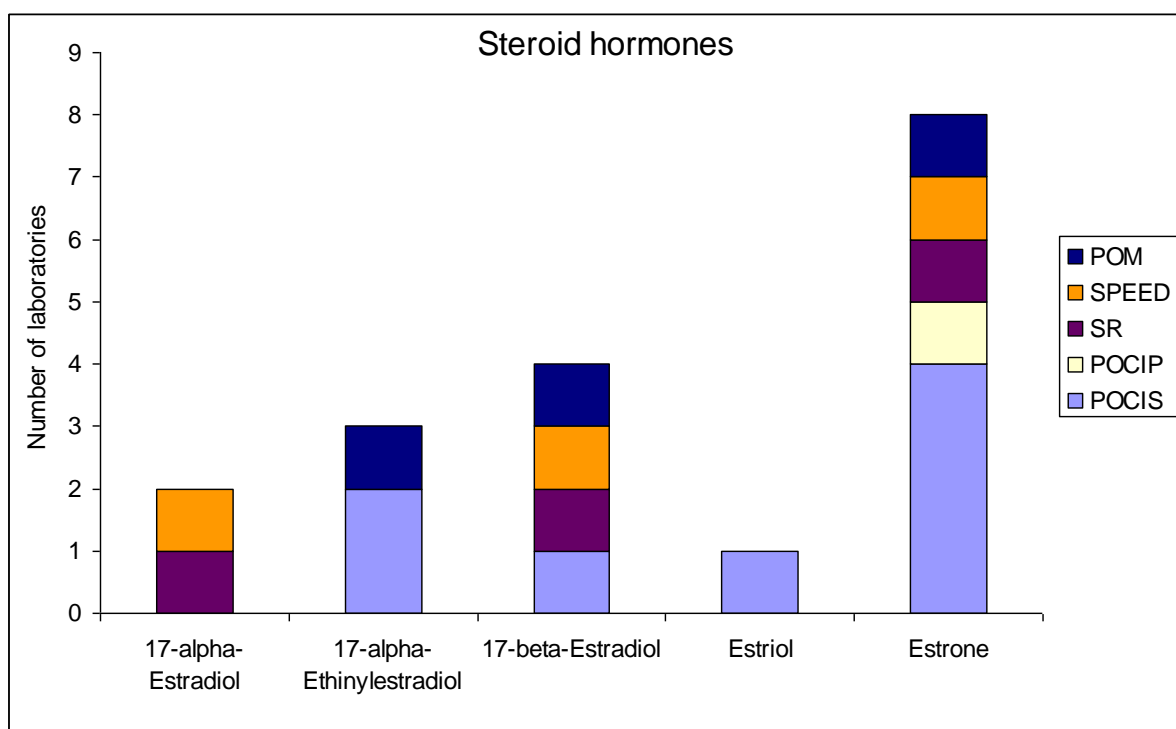


Figure 47 Various categories of participant passive samplers successfully applied in analysis of steroid hormones. Sampler was counted only when a particular compound was measured above method LOQ. A brief description of sampler category (shown as abbreviation in the legend) is given in Table 18.

11.3.11 Field blanks

Concentrations of steroid hormones in field blank samplers were low, always <10% of the concentration found in field exposed samplers and close to method detection limits (Table 32).

11.3.12 Sample variability

The within laboratory variability of analysis of steroids in *participant samplers* (ng/cm²) was observed with the mean CV between 3 and 60% for sampler uptake and between 3 and 163% for the related water concentration estimate, respectively (Table 29).

The between laboratory variability (excluding outliers) was high for all compounds, higher than 154% for sampler uptake (ng/cm²) and higher than 65% for the water concentration estimate (ng/L), respectively.

As was stated for *provided samplers*, this reflects well the fact that measurement uncertainty increases when concentrations are close to method detection limit.

Individual laboratories found in most cases well comparable results (close to equality) for *participant* and *provided sampler* for uptake per surface area (left-hand biplots), as well as the resulting water concentration (C_w , right-hand biplot) (Figure 41-Figure 45). Points that lie near the equality line but far from the median values indicate a large systematic error introduced by the laboratory. Points far from the equality line for uptake are mostly data from samplers that significantly differ from *provided sampler* working principle (e.g. POM).

Table 32. Concentrations of steroid hormones reported in field blank participant sampler (ng/sampler)*.

Laboratory	17-alpha-Estradiol	17-alpha-Ethinylestradiol	17-beta-Estradiol	Estriol	Estrone
19					
20		1.71	1.02		1.55
23					
26					
33					
36					
37					
39					
43	<5		<5		<5
43a	<5		<5		<5
44					
45					
49	<0.25	<2.5	<0.13	<0.5	<0.13
51					

11.3.13 Spot samples

Results of water sample analysis are given in Table 33. Steroid hormone concentrations in water, reported from spot samples, were in most cases below method LOQ. The only exception was 17-beta-estradiol, however, also this value was very close to method LOQ. A comparison of these concentrations with water concentration estimates from passive samplers is displayed in bottom bar charts and right hand biplot charts in Figure 41-45. The reported data (< LOQ) of composite spot samples was always within the range comprised by the water concentration estimates from passive sampler results (median \pm 2 standard deviations excluding outliers).

Table 33 Concentrations of steroids in weekly composite water samples.

Sample/Compound	Filtration blank (20.6.-26.6.)	Filtration blank (27.6.-4.7.)	Weekly composite (20.6.-26.6.)	Weekly composite (27.6.-4.7.)	units
17-alpha-Estradiol	<1.3	<0.9	<1.1	<0.9	ng/L
17-alpha-Ethinylestradiol	<17	<14	<10	<12	ng/L
17-beta-Estradiol	0.7	<0.5	0.5	0.6	ng/L
Estriol	<2.9	<2.8	<7.5	<8.3	ng/L
Estrone	<1.1	<0.9	<0.9	<0.7	ng/L

11.3.14 Conclusions for steroids

1. An acceptable within laboratory variability was observed for standard solution of steroids and only in a few cases laboratories reported results outside the between laboratory variability range. In all cases the reference concentration of steroids was within the range comprised by the participant results (median \pm 2 standard deviations excluding outliers). The between laboratory variability of was acceptable, with exception of 17-alpha-ethinylestradiol (CV of 53%). With these few exceptions, calibration of instrumental methods applied for steroids was not expected to cause excessive variability in reported data. However, it has to be admitted that the selected test concentration (20 ng/mL) was in most cases higher than concentration levels in real samples analysed by laboratories and uncertainty of instrumental measurement is expected to increase with decreasing concentration.
2. Analysis of steroids in passive samplers was much more challenging than the analysis of polar pesticides or pharmaceuticals. There was a high within laboratory variability of analysis of *provided* as well as *participant samplers*. This is not surprising since concentrations found in *provided samplers* were in most cases close to participant method LOQs, where variability is elevated by definition. The lower concentrations than those analysed in standard solution, combined with a more complex sample matrix, can explain the observed increased variability.
3. Similar results for estrone (a compound analysed above LOQ by the highest number of laboratories in both types of samplers) analysed by individual laboratories by different passive samplers indicate that the PS process itself is not causing excessive variability. For other compounds the results were close to the LOQ not allowing such evaluation.
4. Considering the high between laboratory variability in sampler uptake no realistic estimation is possible of the contribution to the overall variability of different approaches in translation from passive sampler uptake to water concentration.
5. A direct comparison of PS data with spot sampling was precluded since spot sample data were below LOQ. However, there is no contradiction between PS and spot sampling method.
6. Although results from individual laboratories indicate that PS method allows measurement of concentrations lower than spot sampling method LOQs, the interlaboratory method precision needs a significant improvement.

11.4 Brominated diphenyl ethers – PBDEs

Up to 14 laboratories participated in the exercise, but the numbers varied depending on target analytes and matrices analysed. Results for individual compounds are displayed in Figure 49 -54. The explanation of data projection applied is described in chapter 10.

11.4.1 Overall data variability

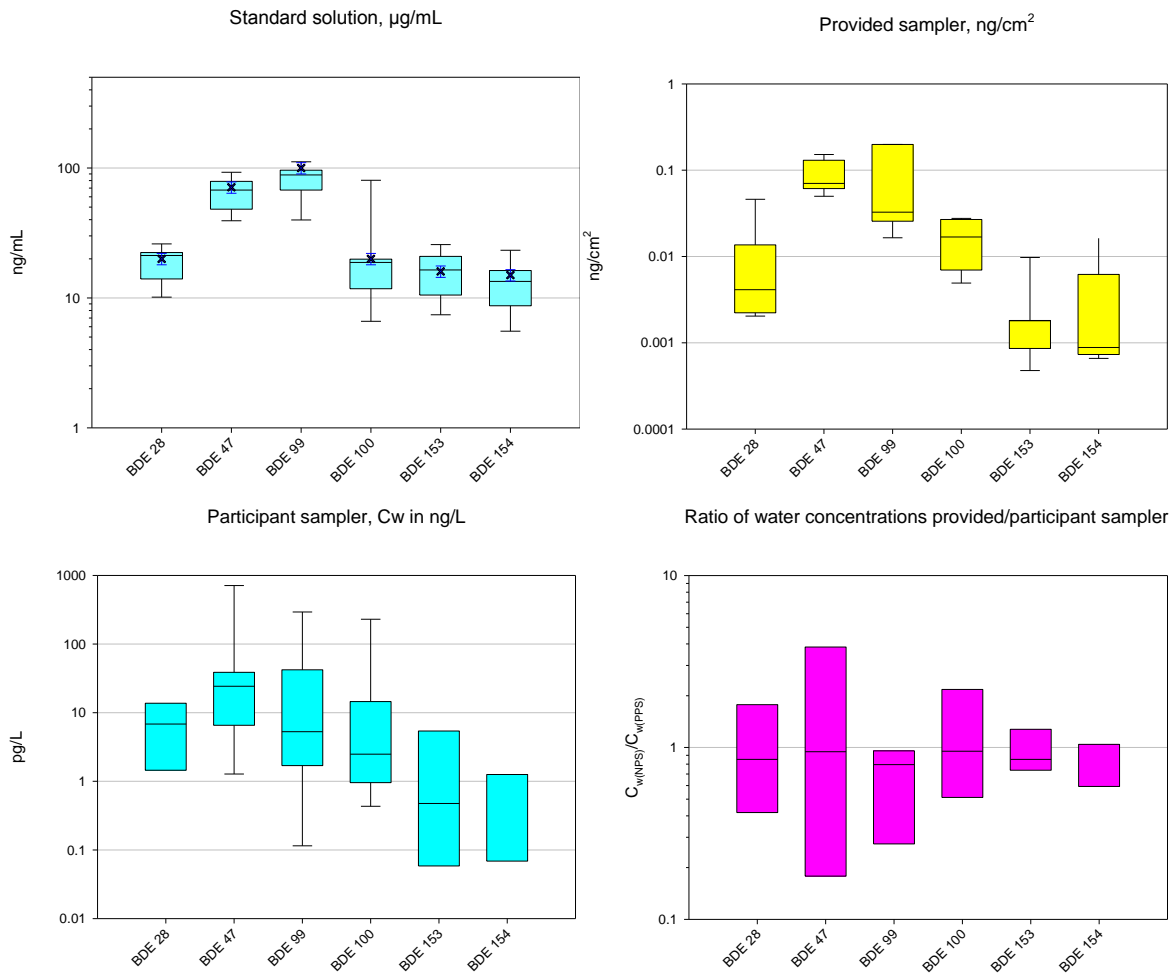


Figure 48 Concentrations of brominated diphenyl ethers in various analysed matrixes: standard solution (top left), provided sampler (top right), water concentration estimated from the participant sampler (bottom left) and the ratio of water concentrations determined in provided and participant passive sampler (bottom right), respectively. For explanation of symbols see legend to Figure 19.

11.4.2 Results by laboratories - PBDEs

BDE 28

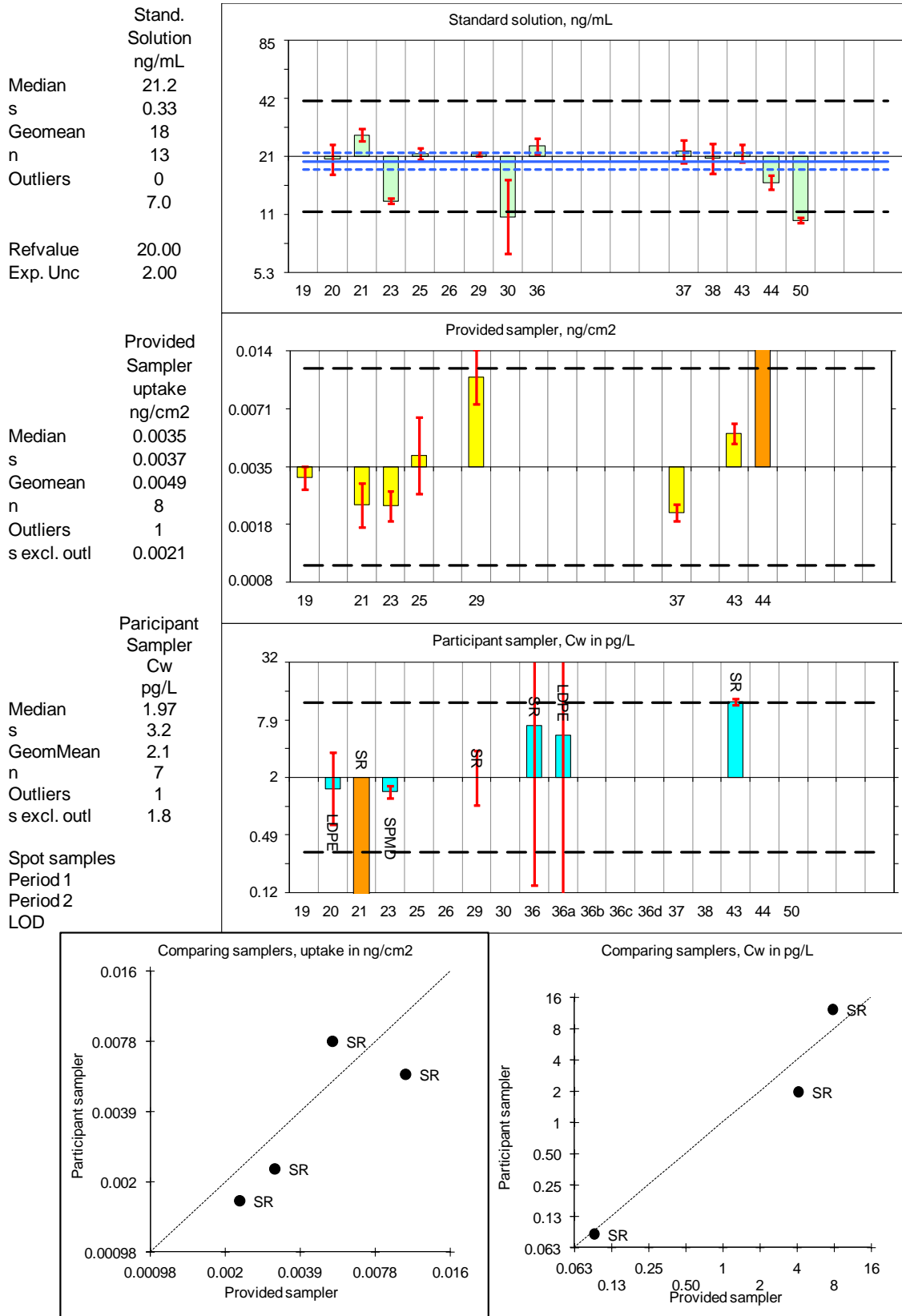


Figure 49 Results of analysis of BDE 28. Graph explanation is given in 10.2 and 10.3.

BDE 47

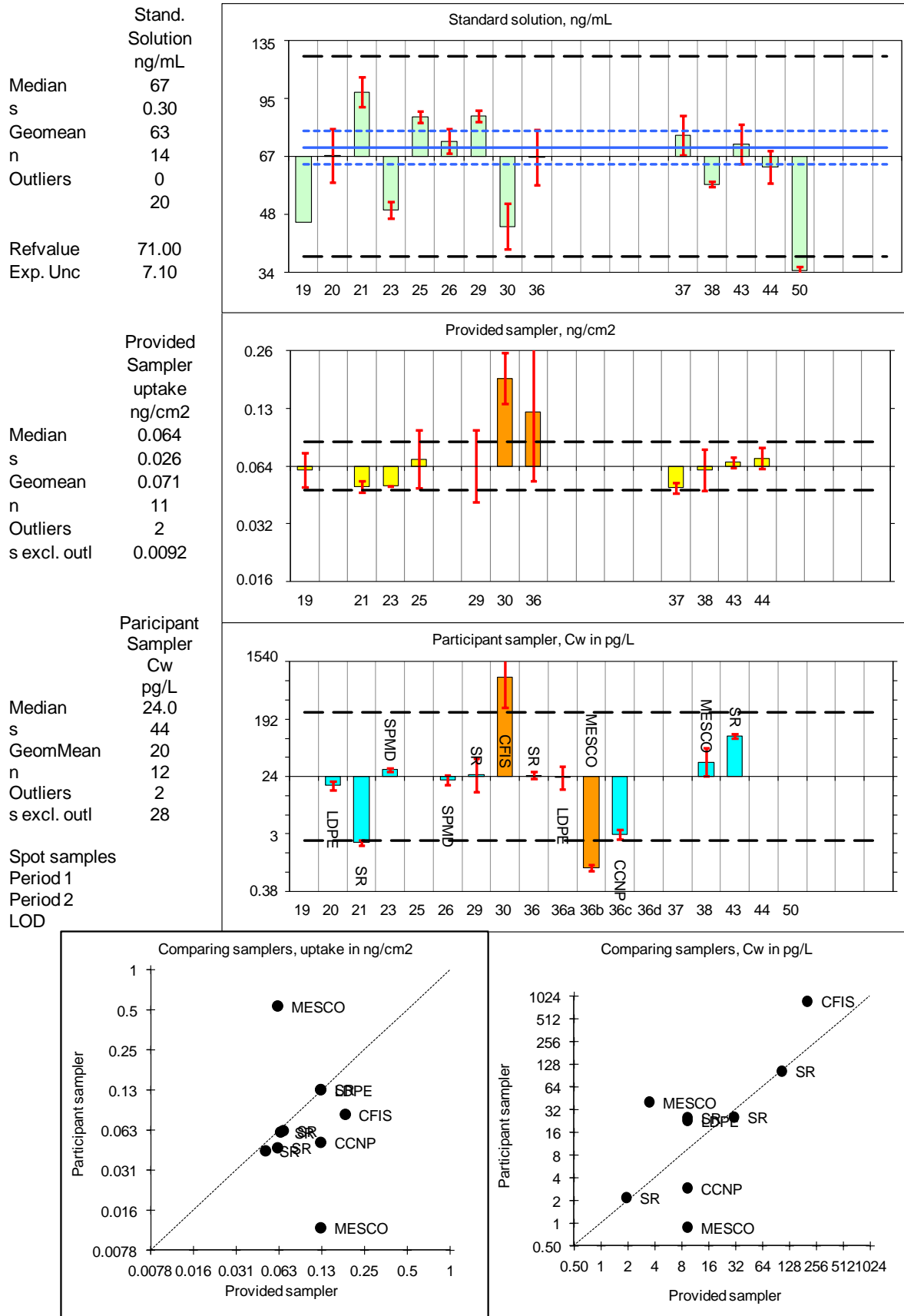


Figure 50 Results of analysis of BDE 47. Graph explanation is given in 10.2.and 10.3.

BDE 99

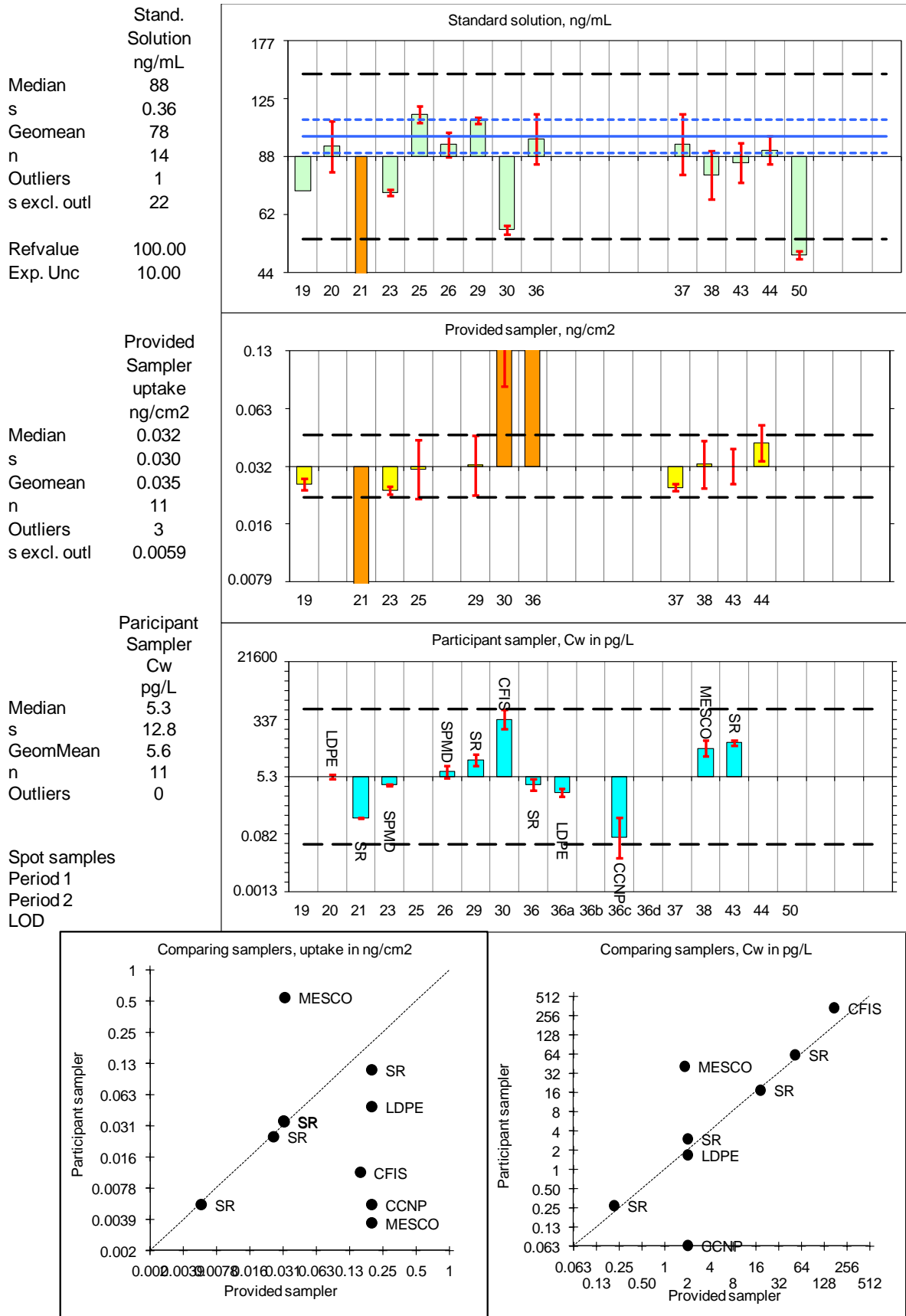


Figure 51 Results of analysis of BDE 99. Graph explanation is given in 10.2 and 10.3.

BDE 100

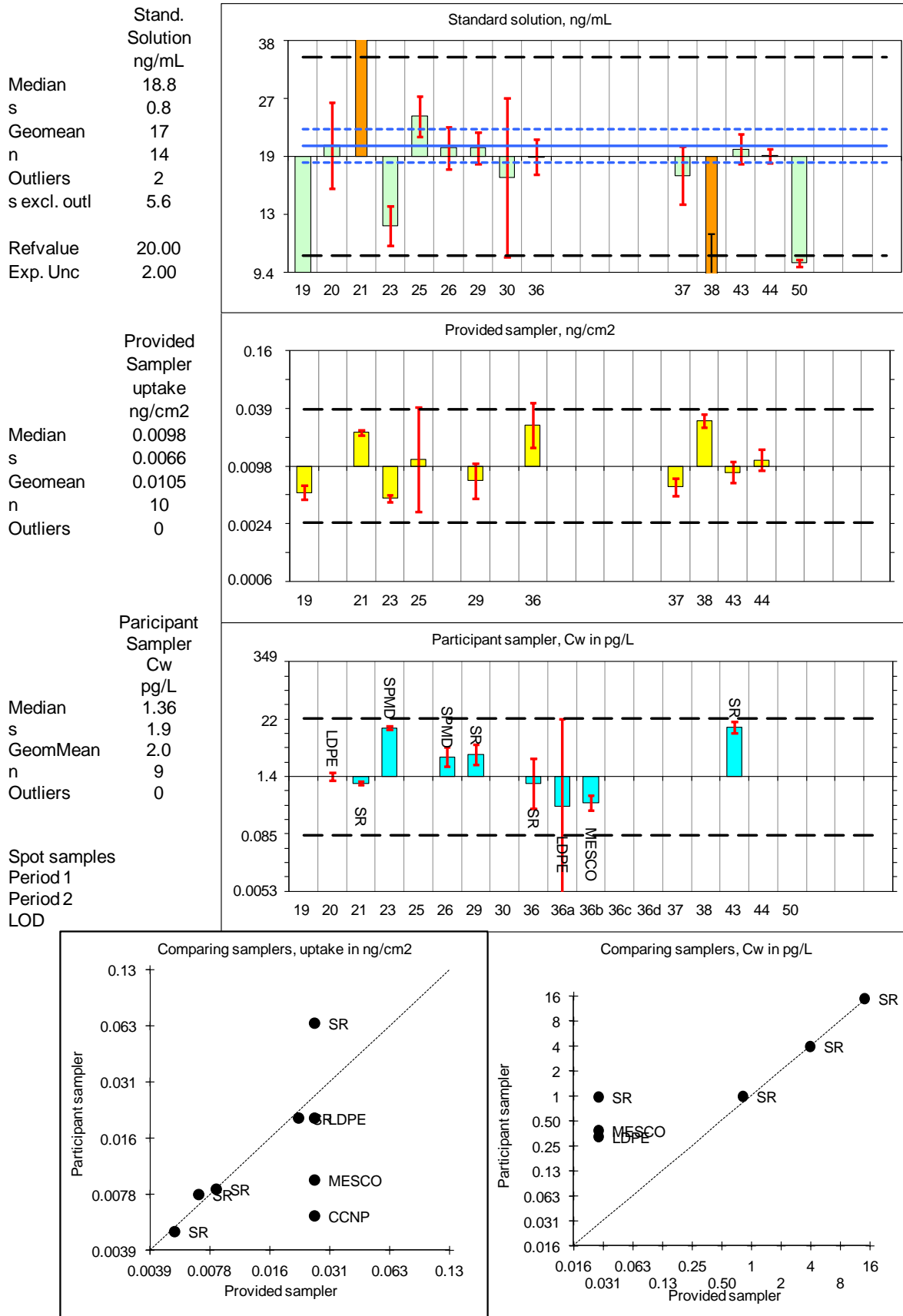


Figure 52 Results of analysis of BDE 100. Graph explanation is given in 10.2.and 10.3.

BDE 153

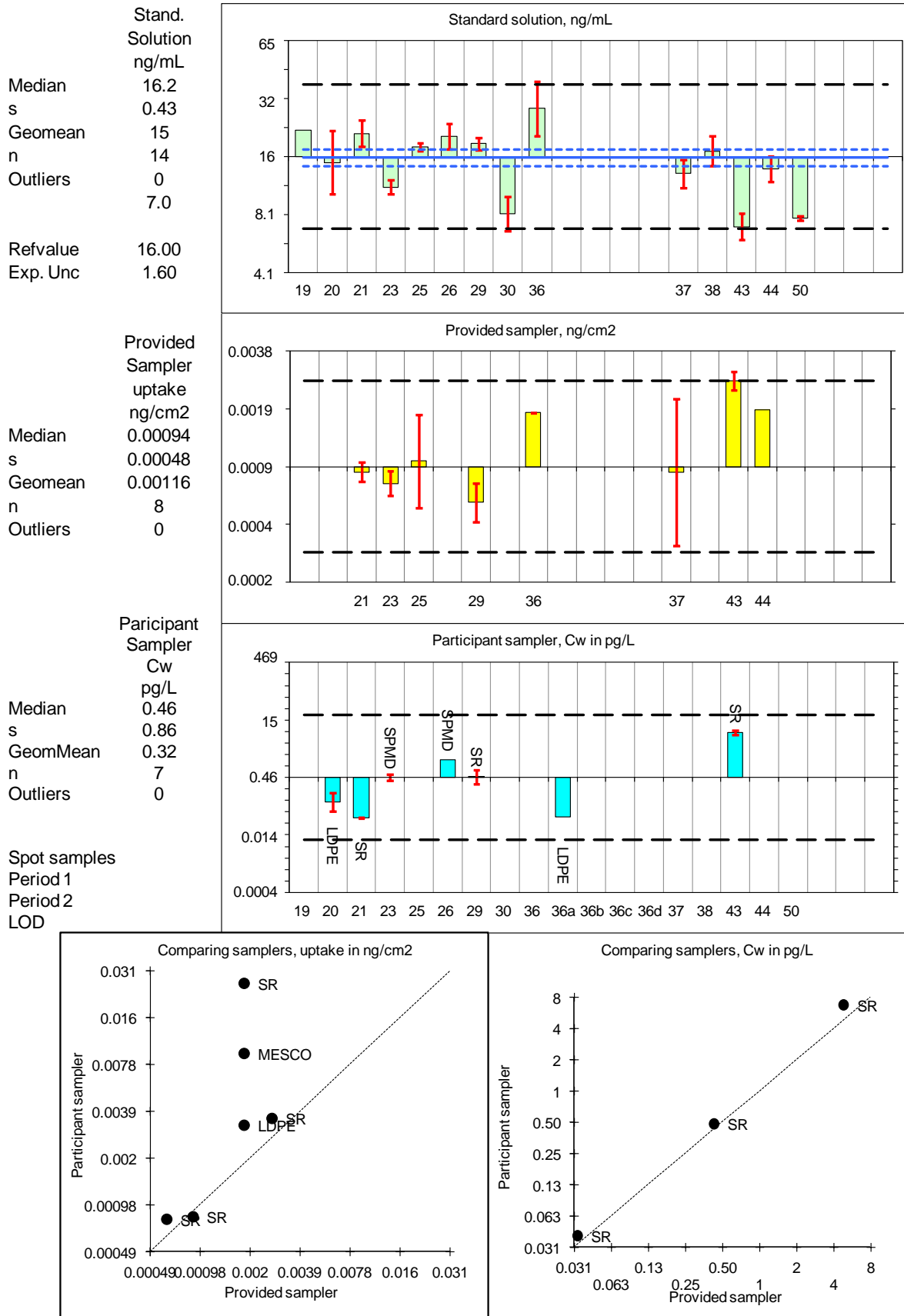


Figure 53 Results of analysis of BDE 153. Graph explanation is given in 10.2.and 10.3.

BDE 154

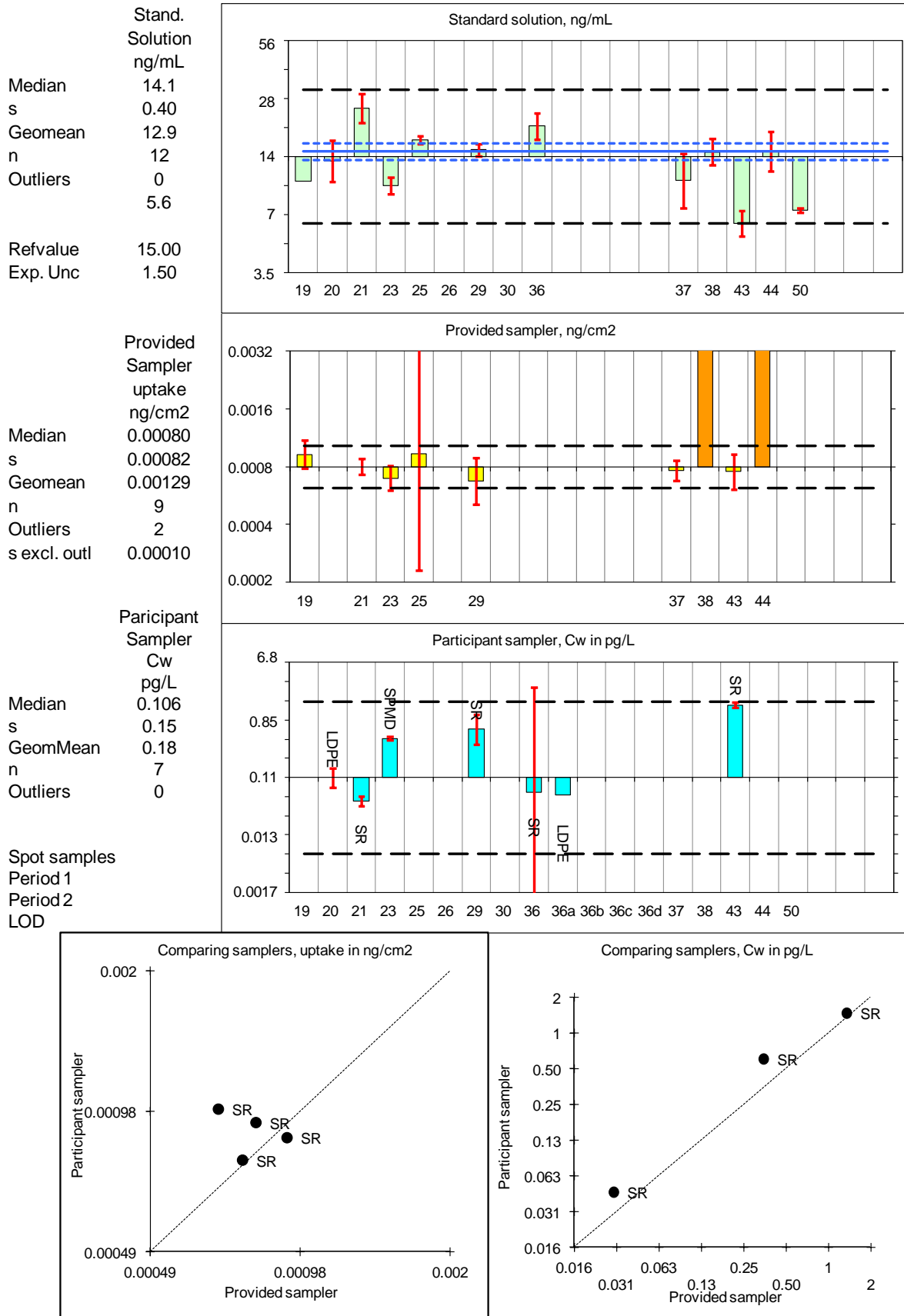


Figure 54 Results of analysis of BDE 154. Graph explanation is given in 10.2.and 10.3.

11.4.3 Sample variability

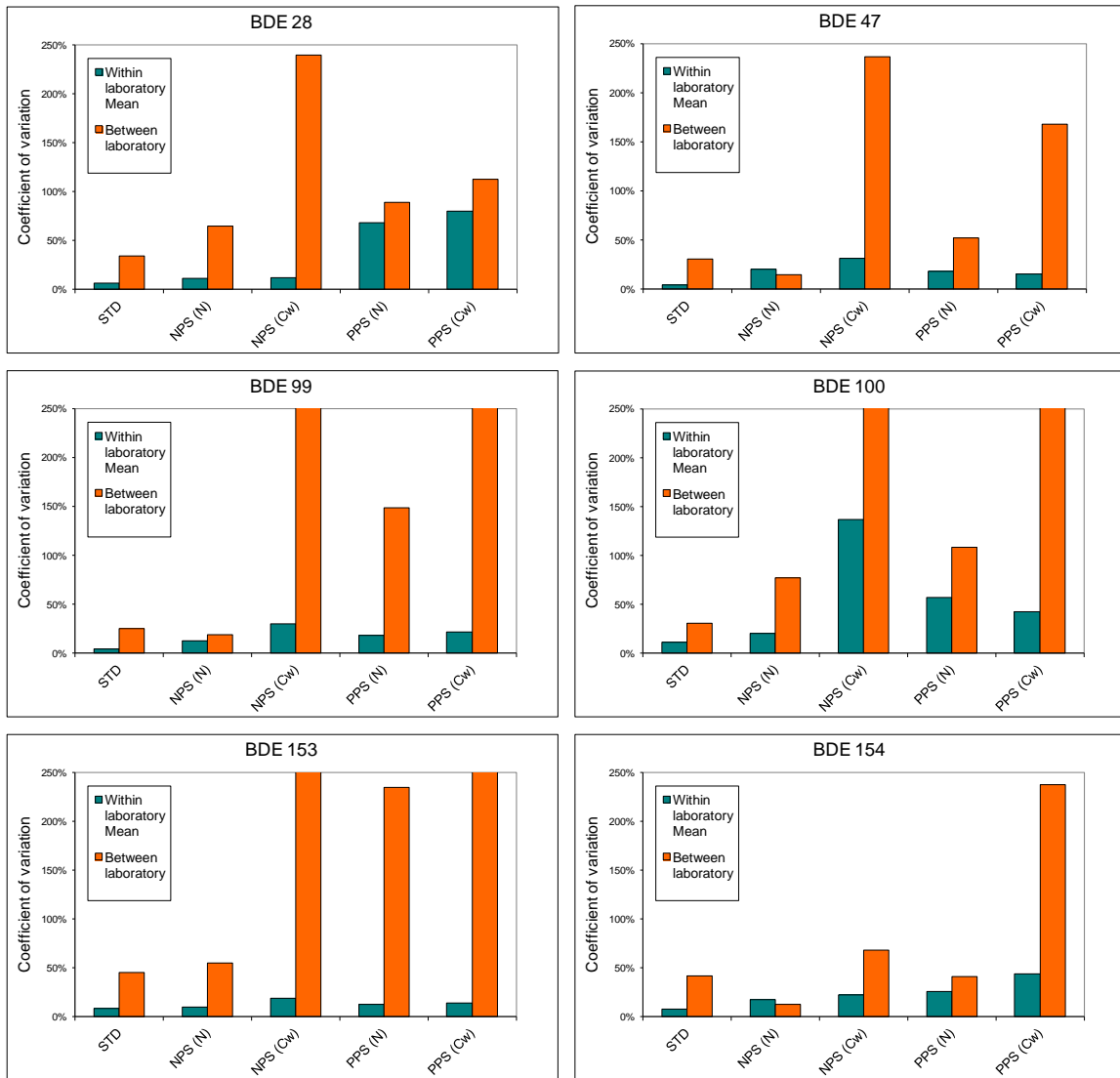


Figure 55 Variability of reported PBDE results at different procedure levels. Results are the coefficients of variation for individual compounds. NPS – provided passive sampler; PPS – participant passive sampler. (N) – amount; (C_w) – water concentration

Table 34 Variability range at different procedure levels for PBDEs.

PBDEs					
		Coefficient of variation (%)			
Variability:		Within laboratory		Between laboratory	
Matrix analysed:		Min.	Max.	Min.	Max.
Standard solution		4%	11%	25%	45%
Provided sampler	NPS amount (ng/cm ²)	9%	20%	13%	77%
	NPS water concentration	11%	137%	68%	>200%

<i>Participant sampler</i>	PPS amount (ng/cm ²)	12%	68%	41%	>200%
	PPS water concentration	14%	79%	112%	>200%

11.4.4 Standard solution

Results provided by participating laboratories for the standard solution are shown in the top bar charts in Figure 49-54. The range of variability of reported results is given in Table 34. Variability observed for individual compounds is also shown in Figure 55.

A good within laboratory variability of analysis of individual compounds in PBDE standard solution was observed with the mean CV from 4 to 11% (Table 34). The between laboratory variability (excluding outliers) was satisfactory, too, ranging between 25 and 45%. In all cases the reference concentration of PBDEs was within the range comprised by the participant results (median \pm 2 standard deviations excluding outliers) and with exception of BDE 99, the median and geometric mean of participant results were within the uncertainty range stated by the central laboratory. Several outlier results were observed, but this bias was not systematic (not occurring for all compounds reported by one laboratory).

11.4.5 Provided sampler

The results provided by participating laboratories are shown in the middle bar charts in Figure 49-54.

11.4.6 Field blank

Concentrations of PBDEs in field blank samplers were low, in most cases less than 10% of the concentration found in field exposed samplers (with exception of BDE 99, BDE 100, BDE 153 in lab 36) and close to method detection limits (Table 35).

11.4.7 Spiked field blank

Results of analysis of PBDEs in spiked field blanks are shown in Figure 56. Relatively high between laboratory variability was observed in analysis of spiked field blanks. Coefficients of variation for BDE47, BDE 99, BDE 100 and BDE 153 were 44%, 72%, 59% and 68%, respectively. The high variability indicates that some laboratories had difficulties in analysis of PBDEs in the silicone rubber matrix.

11.4.8 Sampling variability

An excellent within laboratory variability of analysis of PBDEs in *provided samplers* was observed with the mean CV between 9 and 20% for sampler uptake. The between laboratory variability of for the water concentration estimate was higher, ranging from 11 to 137% (Table 34).

The between laboratory variability (excluding outliers) for sampler uptake was higher, ranging from 13 to 77% for different compounds. Even higher (higher than 68%) variability was observed for the water concentration estimate.

Analysis of individual compounds in *provided samplers* was affected by between laboratory variation up to 2.5 times larger than the analysis of standard solution. This can be explained by lower concentrations and potential interferences originating from a more complex matrix analysed.

Participants can check whether results reported by their laboratory are comparable (within the study variability) with results provided by the other laboratories (Figure 49-54). Participants also may check whether a bias in instrument calibration (outlier result in analysis of standard solution) may have contributed to the bias of *provided sampler*

data reported by this laboratory. For example, for BDE 99 results by laboratory 21 were evaluated as outliers for both analysis of standard solution and the *provided sampler*, respectively.

11.4.9 Contribution of the calculation procedure to data variability

Coefficient of variation of the applied calculation procedure was estimated using the approach described in 10.5. For PBDEs, the variability of applied calculation procedure and sampler calibration procedure is the main factor causing the elevated between laboratory variability of water concentration estimates from *provided sampler* data. This is somewhat surprising since the procedures to reduce uncertainty of estimation of free dissolved concentrations from accumulation in silicon rubbers have been described in the literature (see chapter 1.7 for details) and are routinely used in monitoring programmes. Besides difficulties in proper application of the sampler uptake models, difficulties with the analysis of PRC compounds may have contributed to the high variability of reported water concentration. Accurate measurement of the % of PRCs remained in the sampler after exposure are an absolute requirement for obtaining unbiased estimates of PBDE sampling rates in the field.

Table 35 Concentrations of PBDEs in field blank sampler (ng/sampler) provided by the organizer..

Laboratory	BDE 28	BDE 47	BDE 99	BDE 100	BDE 153	BDE 154
19	<0.1	0.16	0.06	0.04	<0.10	<0.10
20						
21						
23	<0.01	0.05	0.02	<0.01	0.02	<0.01
25	<0.04				0.25	0.15
26						
29	<0.05	<0.05	<0.05	<0.05	<0.05	0.05
30	<5	<5	<5	<5	<5	<5
36	1.03	2.26	20.15	7.05	0.53	1.03
36a	1.03	2.26	20.15	7.05	0.53	1.03
36b	1.03	2.26	20.15	7.05	0.53	1.03
36c	1.03	2.26	20.15	7.05	0.53	1.03
36d	1.03	2.26	20.15	7.05	0.53	1.03
37		0.02	0.01	0.002	0.01	0.00
38						
43						
44						
50	0.27	0.39	<0.05	<0.05	<0.05	<0.05

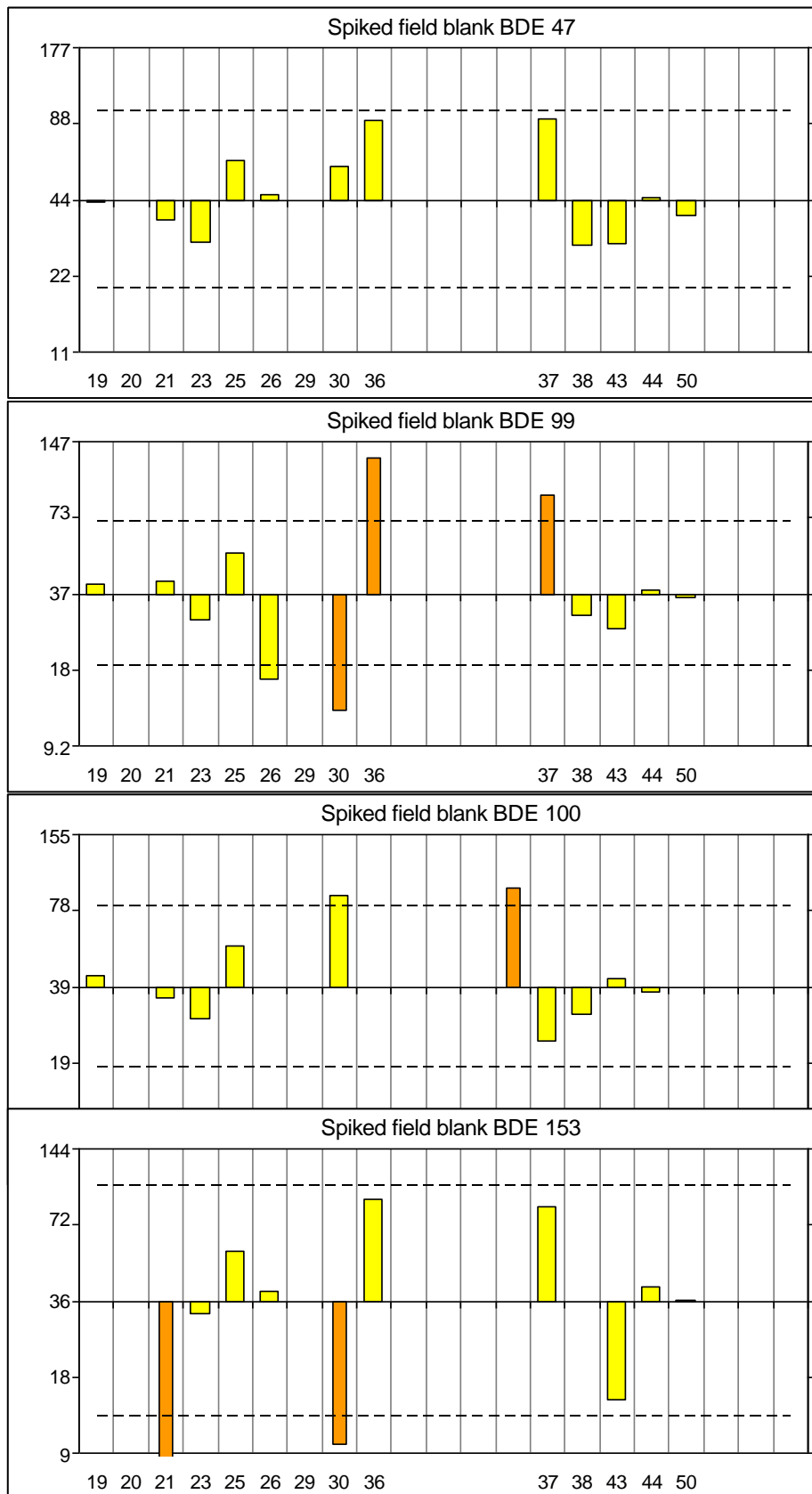


Figure 56 Concentrations of PBDEs in spiked field blank sampler provided by the organizer (ng/sampler). The central line shows the median value and the dashed lines ± 2 standard deviations of log 2 transformed values without outliers. Outlier values are labelled in darker colour.

Table 36 Estimated CV(R_s) for C_w calculation for *provided sampler*, PBDEs.

Compound	CV(N _{NPS}) (%)	CV(C _{w;NPS}) (%)	CV(R _s) (%)
BDE 28	62	187	176
BDE 47	14	231	230
BDE 99	19	549	548
BDE 100	74	572	569
BDE 153	53	665	663
BDE 154	13	66	65

11.4.10 Participant sampler

Figure 57 shows the different sampler types (above method LOQ) applied by participants in sampling of BDEs. The most frequently applied design of sampler applied in the study was based on the use of silicone rubber. The same design as the *provided passive sampler*. Other types of samplers applied included SPMD, LDPE, CFIS, MESCO, and the non-polar version of Chemcatcher. Laboratory 36 applied several designs of passive samplers. Details on other samplers applied by participants and their processing are given in Annex VIII.

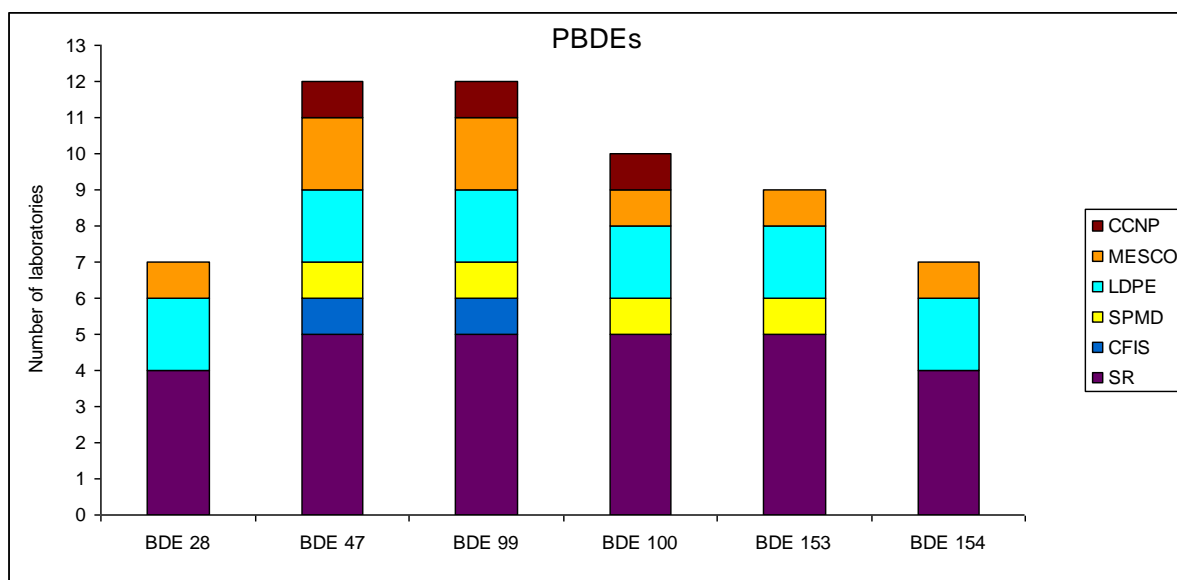


Figure 57 Various categories of participant passive samplers applied in analysis of PBDEs. A sampler was counted only when a particular compound was measured above method LOQ. A brief description of sampler category (shown as abbreviation in the legend) is given in Table 18.

The results provided by participating laboratories are shown in the bottom bar charts in Figure 49-54.

11.4.11 Field blank

Concentrations of PBDEs in field blank samplers were low, in most cases less than 10% of the concentration found in field exposed samplers (with exception of BDE28, BDE 99, BDE 100, BDE 153 in CFSIS sampler; lab 30; BDE 99, BDE 100, BDE 153 and BDE 154 in lab 36) and close to method detection limits (Table 37).

11.4.12 Sample variability

A good within laboratory variability of analysis of PBDEs in *participant samplers* was observed with the mean CV between 10 and 33% for sampler uptake and between 9 and 21% for the related water concentration estimate, respectively (Table 24).

The between laboratory variability (excluding outliers) for sampler uptake (ng/cm²) was higher, ranging from 13 to 117% for different compounds. Even higher (68 to 205%) variability was observed for the water concentration estimate.

In most cases the between laboratory variability of water concentration estimates derived from participant passive samplers was comparable to that derived from *provided samplers*.

Individual laboratories found in most cases well comparable results (close to equality) for participant and *provided sampler* for uptake per surface area (left-hand biplots), as well as the resulting water concentration (C_w, right-hand biplot) (Figure 49-Figure 54). Points that lie near the equality line but far from the median values indicate a large systematic error introduced by the laboratory.

Table 37. Concentrations of PBDEs in field blank participant sampler (ng/sampler)*.

Laboratory	Sampler	BDE 28	BDE 47	BDE 99	BDE 100	BDE 153	BDE 154
19	SR	<0.10	0.2	0.1	0.02	<0.10	<0.10
20	LDPE	0.01	0.01	0.02	0.03	0.04	0.02
21	SR						
23	SPMD	0.02	0.1	0.1	0.01	0.01	<0.01
26	SPMD		1.0	0.9			
29	SR	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
30	CFIS	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
36	LDPE	0.02	3.9	4.7	11	9.1	5.0
36a	MESCO	0.7	0.9	1.1	1.4		0.3
36b	SR			0.02	0.01	0.03	
36c	CCNP				0.02		
36d	SR						
38	MESCO						
43	SR		0.2	0.4			

*Empty fields indicate cases where participants did not report any value.

11.4.13 Water samples

This step was not performed for brominated diphenylethers since alternative methods (other than PS) for measurement of their dissolved concentrations in water are not available. Furthermore, because of very low PBDE concentrations large volumes of water would be required for analysis of concentrations at pg/L level.

11.4.14 Conclusions for PBDEs

1. An acceptable within laboratory variability was observed for standard solution of PBDEs and only in a few cases laboratories reported results outside the between laboratory variability range. The between laboratory variability of the analysis of the standard solution was satisfactory, too. Thus, calibration of instrumental methods applied for PBDEs was not expected to cause excessive variability in reported data.
2. Sampling with *provided samplers* was homogeneous. This is supported by a very low within laboratory variability of analysis of *provided samplers*. Thus, the contribution to total result variability that may have been introduced by non-homogeneity of the distributed samples can be considered minor.
3. Analysis of individual compounds in *provided samplers* was affected by between laboratory variability up to 2.5 times larger than the analysis of standard solution. A similar observation was made also when results of analysis of homogeneously spiked field blanks were compared between laboratories. The elevated variability can be explained by much lower concentrations and higher potential interferences originating from a more complex matrix analysed.
4. The increase of the between laboratory variability in water concentration estimates in comparison to sampler uptake per surface area can be attributed to errors introduced by different approaches in data translation from uptake to water concentration. For PBDEs, the variability of applied calculation procedure and sampler calibration procedure is the main factor causing the elevated between laboratory variability of water concentration estimate from *provided sampler* data. Besides difficulties the laboratories experienced in proper application of the sampler uptake models, difficulties with the analysis of PRC compounds may have contributed to the variability of reported water concentration. Training of laboratories in proper analysis of PRCs and application of published uptake models may in future help to significantly reduce this source of variability.
5. Similar results for different passive samplers analysed by individual laboratories indicate that the PS process is not causing excessive variability.
6. The higher between laboratory variability of water concentration estimates in comparison to within laboratory precision is likely related to systematic error in results of individual laboratories, which in turn can be related to both difficulties with analysis in the complex matrix of the field exposed passive sampler as well as application of biased uptake models and/or calibration data.

11.5 Fluorinated surfactants

Up to 9 laboratories participated in the exercise, but the numbers varied depending on target analytes and matrices analysed. Results for individual compounds are displayed in Figure 59-60. The explanation of data projection applied is described in chapter 7.5.

11.5.1 Overall data variability

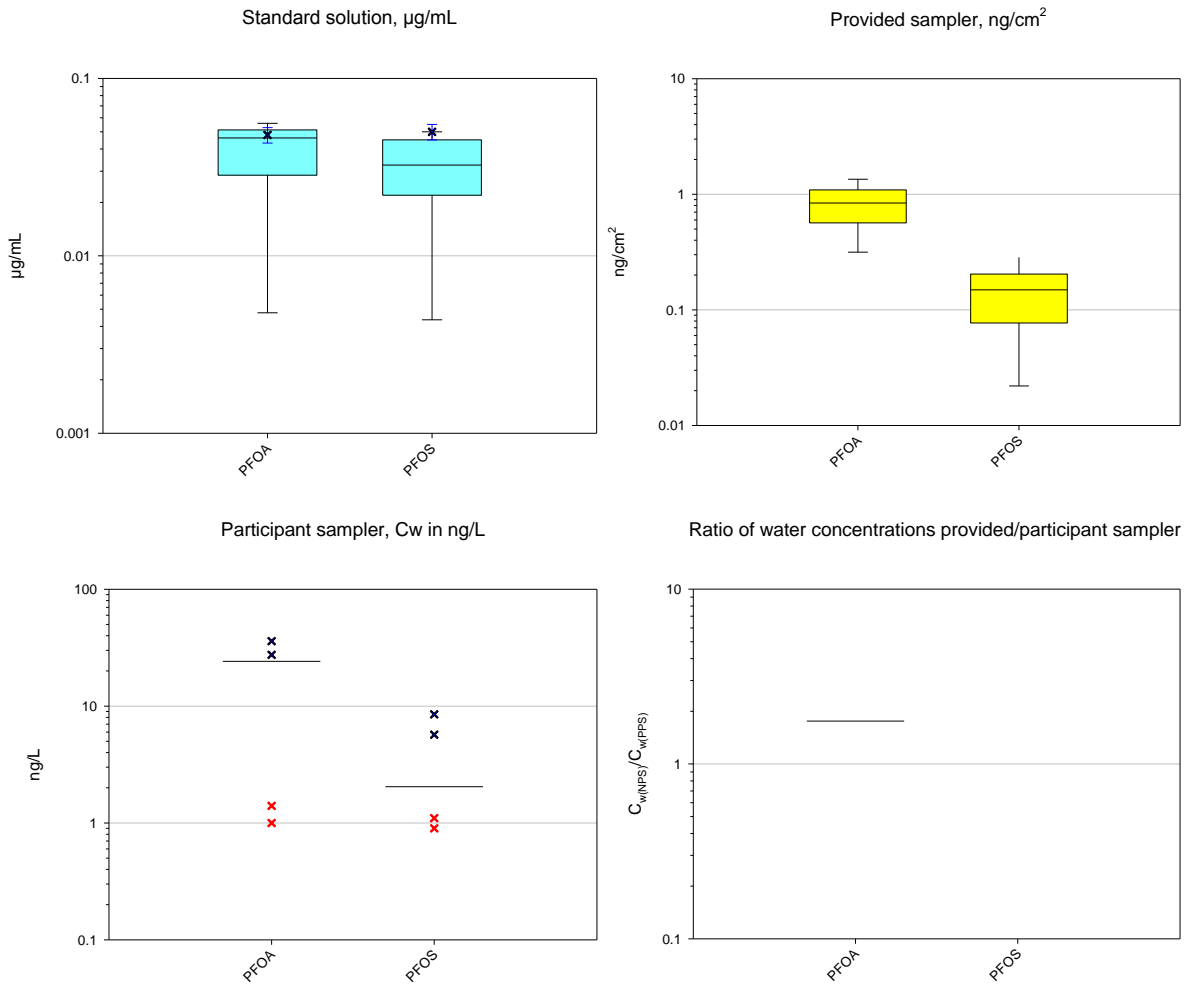


Figure 58 Concentrations of PFOA and PFOS in various analysed matrixes: standard solution (top left), provided sampler (top right), water concentration estimated from the participant sampler (bottom left) and the ratio of water concentrations determined in provided and participant passive sampler (bottom right), respectively. For explanation of symbols see legend to Figure 19.

11.5.2 Results by laboratories – fluorinated surfactants

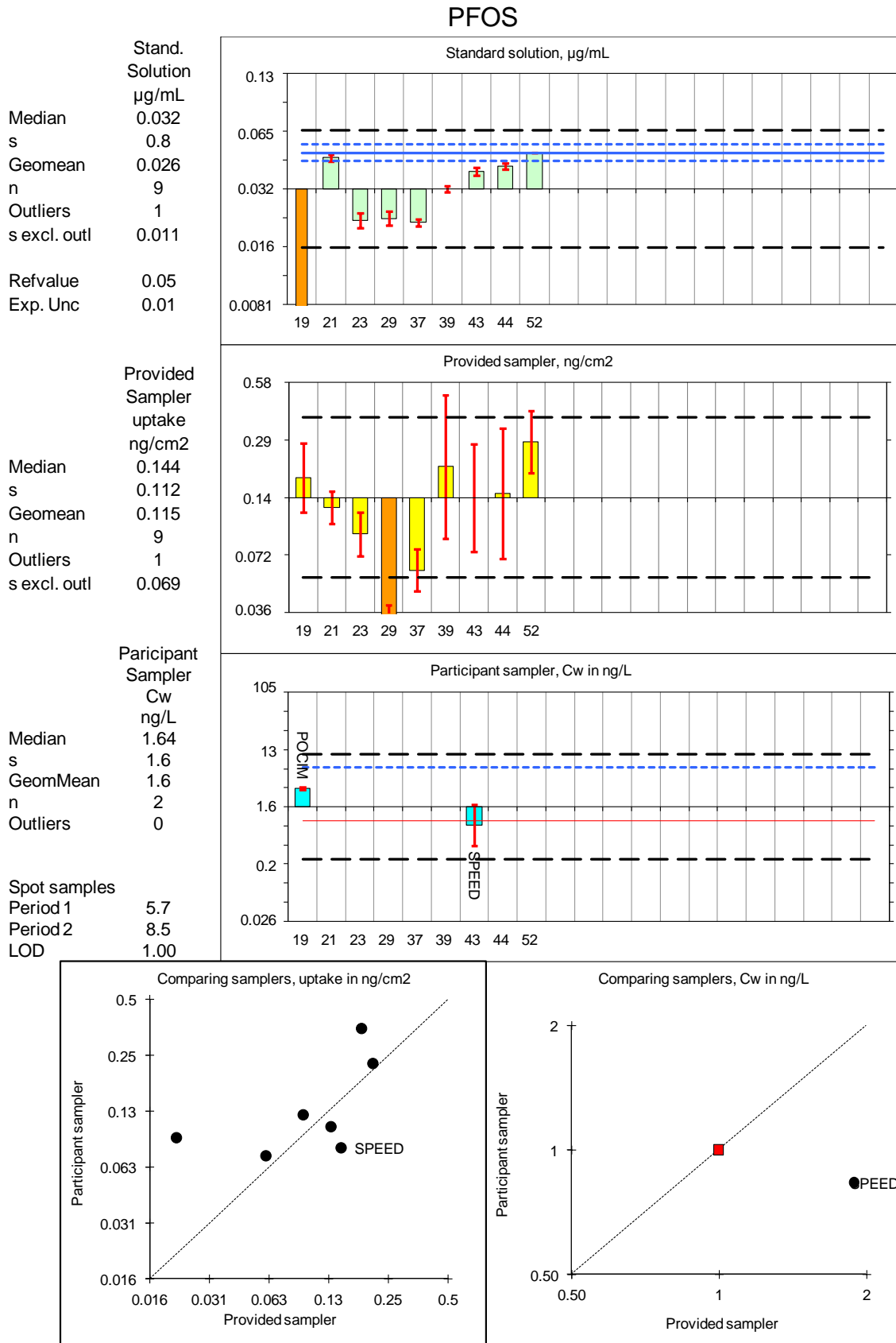


Figure 59. Results of analysis of PFOS. Graph explanation is given in 10.2.and 10.3.

PFOA

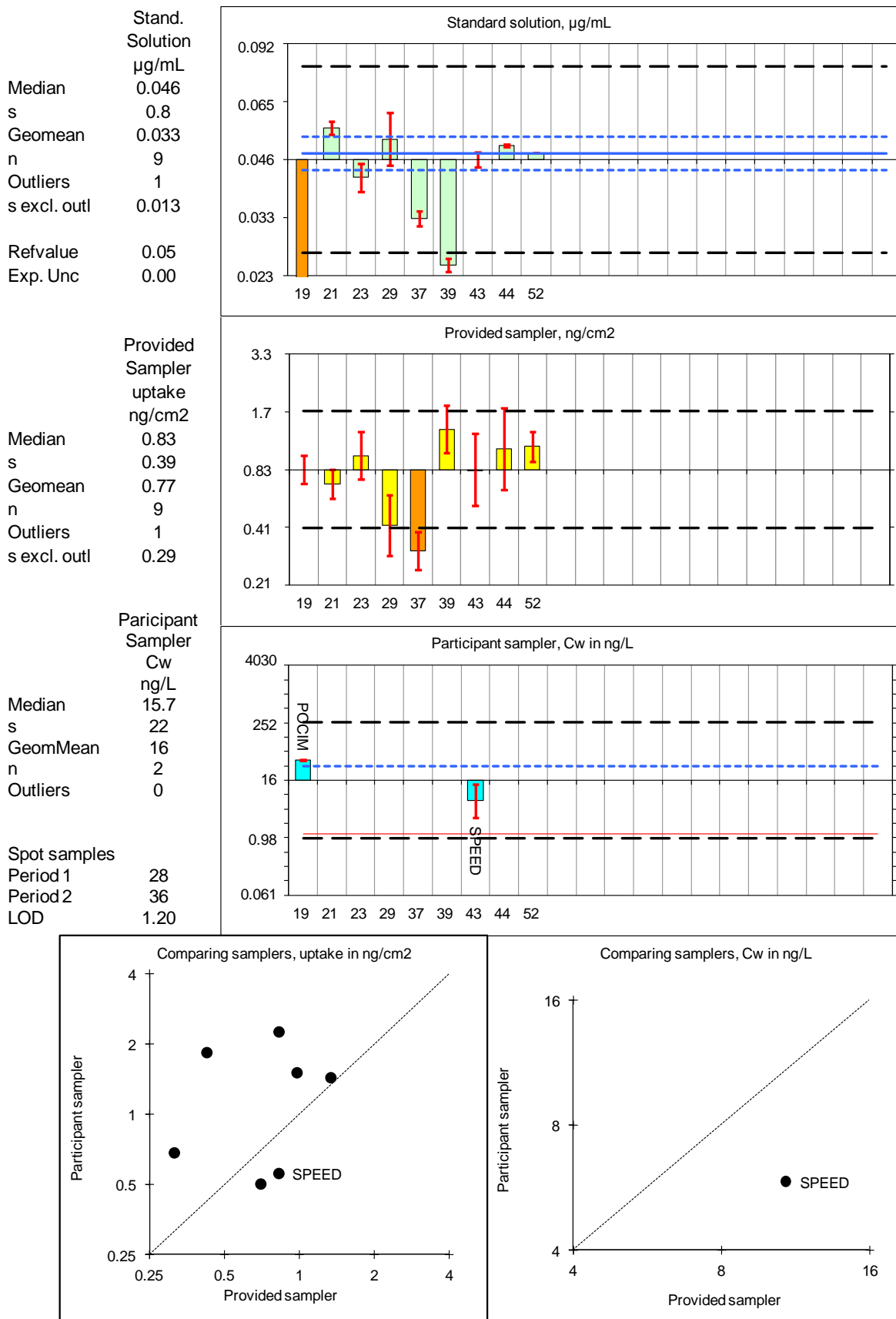


Figure 60. Results of analysis of PFOA. Graph explanation is given in 10.2.and 10.3.

11.5.3 Sample variability

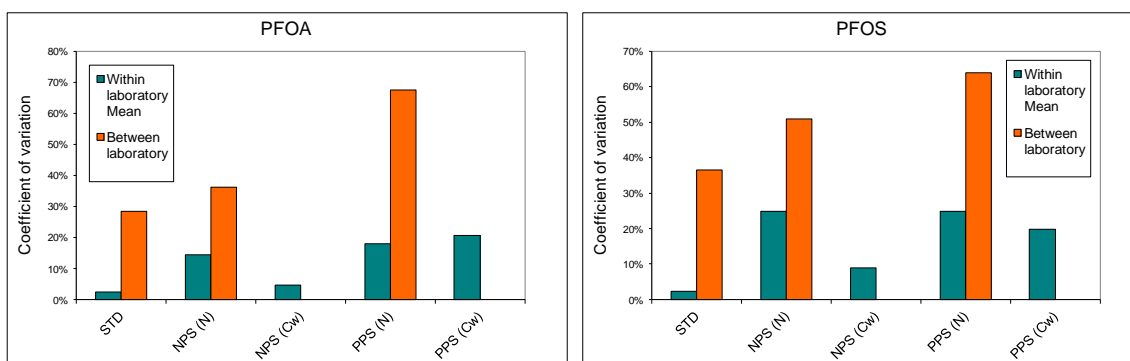


Figure 61 Variability of reported results for fluorinated surfactants at different procedure levels. Results are the coefficients of variation for individual compounds. NPS – provided passive sampler; PPS – participant passive sampler. (N) – amount; (C_w) – water concentration.

Table 38. Variability range at different procedure levels for fluorinated surfactants.

Fluorinated surfactants					
		Coefficient of variation (%)			
Variability:		Within laboratory		Between laboratory	
Matrix analysed:		Min.	Max.	Min.	Max.
	Standard solution	2%	2%	28%	37%
Provided sampler	NPS amount (ng/cm ²)	15%	25%	36%	51%
	NPS water concentration	5%	9%	n.d.	n.d.
Participant sampler	PPS amount (ng/cm ²)	18%	25%	64%	67%
	PPS water concentration	20%	21%	n.d.	n.d.

11.5.4 Standard solution

Results provided by participating laboratories for the standard solution are shown in the top bar charts in Figure 59-60. The range of variability of reported results is given in Table 38. Variability observed for individual compounds is also shown in Figure 61 .

An excellent within laboratory variability of analysis of individual compounds in standard solution of PFOA and PFOS was observed with the mean CV not higher than 2% (Table 38). The between laboratory variability (excluding outliers) was satisfactory, too, ranging between 28 and 37%. For both compounds the reference concentration was within the range comprised by the participant results (median ± 2 standard deviations excluding outliers), but only in case of PFOA the median and geometric mean of participant results were within the uncertainty range stated by the central laboratory.

11.5.5 Provided sampler

The results provided by participating laboratories are shown in the middle bar charts in Figure 59-60.

11.5.6 Field blanks

Concentrations of fluorinated surfactants in field blank samplers were low, in most cases less than 10% of the concentration found in field exposed samplers and close to method detection limits (Table 39).

11.5.7 Sample variability

A good within laboratory variability of analysis of fluorinated surfactant in *provided samplers* was observed with the mean CV between 15 and 25% for sampler uptake (Table 38). The between laboratory variability (excluding outliers) for sampler uptake (ng/cm²) was higher, ranging from 36 to 51%.

The evaluation of between laboratory variability for water concentration estimate cannot be made because only 2 laboratories reported results for water concentration. This is because passive sampler calibration data for fluorinated surfactants were scarce at the time when the study was performed.

Comparison of results for participant and *provided sampler* for uptake per surface area (left-hand biplots), as well as the resulting water concentration (C_w , right-hand biplot) can be seen in Figure 60. Points that lie near the equality line but far from the median values indicate a large systematic error introduced by the laboratory.

11.5.8 Contribution of the calculation procedure to data variability

Since very few participants estimated water concentration from PS data, the estimation of sampling rate uncertainty was not performed.

Table 39. Concentrations of PFOA and PFOS in field blank sampler (ng/sampler) provided by the organizer.

Laboratory	PFOA	PFOS
19	0.2	
21	0.1	0.003
23	0.4	0.1
29		
37		
39	1.2	
43	<0.5	<0.5
44	0.3	0.1
52	3.7	0.5

11.5.9 Participant sampler

Figure 62 shows the different types of samplers that were (above method LOQ) applied by participants in sampling of fluorinated surfactants. The most frequently applied design of sampler applied in the study corresponded with the standard configuration of the

POCIS with OASIS HLB adsorbent and fitted with polyethersulphone membrane. Other types of samplers applied included POCIS modifications with different adsorbent materials and Speeddisks. Details on other samplers applied by participants and their processing are given in Annex XIV. The results provided by participating laboratories are shown in the bottom bar charts in Figure 59-60.

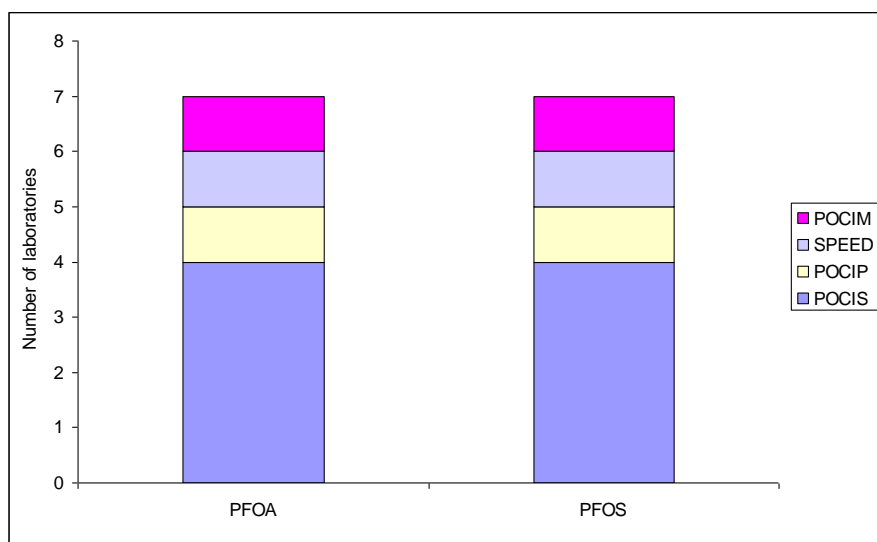


Figure 62 Various categories of participant passive samplers applied in analysis of fluorinated surfactants. A sampler was counted only when a particular compound was measured above method LOQ. A brief description of sampler category (shown as abbreviation in the legend) is given in Table 18.

11.5.10 Field blank

Concentrations of fluorinated surfactants in field blank samplers were low, in most cases less than 10% of the concentration found in field exposed samplers and close to method detection limits (Table 40).

11.5.11 Sample variability

The within laboratory variability of analysis of fluorinated surfactants in *participant samplers* (ng/cm²) was observed with the mean CV between 18 and 25% for sampler uptake. The between laboratory variability (ng/cm²; excluding outliers) was higher, between 64 and 67% for sampler uptake.

The evaluation of between laboratory variability for water concentration estimates cannot be made because only 2 laboratories reported results for water concentration. This is because passive sampler calibration data for fluorinated surfactants are scarce.

Table 40. Concentrations of PFOA and PFOS in field blank participant sampler (ng/sampler).

Laboratory	Sampler	PFOA	PFOS
19	POCIM	0.29	
21	POCIS	0.04	0.003
23	POCIP		
29	POCIS	<3	<3

37	POCIS	0.3	
39	POCIS		
43	SPEED	<0.5	<0.5
44	(blank)		
52	(blank)		

11.5.12 Water samples

Results of water sample analysis are given in Table 41. Concentrations in water, reported from analysis of weekly composite water samples, were above the method limit of quantification. A comparison of these concentrations with water concentration estimates from passive samplers is displayed in the bottom bar charts and right hand biplot charts in Figure 60. The concentration of compounds in composite spot samples was always within the range comprised by the water concentration estimates from passive sampler results (median \pm 2 standard deviations excluding outliers).

Table 41 Concentrations of fluorinated in weekly composite water samples, analysed by a central laboratory

Sample/Compound	Filtration blank (20.6.-26.6.)	Filtration blank (27.6.-4.7.)	Weekly composite (20.6.-26.6.)	Weekly composite (27.6.-4.7.)	units
PFOA	1.4	1.0	27.5	36.0	ng/L
PFOS	1.1	0.9	5.7	8.5	ng/L

11.5.13 Conclusions for fluorinated surfactants

1. An excellent within laboratory variability of analysis of individual compounds in standard solution of PFOA and PFOS was observed and the between laboratory variability was satisfactory, too. Thus, calibration of instrumental methods applied for pharmaceuticals was not expected to cause excessive variability in reported data.
2. Sampling with *provided samplers* was homogeneous. This is supported by a very low within laboratory variability of analysis of *provided samplers*. Thus, the contribution to total result variability that may have been introduced by non-homogeneity of the distributed samples can be considered minor.
3. As for pesticides and pharmaceuticals, the low within laboratory variability of data from *provided samplers* was likely facilitated by the use of a uniform deployment system (deployment cages).
4. The between laboratory variability of analysis was 2-3 x higher than the within laboratory variability.
5. Since passive sampler calibration data for fluorinated surfactants were scarce at the time when the study was performed, effect of the water concentration estimation procedure on data variability was not evaluated.

11.6 Bisphenol A and Triclosan

Up to 6 laboratories participated in the exercise for bisphenol A. Triclosan was measured only by 3 laboratories. Although the number of registered participants in this part of exercise was small, the data illustrate the applicability of PS for monitoring of these compounds. Results for bisphenol A and triclosan are displayed in Figure 64-65. The explanation of data projection applied is described in chapter 10.

11.6.1 Overall data variability

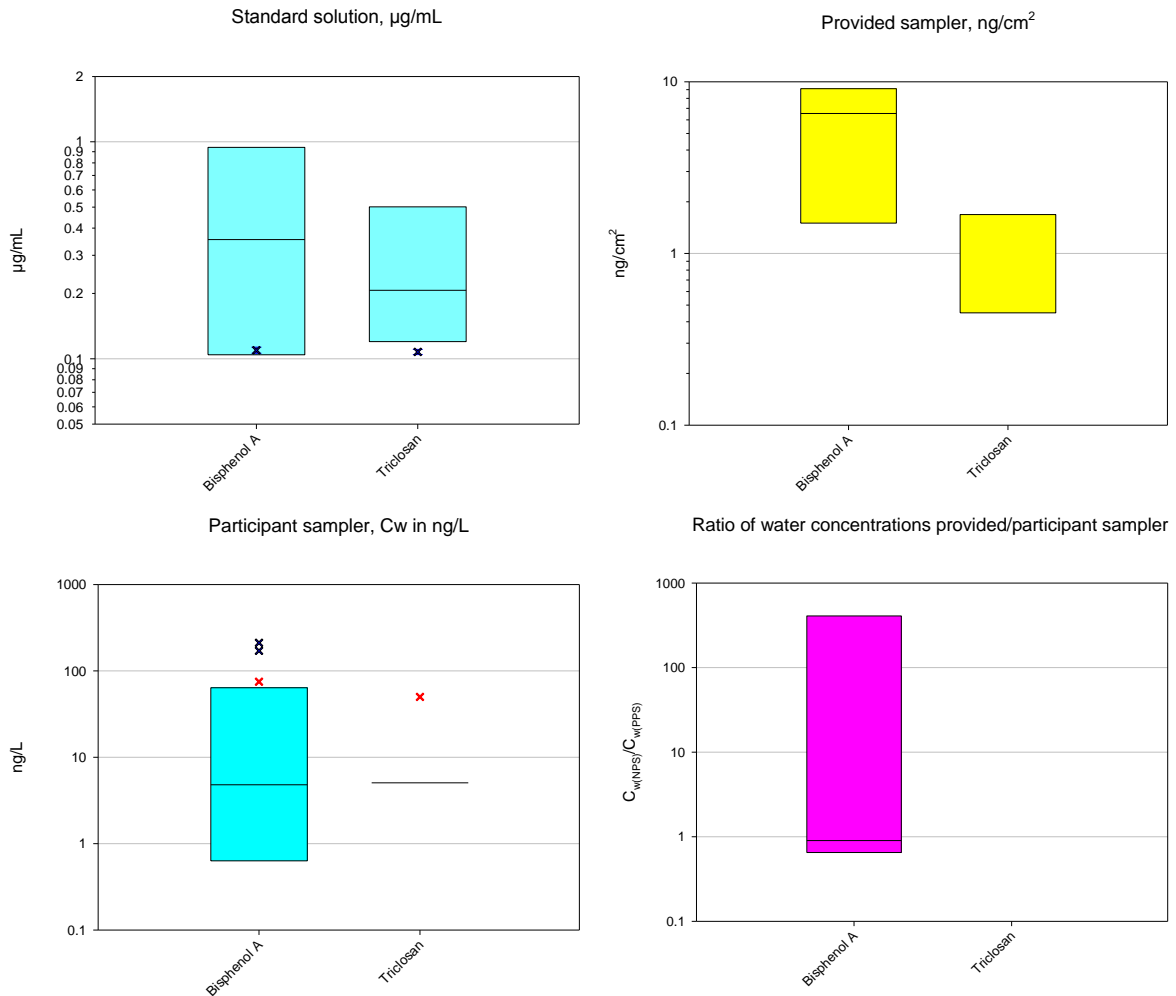


Figure 63 Concentrations of bisphenol A and triclosan in various analysed matrixes: standard solution (top left), provided sampler (top right), water concentration estimated from the participant sampler (bottom left) and the ratio of water concentrations determined in provided and participant passive sampler (bottom right), respectively. For explanation of symbols see legend to Figure 19.

11.6.2 Results by laboratories – bisphenol A and triclosan

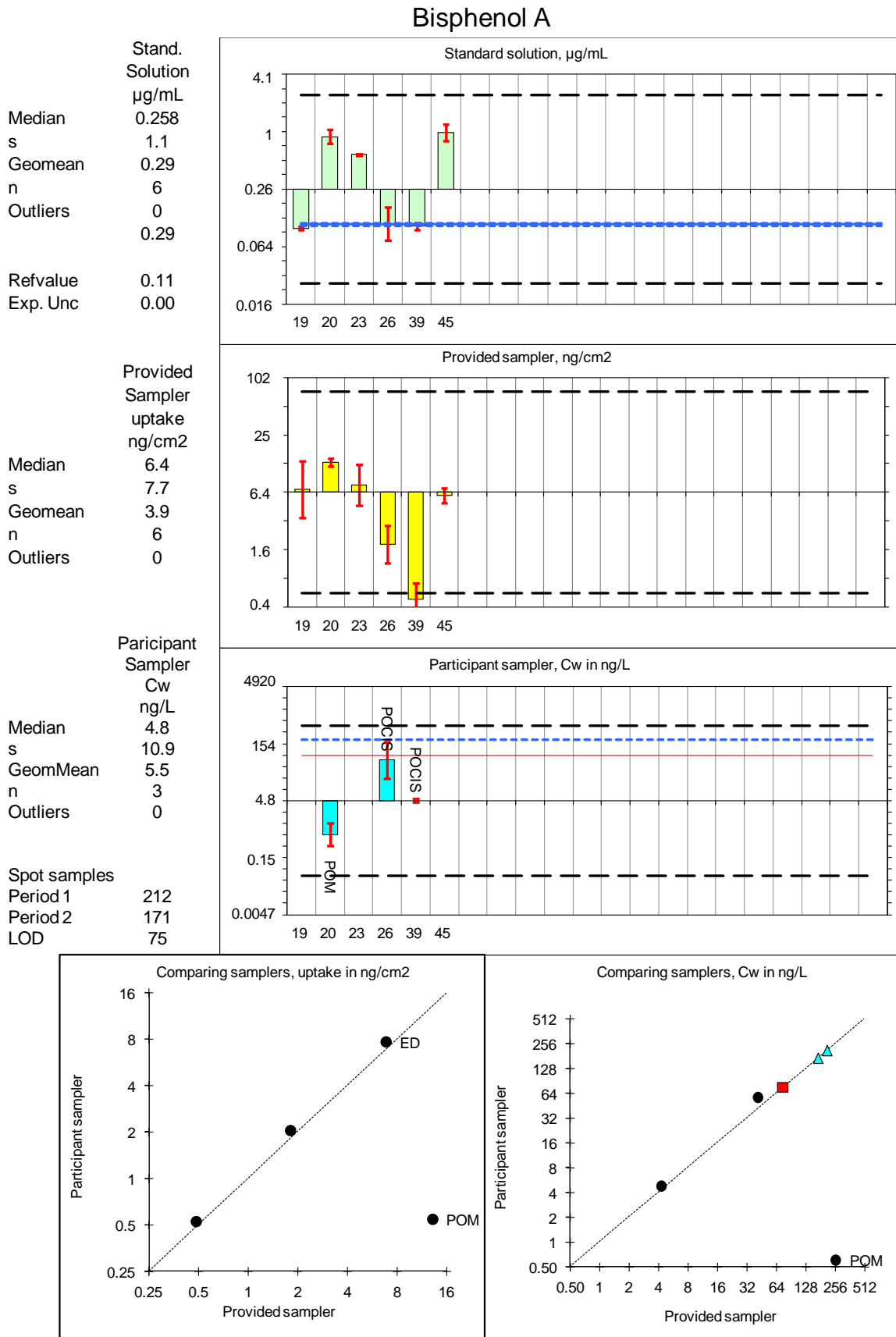


Figure 64 Results of analysis of bisphenol A. Graph explanation is given in 10.2. and 10.3.

Triclosan

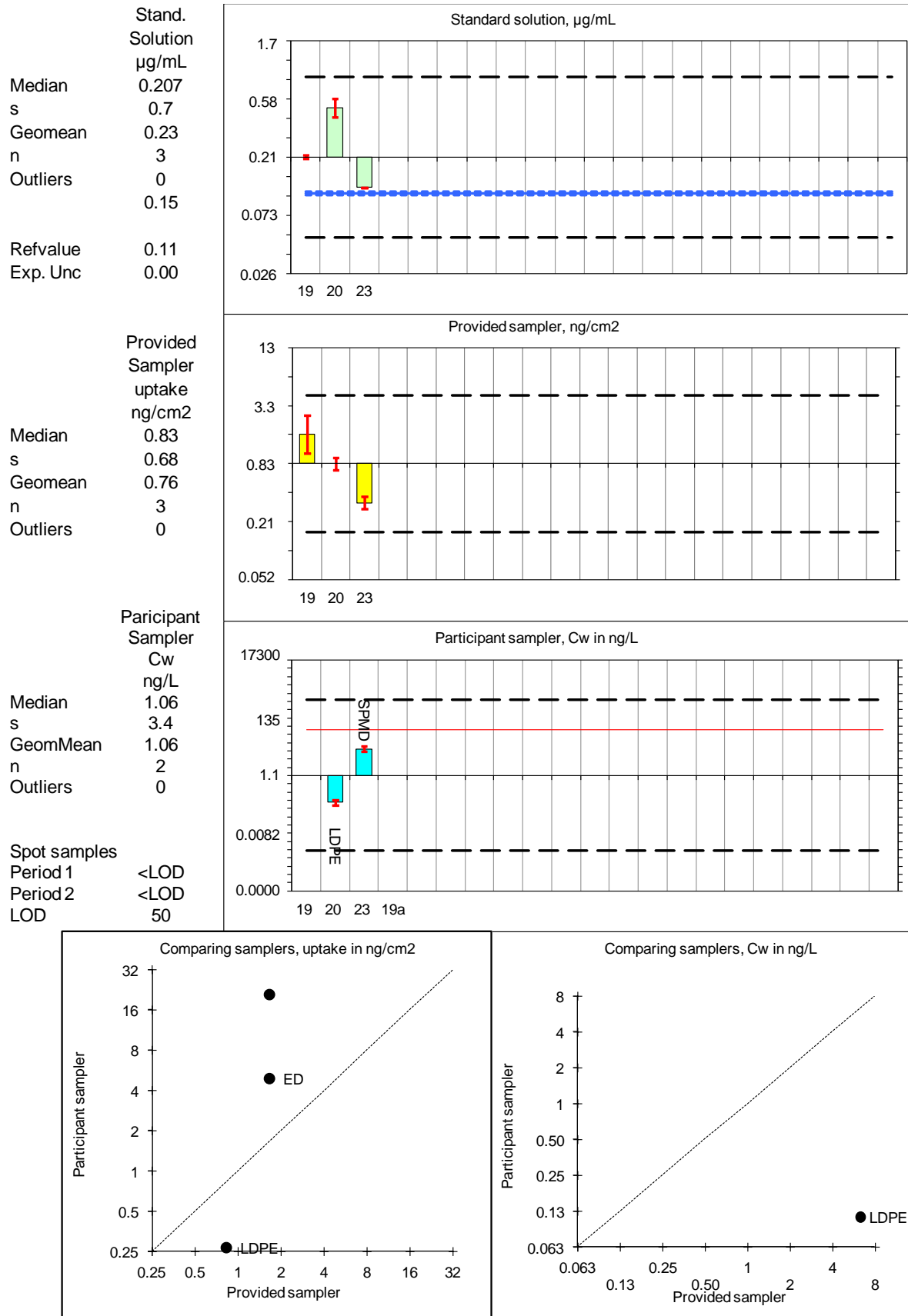


Figure 65 Results of analysis of triclosan. Graph explanation is given in 10.2.and 10.3.

11.6.3 Sample variability

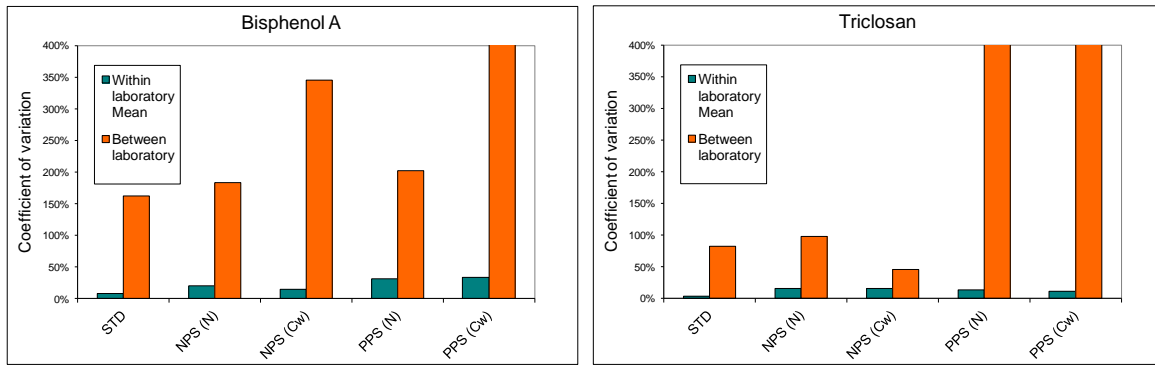


Figure 66 Variability of reported results for bisphenol A and triclosan at different procedure levels. Results are the coefficients of variation for individual compounds. NPS – provided passive sampler; PPS – participant passive sampler. (N) – amount; (C_w) – water concentration.

Table 42 Variability range at different procedure levels for bisphenol.

Compound:	Bisphenol A				
	Coefficient of variation (%)				
Variability:	Within laboratory			Between laboratory	
Matrix analysed:	Mean	Min.	Max.		
	Standard solution	8%	1%	20%	162%
Provided sampler	NPS amount (ng/cm ²)	19%	5%	36%	183%
	NPS water concentration	14%	5%	30%	>200%
Participant sampler	PPS amount (ng/cm ²)	31%	10%	60%	>200%
	PPS water concentration	33%	6%	60%	>200%

Table 43 Variability of triclosan results at different procedure levels.

Compound:	Triclosan				
	Coefficient of variation (%)				
Variability:	Within laboratory			Between laboratory	
Matrix analysed:	Mean	Min.	Max.		
	Standard solution	3%	0%	8%	82%
Provided sampler	NPS amount (ng/cm ²)	15%	7%	23%	98%
	NPS water concentration	16%	7%	20%	45%
Participant sampler	PPS amount (ng/cm ²)	13%	11%	14%	>200%
	PPS water concentration	11%	10%	11%	>200%

11.6.4 Standard solution

Results provided by participating laboratories for the standard solution are shown in the top bar charts in Figure 64-65. The range of variability of reported results is given in

Table 42 and

Table 43. Variability observed for individual compounds is also shown in Figure 66.

A good within laboratory variability of analysis of individual compounds in standard solution was observed with the mean CV from 8 and 3% for bisphenol A and triclosan, respectively. The between laboratory variability was much higher, 162% for bisphenol A and 82% for triclosan, respectively. For bisphenol A, 3 of 6 participating laboratories (labs 20, 23 and 45 provided positively biased results. For triclosan, only 1 of the 3 laboratories provided unbiased result. This means that laboratories experienced difficulty already with the analysis of the standard solution, which is the simplest step in the analytical process.

11.6.5 Provided sampler

The results provided by participating laboratories are shown in the middle bar charts in Figure 64-65.

11.6.6 Field blanks

Concentrations of bisphenol A and triclosan in field blank samplers was low, in most cases less than 10% of the concentration found in field exposed samplers (with exception of bisphenol A in laboratory 19) and close to method detection limits (Table 44).

11.6.7 Sample variability

A good within laboratory variability of analysis of in for uptake to *provided samplers* was observed with mean CV 19% and 15% for bisphenol A and triclosan, respectively. The between laboratory variability for sampler uptake (ng/cm^2) was higher, 183% and 98% for bisphenol A and triclosan, respectively.

A reasonable evaluation of between laboratory variability for water concentration estimate cannot be made because in both cases maximum 3 laboratories reported results for water concentration. This is because passive sampler calibration data for these compounds are scarce.

Comparison of results for participant and *provided samplers* for uptake per surface area (left-hand biplots), as well as the resulting water concentration (C_w , right-hand biplot) can be seen in Figure 64 and Figure 65. Points that lie near the equality line but far from the median values indicate a large systematic error introduced by the laboratory.

11.6.8 Contribution of the calculation procedure to data variability

Coefficient of variation of the applied calculation procedure was estimated only for bisphenol A using the approach described in 10.5. Both the analytical variability (CV=153%) and the variability of calibration data (CV=181%) contributed equally or similarly to the overall variability of water concentration estimates.

11.6.9 Participant sampler

Figure 67 shows the different types of samplers that were (above method LOQ) applied by participants in sampling of target compounds. The most frequently applied design of sampler applied for bisphenol A corresponded with the standard configuration of the POCIS with OASIS HLB adsorbent and fitted with polyethersulphone membranes. The same design was also applied in the *provided passive sampler*. Other types of samplers applied included polyoxymethylene (POM) and Empore disks. For triclosan, Empore disks, SPMDs and LDPE sheets were applied. Details on other samplers applied by participants

and their processing are given in Annex XII. The results provided by participating laboratories are shown in the bottom bar charts in Figure 64-65.

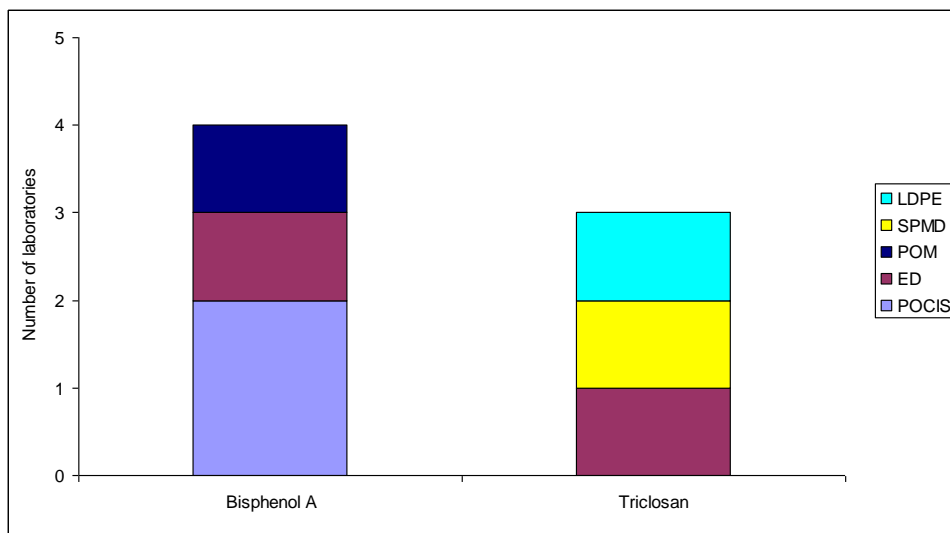


Figure 67 Various categories of participant passive samplers applied in analysis of bisphenol A and triclosan. A sampler was counted only when a particular compound was measured above method LOQ. A brief description of sampler category (shown as abbreviation in the legend) is given in Table 18.

Table 44 Concentrations of PFOA and PFOS in field blank sampler (ng/sampler) provided by the organizer .

Laboratory	Bisphenol A	Triclosan
19	130	8.5
20	6.6	1.8
23	<14	0.82
26	1.1	
39	0.80	
45	6.1	

11.6.10 Field blanks

Concentrations of bisphenol A and triclosan in field blank samplers were low, in most cases less than 10% of the concentration found in field exposed samplers (with exception of triclosan samplers from laboratory 19 and 20) and close to method detection limits (Table 39).

11.6.11 Sample variability

The within laboratory variability of analysis in *participant samplers* (ng/cm) was observed with the mean CV 31% and 13% for sampler uptake of bisphenol A and triclosan, respectively. The between laboratory variability for sampler uptake was higher than 200%.

The evaluation of between laboratory variability for water concentration estimate cannot be made because maximum 3 laboratories reported results for water concentration.

11.6.12 Water samples

Results of water sample analysis are given in Table 46. Concentration of triclosan was lower than the spot sampling method LOQ. A comparison of these concentrations with water concentration estimates from passive samplers is displayed in bottom bar charts and right hand biplot charts in Figure 64-65.

Table 45. Concentrations of bisphenol A and triclosan in field blank participant sampler (ng/sampler).

Laboratory	Sampler	Bisphenol A	Triclosan
19	ED		21
20	POM	14	60
23	SPMD	<18	3.2
26	POCIS	3.3	
39	POCIS	2.9	

The concentration of compounds in composite spot samples for bisphenol A was within the range comprised by the water concentration estimates from passive sampler results (median \pm 2 standard deviations). For triclosan, concentration estimates from passive sampler results were lower than the LOQ of the spot sampling method.

Table 46 Concentrations of bisphenol A and triclosan in weekly composite water samples, analysed by a central laboratory

Sample/Compound	Filtration blank (20.6.-26.6.)	Filtration blank (27.6.-4.7.)	Weekly composite (20.6.-26.6.)	Weekly composite (27.6.-4.7.)	units
Triclosan	<50	<50	<50	<50	ng/L
Bisphenol A	<75	<75	210	120	ng/L

11.6.13 Conclusions for bisphenol A and triclosan

1. An acceptable within laboratory variability was observed for standard solution showing that calibration of instrumental methods was not expected to cause excessive variability in reported data. Some laboratories experienced difficulty already with the analysis of the standard solution, which is the simplest step in the analytical process.
2. Sampling with *provided samplers* was homogeneous based on the acceptable within laboratory variability in analysis of *provided samplers*.
3. Considering the high between laboratory variability in sampler uptake it is difficult to make statements about the contribution to the overall variability of different approaches in the translation of passive sampler uptake data to water concentration. For bisphenol A and triclosan it seems that the contribution of

uncertainty in calculation procedure to the overall uncertainty of water concentration was of the same level as the uncertainty of sampling and analysis.

4. For bisphenol A comparable results for different passive sampler designs analysed by individual laboratories indicate that the PS process is causing less variability than the analysis.
5. Although results from individual laboratories indicate that PS method allows measurement of concentrations lower than spot sampling method LOQs, the interlaboratory method precision needs a significant improvement.

12. Variability of DIA-D5 dissipation from *Provided samplers*

The analysis of the *provided samplers* for polar pesticides also included the analysis of deuterated desisopropylatrazine (DIA-D5). Mazzella et al., (2010) suggested applicability of DIA-D5 as a suitable PRC for compensation of effects of environmental conditions (especially flow velocity) on performance of POCIS fitted with OASIS HLB sorbent. The applicability of this approach was tested in this study from the results of provided exposed and blank samplers supplied by the organiser that allowed to assess the DIA-D5 concentration in samplers before and after exposure.

The % of DIA-D5 (PRC) retained in the sampler after exposure was calculated as:

$$\%PRC = \frac{N_{PS\ NPS}}{N_{B\ NPS}} \quad \text{Equation 6}$$

where $N_{PS\ NPS}$ and $N_{B\ NPS}$ is the mean amount of DIA-D5 in triplicate exposed and blank *provided passive samplers*, respectively. The associated coefficient of variation was calculated from error propagation law.

Fifteen laboratories reported data for DIA-D5 concentrations in *provided samplers*. The within laboratory variability of retained DIA-D5 fraction was acceptable, less than 22% (median 15%). Two exceptions were laboratories 43 and 44 with much higher variability of 44 and 103%, respectively. Surprisingly, the high variability in these 2 cases was caused not only by difficulties with analysis of the matrix-affected exposed samplers, but also by high variability in reported initial DIA-D5 levels reported in not exposed samplers.

The between laboratory variability of reported %PRC was 69%. The low within laboratory and high between laboratory variability indicates difficulties with accuracy of DIA-D5 determination in samplers. Attention has to be paid to a reliable analysis of the compound in the passive samplers before further application as a PRC can be evaluated. It is difficult to find a suitable labelled surrogate to check the procedural recovery of DIA-D5, since the compound is already isotopically labelled. A compound labelled with ^{13}C carbon atoms would be required that would allow correction for ion suppression, which is expected to differ between field exposed and the blank sample.

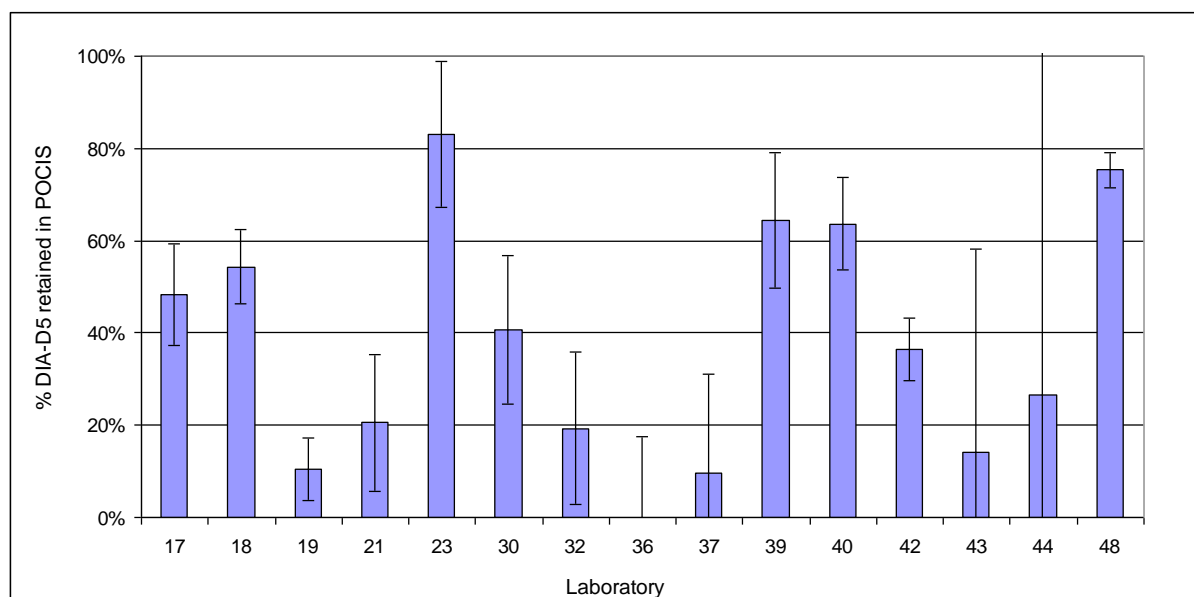


Figure 68 Percentage of DIA-D5 retained in exposed provided samplers

13. Correlation between result deviation from median and level of expertise of participating laboratories

Individual laboratories seem to have introduced a systematic bias to their results by chemical analysis and also by the following estimation of water concentration. A poor between laboratory precision was observed especially for compounds with environmental concentrations approaching method detection limit (e.g. steroids). This observation points at difficulties that some laboratories experienced with the analysis of complex environmental matrices. The study organiser did not restrict the participation only to expert laboratories that routinely analyse the target compounds in passive samplers and have a fully operational QA/QC system. Thus, the observed between laboratory variability may be partially attributed to the limited experience among laboratories with the analysis of emerging substances in the complex analysed matrix.

During registration process, most of the participating laboratories provided a statement on level of expertise in analysis of selected compounds in passive samplers (Table 8). This information enabled to investigate whether there is a correlation between the stated level of expertise of participating laboratory and deviations of reported results. For the purpose of assessment, numeric levels 1, 2, and 3 were used for the higher to lower expertise levels A, B and C respectively. Then the absolute differences of the $^2\log$ transformed results reported by the laboratory and the median were correlated with the numeric expertise level. This was done separately for the results obtained for the standard solution (ng/mL), the *provided sampler* (ng/cm²) and the water concentration estimated by the participant from *participant samplers* (ng/L).

Results of the correlation are shown in Figure 69-73. Positive as well as negative correlations with the level of experience were observed, which were in most cases weak and not significant. Figure 74 shows the few correlations between expertise level and deviations that were found significant. These were observed only for water concentrations estimated from the *participant samplers*.

Several conclusions can be drawn from the results.

1. Deviations of laboratory's results for the standard solution from the median were not related to their indicated level of expertise on passive sampling.
2. For the analysis of the *provided sampler*, where the difference from the median were much larger, also no relation with the expertises level was observed, i.e. both the inexperienced laboratories and those that claimed to be skilled in the analysis of passive samplers equally contributed to the observed high between laboratory variability.
3. Only for C_w data reported from *participant samplers* showed deviations from the median a significant positive correlation with the self assessed level of expertise was observed, but only for a limited number of compounds (terbutylazine, S-metolachlor, BDE 99 and PFOA). We could assume that experienced labs have a better estimates of the sampling rate.

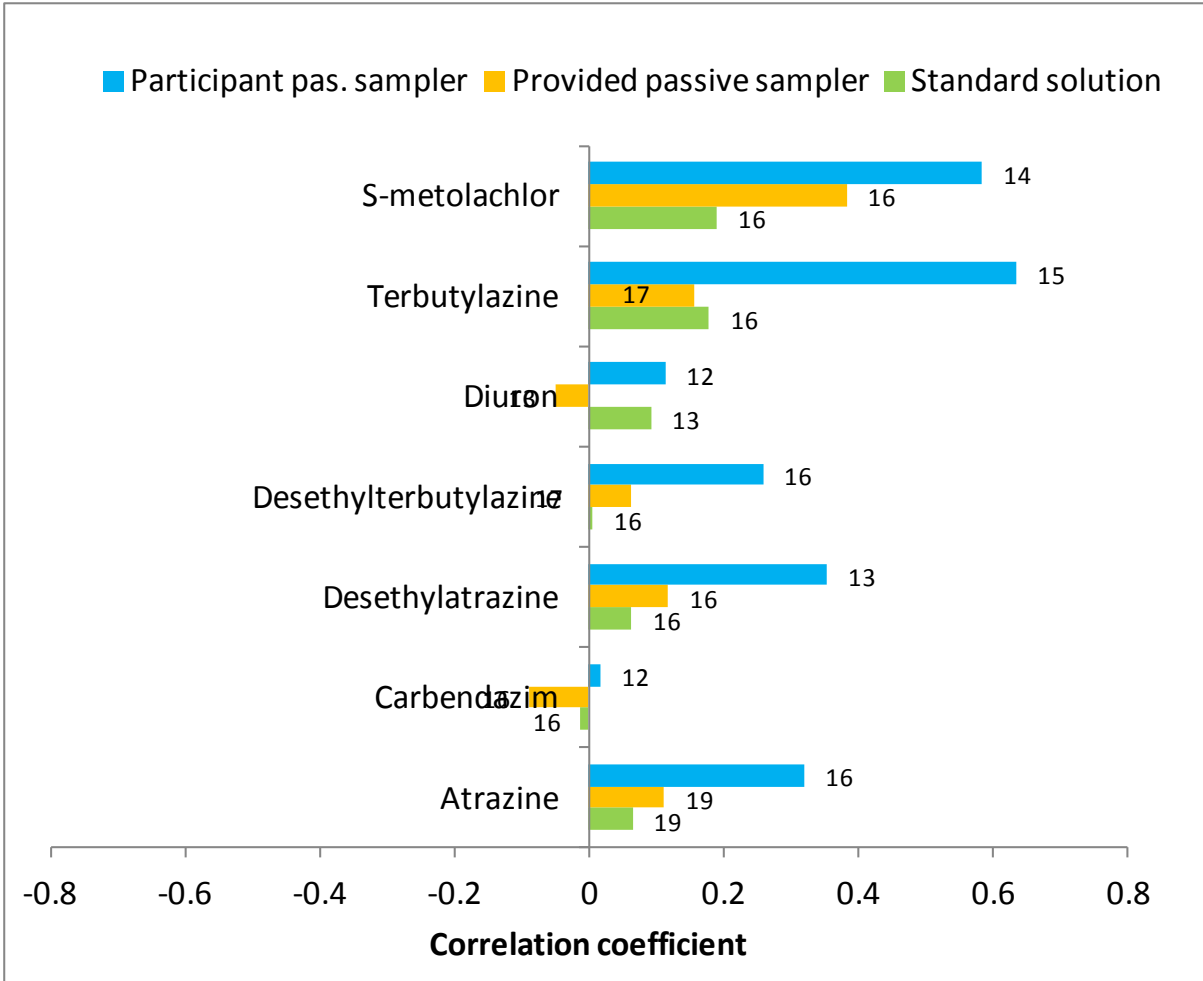


Figure 69 Correlation between absolute deviations from median (log transformed data) and laboratory level of expertise for polar pesticides. Analysed matrices included standard solution, provided sampler (ng/cm²) and water concentration estimated from the participant sampler (ng/L). The numbers next to bars indicate number of laboratories that analysed the sample.

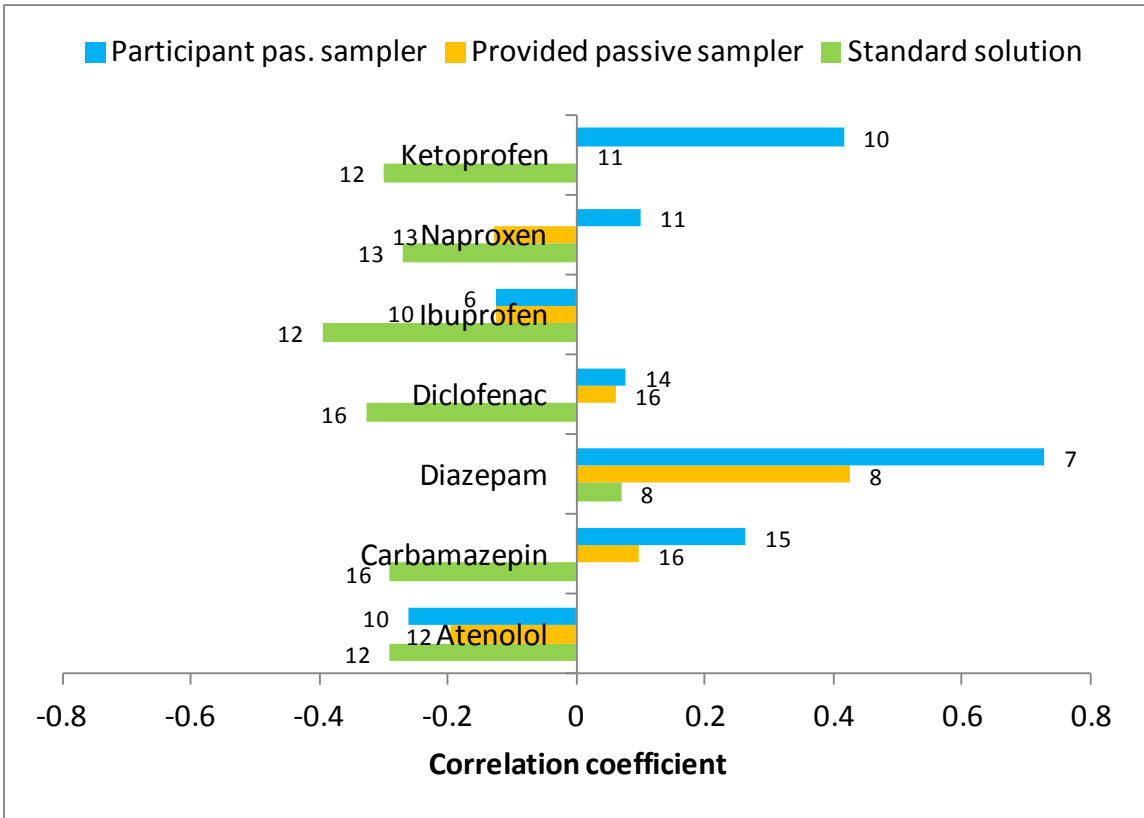


Figure 70 Correlation between absolute deviations from median (log transformed data) and laboratory level of expertise for pharmaceuticals. Explanation is given in Figure 69.

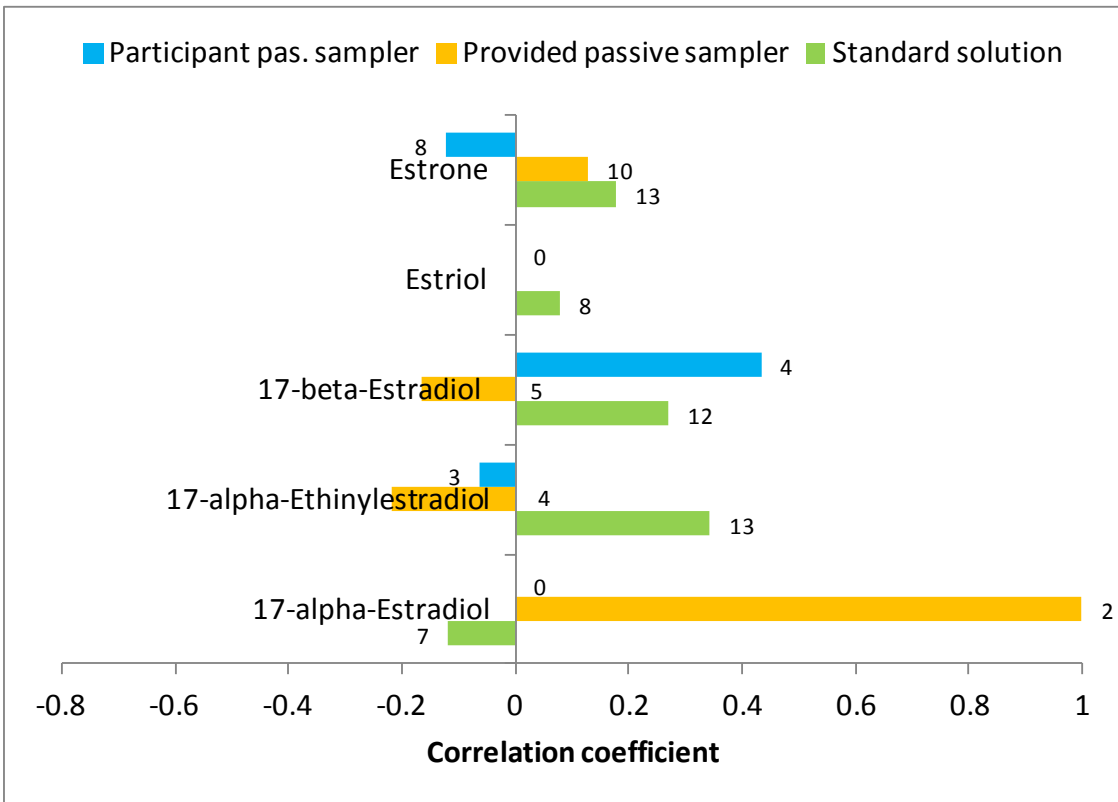


Figure 71 Correlation between absolute deviations from median (log transformed data) and laboratory level of expertise for steroids. Explanation is given in Figure 69.

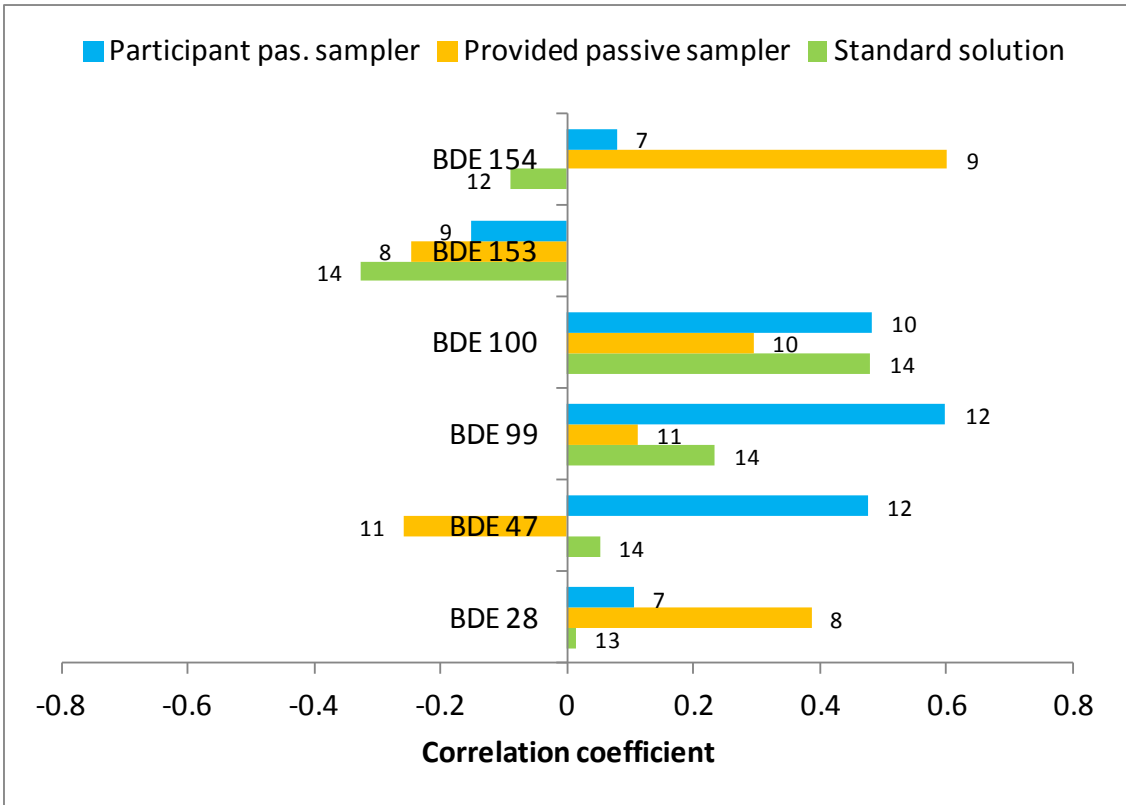


Figure 72 Correlation between absolute deviations from median (log transformed data) and laboratory level of expertise for BDEs. Explanation is given in Figure 69.

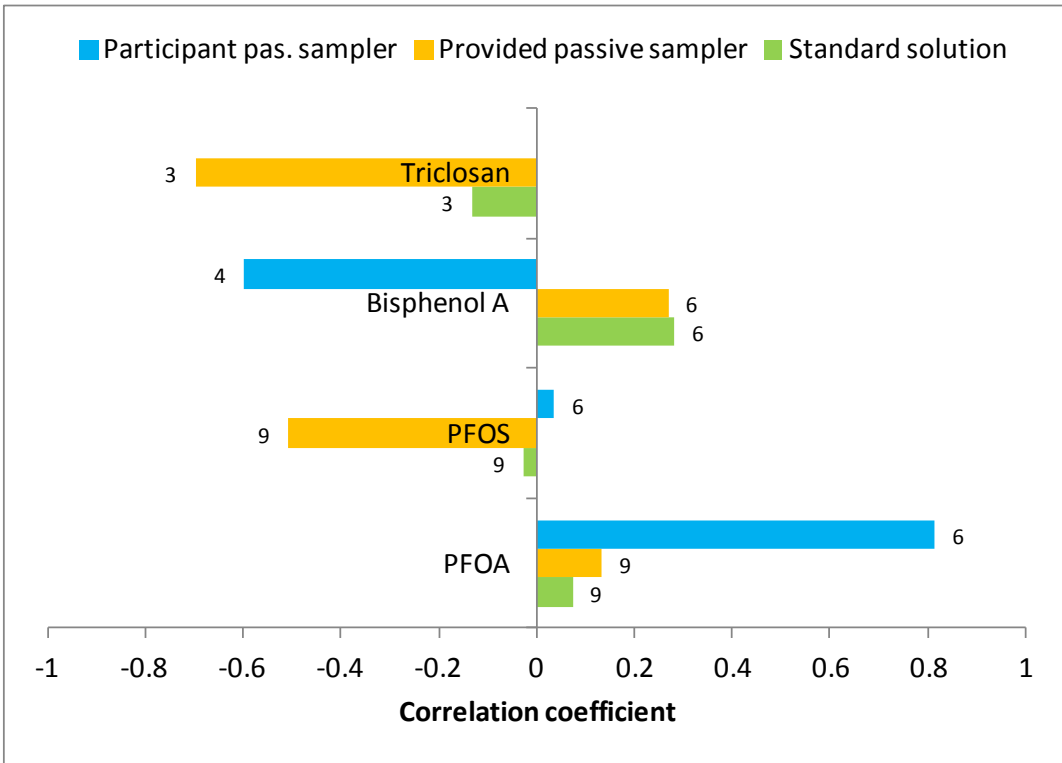


Figure 73 Correlation between absolute deviations from median (log transformed data) and laboratory level of expertise for PFOA, PFOS, bisphenol A and triclosan. Explanation is given in Figure 69.

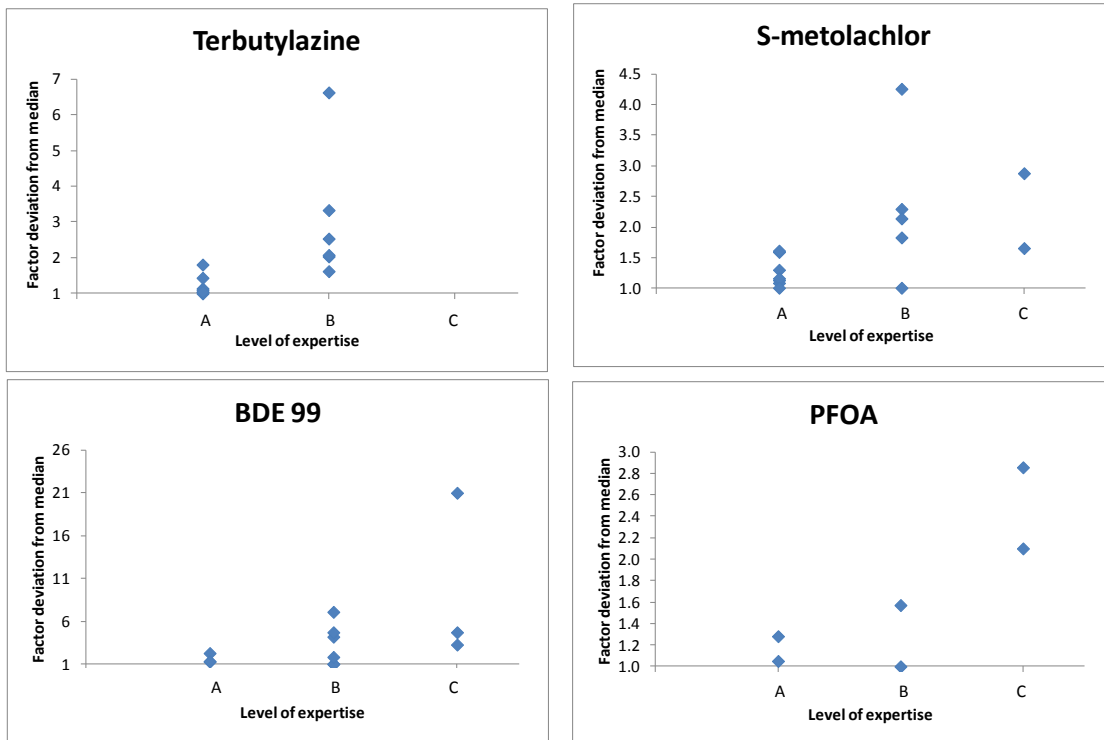


Figure 74 Relation between result deviations from median (log transformed data) and laboratory level of expertise expertise for compounds where the correlation was statistically significant ($\alpha=0.05$). Analysed matrix was the water concentration estimated from the participant sampler (ng/L).

Conclusions

Conclusions made for individual compound groups investigated in the interlaboratory study can be generalised:

1. With a few exceptions an acceptable within laboratory precision and also between laboratory variability was observed for analysis of target compounds in standard solution. For most compounds the reference concentration of analytes was within the range comprised by the participant results. Thus, in most cases calibration of instrumental methods did not cause excessive variability or bias in reported data.
2. For most classes of polar compounds sampling with *provided samplers* (POCIS) was homogeneous, which was confirmed by the low within laboratory variability in their analysis. This implies that the compound uptake by these samplers was not depending on the position of samplers in the sampled system. Use of uniform deployment cages seems to help buffering differences in local water velocity/turbulence and thus facilitate uniform sampler uptake. Lower within laboratory precision of steroids in *provided samplers* can be explained by the very low concentrations that were close to the method limit of detection.
3. In cases where *provided* and *participant sampler* uptake mechanisms were expected to be similar, the obtained within laboratory results for surface specific uptake (ng/cm²) by the different passive samplers were well comparable. This indicates that the PS process is causing less variability than the between laboratory chemical analysis and subsequent data translation to water concentration.
4. In most cases the between laboratory variability of results from passive samplers was roughly a factor 5 larger than the within laboratory variability.
5. The higher between laboratory variability of water concentration estimates in comparison to sampler uptake in *provided samplers* indicates that there is no agreement on approaches in translation of sampler uptake data to water concentrations. This observation reflects the limited agreement of sampler calibration data published for adsorption PS devices as has been reviewed recently by Harman et al., 2011, 2012). For most polar compounds both the analytical variability and the variability of applied calibration data contribute similarly to the overall variability of water concentration estimates.
6. Only for a limited number of compounds there has been a significant positive correlation between the accuracy of results reported from *participant samplers* and the self assessed level of expertise.
7. For PBDEs, which were sampled by partitioning-based passive samplers (silicone rubber), the variability of applied calculation procedures is the main factor causing the elevated between laboratory variability of water concentration estimates from *provided sampler* data. Besides difficulties the laboratories experienced in application of the sampler uptake models available in the literature (see chapter 1.7), difficulties with the analysis of PRC compounds also significantly contributed to the total variability of reported water concentration. Training of laboratories in proper analysis of PRCs and application of published uptake models will help to significantly reduce this source of variability.
8. In most cases, discrepancies between water concentrations obtained by PS and spot sampling were not observed, however, the precision of the PS method needs improving. In several cases (e.g. S-metolachlor, triclosan) it has been demonstrated that PS is able to detect contaminant concentrations that are below method detection limits of conventional spot sampling methods.

The overall conclusion of this exercise is that the passive sampling process works as expected, but participating laboratories experienced difficulties in accurately determining

the analyte amount sorbed by the sampler as well as in deriving aqueous concentrations from the amount in passive sampler.

Recommendations

The exercise revealed several weak points of the methods currently applied in analysis and passive sampler data evaluation. In this last chapter we provide some recommendations to tackle these problems in future.

Accuracy of analysis of complex samples using LC/MS methods

The study revealed that many laboratories experience difficulties with the accuracy of analysis in passive sampler extracts, when LC/MS methods were applied. The analysis of compounds using LC/MS with electro-spray ionisation (ESI) in the presence of co extracted matrix is and continues to be very susceptible to ion suppression or also ion enhancement. Such problem is not specific for analysis of extracts from adsorption-based passive samplers, but occurs as well in other sample preparation techniques, such as solid phase extraction. Several recommendations can be to make improvements to accuracy and reproducibility of sampler analysis in future:

1. Laboratories should validate their LC/MS methods specifically also for extracts from passive samplers exposed in wastewater or similarly complex environment.
2. Mass labelled standards should be applied whenever possible to control and correct the LC/MS results for the effects of ion suppression. However, it has to be acknowledged that even use of isotopically labelled internal standards does not always solve the problem. In case it is not possible to apply labelled standards for each compound under investigation, the analytical method performance should be verified using analyte standard addition to tested samples.
3. Despite the broadly spread believe that LC/MS/MS techniques are selective and thus, sample cleanup is generally not required, we strongly recommend sample dilution and/or cleanup to reduce the potential matrix effects in the sample analysis.
4. Use of alternative ionisation techniques such as atmospheric pressure chemical ionisation (APCI) instead of ESI may help to reduce problems with ion suppression.

Availability of accurate calibration data for adsorption based PS

Besides the accuracy of applied analytical methods, in most cases the variability of available and applied calibration data contributed similarly to the overall variability of water concentration estimates. The recently organised NORMAN/AQUAREF workshop on passive sampling techniques for monitoring of contaminants in the aquatic environment (Lyon, 27-28 November 2014) concluded that currently, the mechanisms of uptake to adsorption based PS are neither completely understood, nor fully under control. The calibration data that are available from literature are often variable and (unlike in partitioning PS) very substance specific [22]. The exchange of polar compounds between sampler and the aqueous phase was often observed to be anisotropic. In consequence, it is generally not possible to use release of PRC (performance reference compounds) to calibrate the uptake rate for calculation of TWA (time weighted average) water concentrations for a wider range of compounds. In general, simple linear uptake models are applied and are considered sufficient for translation of passive sampler uptake into water concentration, providing the sampler uptake capacity is high enough to allow integrative contaminant uptake during the whole sampler exposure.

1. The understanding and monitoring (or control) of the contaminant uptake to adsorption based samplers is the prerequisite for further decrease of variability from calibration data applied in conversion from sampler-based data to water

concentrations. This issue remains open for further research of adsorption based PS.

2. PRCs still could be used as surrogates to monitor exposure conditions in time and space or link to calibration data (quality controls).
3. Whenever water concentrations are calculated from passive sampler data, existing variability of available calibration data should also be taken into account, besides analytical variability. Ideally, water concentration estimate should be reported as a confidence interval. The upper confidence limit of estimated water concentration (taking into account the minimum assumed sampling rate) can be used as a "worst case" concentration, which may often be sufficient to check compliance with environmental quality standards.

Experience with state-of-the art approaches to evaluate data from partition-based PS of hydrophobic compounds

The study identified that for partitioning based PS many participants had a limited experience with the analysis of PRC compounds in *provided passive samplers*, and also with the application of published procedures and models to estimate water concentration from passive partition PS data. Several general recommendations can be made for a correct application of partitioning PS:

1. In case samplers reach equilibrium with sampled water sampler-water partition coefficient (K_{sw}) are required to derive the concentration of a chemical in the water phase from the amount accumulated in the sampler. Accurate values of PS/water partition coefficients should be available for both target analytes and PRCs applied.
2. In case no equilibrium is attained aqueous concentration can be estimated by sampler/water exchange kinetics models that can be in situ calibrated from the release of performance reference compounds (PRCs) dosed to the sampler prior to exposure [33]. Booij and Smedes (2010) recommend that efforts to reduce the bias and variability in water concentration estimates should primarily focus on reducing the uncertainties in the K_{sw} values of the PRCs. Increasing the number of PRCs that are used is also relevant, however, it is expected to have a smaller effect.
3. The applied uptake kinetics models often consider that uptake is controlled by the water boundary layer (WBL) at the surface of the sampler. This requires that internal transport resistance is sufficiently low, i.e. does not limit the uptake rate. This can be confirmed by measuring the diffusion coefficients inside the sampler material. Thus, it is necessary to know also diffusion coefficients of analytes and PRCs in the polymer used in partitioning PS.

We refer users of partition PS to use freely available guidelines for passive sampling of hydrophobic contaminants in water using silicone rubber samplers [34]. Dissemination of the existing knowledge on the best practice in evaluation of data from partitioning PS by organisation of training courses or workshops is recommended as well.

Organisation of future interlaboratory studies

In future interlaboratory studies, it will be necessary to clearly separate the issue of laboratory analysis from the passive sampling testing.

We propose a two stage interlaboratory study:

1. In preparation of the interlaboratory study, a (certified) **reference material** should be prepared centrally by expert laboratories, e.g. a homogenised extract of passive samplers exposed in a real environment that contains environmentally relevant concentrations of analytes of interest.

2. The first stage of the study would be a **Proficiency Testing (PT) scheme**, where laboratories would analyse the reference material prepared in step 1. Only laboratories that demonstrate acceptable performance in the PT scheme would be admitted to participate in the main interlaboratory study addressing the passive sampling intercomparison. Alternatively, If the PT scheme is performed in parallel with the interlaboratory sampler comparison, passive sampling results of laboratories that failed in the PT scheme would be excluded from evaluation (or, depending on the achieved z-score, their result will have a lower weight). This approach would minimise the effect of laboratory analysis on the variability of passive sampling results.
3. The *second stage* of the study would be an **interlaboratory passive sampler comparison**, with a similar design to the one demonstrated in this study. Provided and participant samplers would again be deployed in parallel at a single sampling site. **Variability of sampled analyte amount** and **water concentrations** derived from various passive samplers selected by the individual participating laboratories would be assessed and compared to the criteria set for routine monitoring methods e.g. under the Water Framework Directive.
4. Assessment of **trueness of water concentrations** calculated from the passive sampling data is the most important objective of future interlaboratory studies. Such assessment can be practically performed in real environment only for those compounds, where water concentration measurements obtained by an alternative sampling method (giving comparable results to PS) can be accepted as a "true" or **reference value**. For polar compounds, an acceptable alternative method is based on continuous active sampling of water e.g. using automatic water sampler, followed by preparation of a composite water sample in an approach similar to the one described in this study (8.6). In order to obtain an acceptable **reference value** of water concentration, several expert laboratories must perform independent representative collection and analysis of water at the test site during the time period of passive sampler exposure. Providing the variability of results obtained from active sampling by expert laboratories is acceptable, the assigned reference value for water concentration can be calculated e.g. as the mean of these results.
5. For hydrophobic compounds, there is currently no alternative method to PS for measurement of free dissolved concentration. Therefore, at the moment the only way to provide a reference value for the assessment of trueness is to set a consensus value measured by passive sampling, and agreed upon by a group of expert laboratories.

List of Tables

Table 1 Target analytes : Polar pesticides	21
Table 2 Target analytes: Pharmaceuticals.....	22
Table 3 Target analytes: Steroid hormones.....	22
Table 4 Target analytes: Brominated flame retardants	22
Table 5 Target analytes: Fluorinated surfactants	23
Table 6 Target analytes: Bisphenol A and Triclosan.....	23
Table 7 Steering group of the inter-laboratory study	23
Table 8 Self assessed level of expertise in analysis of target compound groups in passive samplers.....	25
Table 9 List of participating laboratories.....	27
Table 10 Compound classes analysed in passive samplers from an initial screening of the sampling site.	32
Table 11 Comparison of the variability of measured pesticide amount in POCIS within individual deployment cages with the variability of the mean analyte amount determined in the five deployment cages.....	35
Table 12 Reference concentration of polar pesticides in distributed standard solution, stated by the central laboratory.	42
Table 13 Reference concentration of pharmaceuticals in distributed standard solution, stated by the central laboratory.	42
Table 14 Reference concentration of steroid hormones in distributed standard solution, stated by the central laboratory.	43
Table 15 Reference concentration of PBDEs in distributed standard solution.....	43
Table 16 Reference concentration of fluorinated surfactants in distributed standard solution, stated by the central laboratory.	44
Table 17 Reference concentration of bisphenol A and triclosan in distributed standard solutions, stated by the central laboratory.....	44
Table 18. A brief description and abbreviations of various passive sampler designs applied in the interlaboratory study.....	51
Table 19. Variability range at different procedure levels Polar pesticides.	61
Table 20. Concentrations of polar pesticides in field blank sampler (ng/sampler) provided by the organizer ¹	62
Table 21. Estimated CV(R _s) for C _w calculation for <i>provided sampler</i> , Polar Pesticides	63
Table 22. Concentrations of polar pesticides in field blank participant sampler (ng/sampler) [*]	65
Table 23 Concentrations of polar pesticides in weekly composite water samples.....	66
Table 24 Variability range at different procedure levels for pharmaceuticals.....	77
Table 25 Concentrations of pharmaceuticals in field blank sampler (ng/sampler) provided by the organizer ¹	78
Table 26. Estimated CV(R _s) for C _w calculation for <i>provided sampler</i> , pharmaceuticals.	79
Table 27. Concentrations of polar pharmaceuticals in field blank participant sampler (ng/sampler) [*]	81

Table 28 Concentrations of pharmaceuticals in weekly composite water samples, analysed by a central laboratory	82
Table 29 Variability range at different procedure levels for steroid hormones.	90
Table 30. Concentrations of steroids in field blank sampler (ng/sampler) provided by the organiser. *Empty fields indicate cases where participants did not report any value.	91
Table 31. Estimated CV(R _s) for C _w calculation for <i>provided sampler</i> , steroids.	91
Table 32. Concentrations of steroid hormones reported in field blank participant sampler (ng/sampler)*	93
Table 33 Concentrations of steroids in weekly composite water samples.	94
Table 34 Variability range at different procedure levels for PBDEs.	103
Table 35 Concentrations of PBDEs in field blank sampler (ng/sampler) provided by the organizer.	105
Table 36 Estimated CV(R _s) for C _w calculation for <i>provided sampler</i> , PBDEs.	107
Table 37. Concentrations of PBDEs in field blank participant sampler (ng/sampler)*	108
Table 38. Variability range at different procedure levels for fluorinated surfactants.	113
Table 39. Concentrations of PFOA and PFOS in field blank sampler (ng/sampler) provided by the organizer.	114
Table 40. Concentrations of PFOA and PFOS in field blank participant sampler (ng/sampler).	115
Table 41 Concentrations of fluorinated in weekly composite water samples, analysed by a central laboratory.	116
Table 42 Variability range at different procedure levels for bisphenol.	120
Table 43 Variability of triclosan results at different procedure levels.	120
Table 44 Concentrations of PFOA and PFOS in field blank sampler (ng/sampler) provided by the organizer*.	122
Table 45. Concentrations of bisphenol A and triclosan in field blank participant sampler (ng/sampler).	123
Table 46 Concentrations of bisphenol A and triclosan in weekly composite water samples, analysed by a central laboratory	123

List of Figures

Figure 1	Analysis of standard solution. Result shows the variability of applied instrumental methods and is a first simple step to allow correction of data for analytical deviations.	17
Figure 2	Provided passive sampler. The replicate (3 replicates + blank) provided samplers and their analysis by participating laboratories allows an intercalibration of the analysis of passive samplers. An estimate can be made of the contribution of the analytical (sampler extraction + analysis) component to total variability.	18
Figure 3A	Participant passive samplers. The study consisted of passive samplers deployed to sample the water phase at a single sampling site. Participating laboratories were free and encouraged to send all recently available types/designs of passive samplers for deployment that are believed to be suitable for sampling the selected target analytes.	19
Figure 4	Spot sampling in water. The concentration of analytes measured in 2 weekly composite samples of water during passive sampler deployment provided the comparison with a conventional sampling approach. Spot sampling was not performed for PBDEs.	20
Figure 5.	Layout of the WWTP in Brno-Modřice. The sampling site is located at the discharge of treated wastewater and is marked with the red circle.	30
Figure 6.	Views of the sampling site; discharge of treated wastewater from the WWTP in Brno-Modřice. A suspended sidewalk above the basin with the discharge pipe allowed a convenient deployment of passive samplers. The yellow rectangles in the middle right picture describe horizontal coordinates of possible positions for sampler deployment. The bottom picture illustrates vertical profile of the basin. Samplers were suspended from the sidewalk on ropes and exposed at water depth 0.5-2 m.	31
Figure 7	Sampling homogeneity test using POCIS samplers. Five standard POCIS sampler deployment cages containing 3 POCIS (with Oasis HLB adsorbent) each were deployed at various positions (2 positions and 3 depths) in the outflow object of the WWTP in Brno Modřice.	33
Figure 8	Mean amounts [ng/sampler] (± 1 standard deviation) of pesticides accumulated in triplicate POCIS samplers placed in 5 deployment cages at various positions (2 positions and 3 depths) in the outflow object of the WWTP in Brno Modřice. The various sampling coordinates are outlined in Figure 7 (e.g. AD means horizontal position A and vertical position D).	34
Figure 9	Exposure of samplers for different compound classes.	36
Figure 10	Water discharge.	36
Figure 11	Water temperature.	37
Figure 12	Suspended solids in water samples.	37
Figure 13	pH in water samples.	37
Figure 14	Conductivity in water samples.	38
Figure 15	Total organic carbon in water samples.	38
Figure 16	Water sampling scheme for obtaining 7-day composite water samples for analysis of pesticides and pharmaceuticals.	40
Figure 17	Water sampling scheme for obtaining 7-day composite water samples for analysis of triclosan, bisphenol A, PFOS, PFOA and steroid hormones.	41
Figure 18	Explanation of objects and symbols in bar graphs that display results of analysis of standard solution, provided and participant sampler by participating laboratories.	48

Figure 19 Concentrations of polar pesticides in various analysed matrixes: standard solution (top left), provided sampler (top right), water concentration estimated from the participant sampler (bottom left) and the ratio of water concentrations determined in provided and participant passive sampler (bottom right), respectively. Further graph explanation is given in 10.1.....	52
Figure 20 Results of analysis of atrazine Graph explanation is given in 10.2.and 10.3	53
Figure 21 Results of analysis of carbendazime. Graph explanation is given in 10.2.and 10.3	54
Figure 22 Results of analysis of desethylatrazine. Graph explanation is given in 10.2.and 10.3.....	55
Figure 23 Results of analysis of desethylterbutylazine. Graph explanation is given in 10.2.and 10.3	56
Figure 24 Results of analysis of diuron. Graph explanation is given in 10.2.and 10.3.....	57
Figure 25 Results of analysis of S-metolachlor. Graph explanation is given in 10.2.and 10.3	58
Figure 26. Results of analysis of terbutylazine. Graph explanation is given in 10.2.and 10.3	59
Figure 27 Variability of reported pesticide results at different procedure levels. Coefficients of variation for individual compounds are shown. NPS – provided passive sampler; PPS – participant passive sampler. (N) –amount; (C _w) – water concentration. See also 10.4.....	60
Figure 28 Various categories of participant passive samplers applied in analysis of polar pesticides. Sampler was counted only when a particular compound was measured above the method LOQ. A brief description of sampler category (shown as abbreviation in the legend) is given in Table 18.	64
Figure 29 Concentrations of pharmaceuticals in various analysed matrixes: standard solution (top left), provided sampler (top right), water concentration estimated from the participant sampler (bottom left) and the ratio of water concentrations determined in provided and participant passive sampler (bottom right), respectively. For explanation of symbols see legend to Figure 19.	67
Figure 30 Results of analysis of alprazolam. Graph explanation is given in 10.2.and 10.3 ..	68
Figure 31 Results of analysis of atenolol. Graph explanation is given in 10.2.and 10.3	69
Figure 32 Results of analysis of carbamazepine. Graph explanation is given in 10.2.and 10.3	70
Figure 33 Results of analysis of diazepam. Graph explanation is given in 10.2.and 10.3	71
Figure 34 Results of analysis of diclofenac. Graph explanation is given in 10.2.and 10.3....	72
Figure 35 Results of analysis of ibuprofen. Graph explanation is given in 10.2.and 10.3.	73
Figure 36 Results of analysis of ketoprofen. Graph explanation is given in 10.2.and 10.3. ..	74
Figure 37 Results of analysis of naproxen. Graph explanation is given in 10.2.and 10.3.	75
Figure 38 Variability of reported pharmaceutical results at different procedure levels. Results are the coefficients of variation for individual compounds. NPS – provided passive sampler; PPS – participant passive sampler. (N) –amount; (C _w) – water concentration.	76
Figure 39 Various categories of participant passive samplers applied in analysis of pharmaceuticals. A sampler was counted only when a particular compound was measured above method LOQ. A brief description of sampler category (shown as abbreviation in the legend) is given in Table 18.....	80

Figure 40 Concentrations of steroids in various analysed matrixes: standard solution (top left), provided sampler (top right), water concentration estimated from the participant sampler (bottom left) and the ratio of water concentrations determined in provided and participant passive sampler (bottom right), respectively. For explanation of symbols see legend to Figure 19.....	83
Figure 41 Results of analysis of 17-alpha-estradiol. Graph explanation is given in 10.2.and 10.3.....	84
Figure 42 Results of analysis of 17-alpha-ethinylestradiol. Graph explanation is given in 10.2.and 10.3.....	85
Figure 43 Results of analysis of 17-beta-estradiol. Graph explanation is given in 10.2.and 10.3.....	86
Figure 44 Results of analysis of estriol. Graph explanation is given in 10.2.and 10.3.....	87
Figure 45 Results of analysis of estrone. Graph explanation is given in 10.2.and 10.3.....	88
Figure 46 Variability of reported steroid hormone results at different procedure levels. Results are the coefficients of variation for individual compounds. NPS – provided passive sampler; PPS – participant passive sampler. (N) –amount; (C_w) – water concentration.....	89
Figure 47 Various categories of participant passive samplers successfully applied in analysis of steroid hormones. Sampler was counted only when a particular compound was measured above method LOQ. A brief description of sampler category (shown as abbreviation in the legend) is given in Table 18.....	92
Figure 48 Concentrations of brominated diphenyl ethers in various analysed matrixes: standard solution (top left), provided sampler (top right), water concentration estimated from the participant sampler (bottom left) and the ratio of water concentrations determined in provided and participant passive sampler (bottom right), respectively. For explanation of symbols see legend to Figure 19.....	96
Figure 49 Results of analysis of BDE 28. Graph explanation is given in 10.2.and 10.3.....	97
Figure 50 Results of analysis of BDE 47. Graph explanation is given in 10.2.and 10.3.....	98
Figure 51 Results of analysis of BDE 99. Graph explanation is given in 10.2.and 10.3.....	99
Figure 52 Results of analysis of BDE 100. Graph explanation is given in 10.2.and 10.3....	100
Figure 53 Results of analysis of BDE 153. Graph explanation is given in 10.2.and 10.3....	101
Figure 54 Results of analysis of BDE 154. Graph explanation is given in 10.2.and 10.3....	102
Figure 55 Variability of reported PBDE results at different procedure levels. Results are the coefficients of variation for individual compounds. NPS – provided passive sampler; PPS – participant passive sampler. (N) –amount; (C_w) – water concentration	103
Figure 56 Concentrations of PBDEs in spiked field blank sampler provided by the organizer (ng/sampler). The central line shows the median value and the dashed lines ± 2 standard deviations of log 2 transformed values without outliers. Outlier values are labelled in darker colour.	106
Figure 57 Various categories of participant passive samplers applied in analysis of PBDEs. A sampler was counted only when a particular compound was measured above method LOQ. A brief description of sampler category (shown as abbreviation in the legend) is given in Table 18.....	107
Figure 58 Concentrations of PFOA and PFOS in various analysed matrixes: standard solution (top left), provided sampler (top right), water concentration estimated from the participant sampler (bottom left) and the ratio of water concentrations determined in provided	

and participant passive sampler (bottom right), respectively. For explanation of symbols see legend to Figure 19.	110
Figure 59. Results of analysis of PFOS. Graph explanation is given in 10.2.and 10.3.	111
Figure 60. Results of analysis of PFOA. Graph explanation is given in 10.2.and 10.3.	112
Figure 61 Variability of reported results for fluorinated surfactants at different procedure levels. Results are the coefficients of variation for individual compounds. NPS – provided passive sampler; PPS – participant passive sampler. (N) –amount; (C _w) – water concentration.....	113
Figure 62 Various categories of participant passive samplers applied in analysis of fluorinated surfactants. A sampler was counted only when a particular compound was measured above method LOQ. A brief description of sampler category (shown as abbreviation in the legend) is given in Table 18.....	115
Figure 63 Concentrations of bisphenol A and triclosan in various analysed matrixes: standard solution (top left), provided sampler (top right), water concentration estimated from the participant sampler (bottom left) and the ratio of water concentrations determined in provided and participant passive sampler (bottom right), respectively. For explanation of symbols see legend to Figure 19.....	117
Figure 64 Results of analysis of bisphenol A. Graph explanation is given in 10.2.and 10.3.	118
Figure 65 Results of analysis of triclosan. Graph explanation is given in 10.2.and 10.3.....	119
Figure 66 Variability of reported results for bisphenol A and triclosan at different procedure levels. Results are the coefficients of variation for individual compounds. NPS – provided passive sampler; PPS – participant passive sampler. (N) –amount; (C _w) – water concentration.....	120
Figure 67 Various categories of participant passive samplers applied in analysis of bisphenol A and triclosan. A sampler was counted only when a particular compound was measured above method LOQ. A brief description of sampler category (shown as abbreviation in the legend) is given in Table 18.....	122
Figure 68 Percentage of DIA-D5 retained in exposed provided samplers	125
Figure 69 Correlation between absolute deviations from median (log transformed data) and laboratory level of expertise for polar pesticides. Analysed matrices included standard solution, provided sampler (ng/cm ²) and water concentration estimated from the participant sampler (ng/L). The numbers next to bars indicate number of laboratories that analysed the sample.	127
Figure 70 Correlation between absolute deviations from median (log transformed data) and laboratory level of expertise for pharmaceuticals. Explanation is given in Figure 69.	128
Figure 71 Correlation between absolute deviations from median (log transformed data) and laboratory level of expertise for steroids. Explanation is given in Figure 69.	128
Figure 72 Correlation between absolute deviations from median (log transformed data) and laboratory level of expertise for BDEs. Explanation is given in Figure 69.....	129
Figure 73 Correlation between absolute deviations from median (log transformed data) and laboratory level of expertise for PFOA, PFOS, bisphenol A and triclosan. Explanation is given in Figure 69.....	129
Figure 74 Relation between result deviations from median (log transformed data) and laboratory level of expertise expertise for compounds where the correlation was statistically significant ($\alpha=0.05$). Analysed matrix was the water concentration estimated from the participant sampler (ng/L).....	130

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Annexes

- I. *Provided passive samplers* of polar pesticides: method information
- II. *Participant passive samplers* of polar pesticides: method information
- III. *Provided passive samplers* of pharmaceuticals: method information
- IV. *Participant passive samplers* of polar pharmaceuticals: method information
- V. *Provided passive samplers* of steroids: method information
- VI. *Participant passive samplers* of steroids: method information
- VII. *Provided passive samplers* of BDEs: method information
- VIII. *Participant passive samplers* of BDEs: method information
- IX. *Provided passive samplers* of bisphenol A: method information
- X. *Participant passive samplers* of bisphenol A: method information
- XI. *Provided passive samplers* of triclosan: method information
- XII. *Participant passive samplers* of triclosan: method information
- XIII. *Provided passive samplers* of fluorinated surfactants: method information
- XIV. *Participant passive samplers* of fluorinated surfactants: method information

Annex I

Provided passive samplers of polar pesticides: method information

Table AI- 1 Provided passive samplers of polar pesticides: method information

LAB No.	17	18	19	21	23	30	32	36	37	39	40	42	43a	43	44	47	48	49	50a	50
PS type :	POCIS, pharmaceutical version																			
Receiving phase material:	sorbent Oasis HLB, 60 µm																			
Receiving phase mass (g):	0.200 g; mass of sorbent separated from samplers after exposure is given on each SPE cartridge																			
Receiving phase volume (cm3)																				
Membrane material :	Polyethersulphone; SUPOR 100 Membrane Disc Filters (0.1 µm, 90 mm diameter)																			
Active sampler surface area (or membrane area) (cm2):	45.8 cm2																			
Performance and Reference Compound (PRC) *																				
Passive samplers with PRC :	Deisopropylatrazine (DIA) d5																			
	concentration cca. 4ug/g sorbent																			
Transport and storage																				
Storage conditions before deployment (°C)**:	Fridge (4 degrees C)																			

Table AI -2 Provided passive samplers of polar pesticides: method information

LAB No.	17	18	19	21	23	30	32	36	37	39	40	42	43a	43	44	47	48	49	50a	50
Storage conditions after sampler recovery (°C)**:			Fridge (4 degrees C)	- 20 degrees celsius						-20	-20°C	-20°C			freezer			Storage in freezer at -20°C		
Date of return shipment from the organizer to the participant laboratory:*		26.07.2011	21/07/2011	13/07/2011						18.07.2011	18/07/2011	4 July 2011	~31/8/2011	~31/8/2011				07/07/2011		
Date of receipt by the participant laboratory **:	29/07/2011	28.07.2011	26/07/2011	15/07/2011	21/06/2011					19.07.2011	19/07/2011	6 July 2011	~2/9/2011	~2/9/2011	10/25/11	03/08/2011	22/07/2011	08/07/2011	August, 5th	August, 5th
REMARKS:										-	-		Dates are approximate	Dates are approximate				/		

(continued) Provided passive samplers of polar pesticides: method information

LAB No.	17	18	19	21	23	30	32	36	37	39	40	42	43a	43	44	47	48	49	50a	50	
Sampler deployment and recovery																					
Date and hour of the deployment ** :	30/05/2011		30/05/2011; 10:35am, 11:50am, 12:25pm	5/30/2011 between 10:35 and 12:40	30.5.2011, 10:35	5/30/11 11:50				30.05.2011 11:30	samplers 3, 9 : 30/05/2011 10:35:00 ; sampler 101 : 30/05/2011 12:40	2011-05-30	20/06/2011	20/06/2011	(16) 5/30/11, 10:35 (20) 5/30/11, 10:35 (59) 5/30/11, 11:50		Sampler 43: 30.05.2011 11:10 Sampler 54: 30.05.2011 11:50 Sampler 75: 30.05.2011 12:25	Sample 70: 30/05/2011 at 11:50; sample 74: 30/05/2011 at 12:25; sample 87: 30/05/2011 at 12:25			
Air Temp on deployment (°C)**			Average temp between 10am and 12 pm = 21	21	21	14				22	samplers 3, 9 : 20 ; sampler 101 : 23	20-23°C			(16) 20°C (20) 20°C (59) 21°C		Sampler 43: 21; Sampler 54, 75: 22	Sample 70: 22°C; sample 74: 22,5°C; sample 87: 22,5°C			
Duration of the deployment (exposure to air for field control)*			45mins, 40 mins, 35 mins	+/- 30 minutes	0.03125	40 min				30 min	samplers 3, 9 : 00:45 ; sampler 101 : 00:15	13.96 2			(16) 45 min (20) 45 min (59) 40 min		Sampler 43: 35min Sampler 54: 30min Sampler 75: 35min	Sample 70: 40 min; sample 74: 35 min; sample 87: 35 min			
Air Temp on recovery (°C)**			Average temp between 10am and 12 pm = 20.25	21	19	15				20	samplers 3, 9 : 20 ; sampler 101 : 22	18-22°C			(16) 18°C (20) 18°C (59) 20°C		Sampler 43, 54: 21; Sampler 75: 22	Sample 70: 21°C; sample 74: 21,5°C; sample 87: 21,5°C			

Table AI -2 (continued) Provided passive samplers of polar pesticides: method information

LAB No.	17	18	19	21	23	30	32	36	37	39	40	42	43a	43	44	47	48	49	50a	50
Duration of the recovery (exposure to air for field control)*			39 mins, 16 mins, 30 mins	+/- 30 minutes	0.027777778	17 min				30 min	samplers 3, 9 : 00:39 ; sampler 101 : 00:18				(16) 39 min (20) 39 min (59) 17 min		Sampler 43: 9min Sampler 54: 17min Sampler 75: 30min	Sample 70: 17 min; sample 74: 30 min; sample 87: 30 min		
Date and hour of the recovery** :	13/06/2011		13/6/2011; 9:16am, 10:43am, 11:30pm	6/13/2011 between 9:16 and 12:00	13.6.2011, 9:16	6/13/11 10:43				13.06.2011 10:00	samplers 3, 9 : 13/06/2011 09:16 ; sampler 101 : 13/06/2011 12:00	2011-06-13	04/07/2011	04/07/2011	(16) 6/13/11, 9:16 (20) 6/13/11, 9:16 (59) 6/13/11, 10:43		Sampler 43: 13.06.2011 10:34 Sampler 54: 13.06.2011 10:43 Sampler 75: 13.06.2011 11:30	Sample 70: 13/06/2011 at 10:43; sample 74: 13/06/2011 at 11:30; sample 87: 13/06/2011 at 11:30		
Comment on fouling** :				no fouling						Exposed membranes were spotted and darker than unexposed ones	-							Not much		

Table AI -2 (continued) Provided passive samplers of polar pesticides: method information

LAB No.	17	18	19	21	23	30	32	36	37	39	40	42	43a	43	44	47	48	49	50a	50
Field deployment device used: standard POCIS deployment cage for 6 samplers																				
Analytical aspects																				
Extraction technique:	elution MeOH	SPE, 3 mL of MeOH and 3 mL MeOH: ethyl acetate , 75:25	Elution of cartridges under gentle vacuum with 3mL methanol, 2mL acetonitrile, 2mL acetone	sorbent rinsed with +/- 10 ml milli Q into empty glass column with PTFE frit, drying 10 minutes (-50 kPa), elution with 3x 4ml methanol	liquid extraction	Solvent extraction with methanol	SPE	3 x 15 min ultrasonic extraction with toluene :MeOH :DCM (1:1:8)	according to Alvarez 2004	5 mL MeOH - 5 mL MeOH/DCM (50/50) - 5 mL DCM	elution with Methanol and dichloromethane	3 ml Methanol + 3 mL 75/25 Methanol/Ethyl acetate	Elution with 4 ml methyl tertiary butylether followed by 8 ml methanol	Elution with 4 ml methyl tertiary butylether followed by 8 ml methanol	3x 5ml 100% MeOH	In column extraction with 80/20 Dichloromethane/IPA	5 mL Methanol	SPE	SPE	SPE
Date of extraction:	08/08/2011		29/08/2011	29/09/2011		12/20/11	17/08/2011	15/11/2011	20/10/2011	12.09.2011	12/09/2011	08/12/2011	20/10/2011	20/10/2011	13/12/2011	12/12/2011	19/08/2011	25/07/2011	october , 13th	october , 13th
Date of instrumental analysis:	23/08/2011		05/09/2011	18/10/2011		12/20/11	09/06/2011		21/10/2011	15.09.2011	24/09/2011	08/12/2011	27/10/2011	27/10/2011	05/01/2012	10/01/2012	22/08/2011	23/09/2011	november, 11th	november, 11th

Table AI -2 (continued) Provided passive samplers of polar pesticides: method information

LAB No.	17	18	19	21	23	30	32	36	37	39	40	42	43a	43	44	47	48	49	50a	50
Cleanu p metho d:	no	none			no	The extract obtaine d by extracc tion techniq ue describ ed is filtered with 0.2 µm PVDF membr ane	no cleanu p	NaSO4, 0.45 µm cellulose acetate membr ane	no	No cleanu p	no	OnLine SPE	No	No		No clean up		/	-	-
Instru menta l metho d:	UPLC/ MS/MS	HPLC- MS/MS	LCMS	LC-MS	LC/MS/ MS	HPLC- MS/MS	HPLC- MS/MS	LC- MS/MS	LC- MS/MS	LC-MS- MS	LC- MS/MS	LC- MS/MS	LC- MSMS	LC- MSMS	LC/MS/ MS, ESI+, column : Betasil C18, Mobile phase: gradien t water 5mM NH4CO OH, MeOH 5mM NH4CO OH	LCMS QQQ and GCMS (for Atrazin e)	online SPE (Oasis HLB) HPLC- MS/MS	LC- MS/MS	HPLC- MS/MS	GCMS
Injecti on solven t:	MEOH	Water: MeCN, 90:10	50% methan ol/ water	milli Q	MeOH/ water	Methan ol	MeOH: H2O	MeOH	75% methan ol/25% 5mM ammon ium acetate	MeOH	Methan ol	50/50 methan ol/Milli Q	Acetoni trile- water	Acetoni trile- water	methan ol:water 5mM NH4CO OH (1:1)	In mobile phase	HPLC grade Water, Methan ol	Water	methan ol	dichlor ometha ne

Table AI -2 (continued) Provided passive samplers of polar pesticides: method information

LAB No.	17	18	19	21	23	30	32	36	37	39	40	42	43a	43	44	47	48	49	50a	50
Recovery and internal standards used:	Simazine d10	No correction with recoveries, use of deuterated compounds as internal standards	IS: 25ng d-simazine, RS: 12ng d-atrazine		IS = C13 labelled Simazine, RS not used	Atrazine-D5	none		yes	Simazine d10, Hexazine d6, Diuron d6, Atrazine d5, Terbutylazine d5, Irgarol d9	alachlor-d13, atrazine-d5, hydroxyatrazine-d5, carbofuran-d3, cyanazine-d5, dea-d7, diuron-d6, hexazine-d6, irgarol-d9, isoproturon-d6, simazine-d10, terbutylazine-d5	No recovery test, IS: Atrazine-d5, Isoproturon-d6, Terbutylazine-d5	Several standards used but generally not the target compounds, Therefore no corrections were made.	Several standards used but generally not the target compounds, Therefore no corrections were made.	internal standards: Atrazine D5, Isoproturon D6, Simazine D5, Terbutryn D5	Deuterated (D5) Atrazine, (D6) Diuron and (D3)Carbendazim	Labelled IS used for every compound analysed	/	only check on internal standards	only check on internal standards
REMARKS:										-	-		No corrections for suppression made	No corrections for suppression made		Matrix interference made quantification of Atrazine and Atenolol problematic. Ibuprofen was not present above our detection limits		/	DIA-d5 is not used for quantification	DIA-d5 is not used for quantification

Table AI -2 (continued) Provided passive samplers of polar pesticides: method information

LAB No.	17	18	19	21	23	30	32	36	37	39	40	42	43a	43	44	47	48	49	50a	50
Data evaluation aspects																				
Method for estimation of water concentration from passive sampler:	m/Rst	Data in ng/g, determination of TWA concentrations with application of ku (Lissalde et al. 2011) and PRC (Mazzella et al. 2010) data	$C_w = N_s / (R_s * t)$	according to Mazzella et al. ES&T, vol. 44, no5, 2010 eq 2 and 6, DIAd5 PRC Log Ksw 3.85	please give a short description and relevant references	To determine the average concentration of different analytes in water sampling rate values for POCIS have been searched in bibliography. Knowing the sampling rate, the mass adsorbed and the exposure time the value of the average concentration of water has	The rough estimation of 4,2 L is based upon a report by Roberts & Balaam . Roberts, P.H., Balaam , J.L, 2006. Offline extraction and passive sampling. Modelk ey progress report SSPI-CT-2003-511237-2. They found water extractions between 50 and 300 ml	Rs from Literature	TWA calculated according to Alvarez 2004	Calculation with following formula : $C_s \times 0,2 = C_w R_s t$ (Vrana et al., 2005)	PRC approach using Salbutamol-d3, Caffeine-C13 and DIA-d5	Analyses of DIA-d5	Uptake of Clotrimazole, Carbamazepine, Thiabendazole, transferred to sampled volume using Cw from SR sampling	Uptake of Clotrimazole, Carbamazepine, Thiabendazole, transferred to sampled volume using Cw from SR sampling	N.Mazzella, S. Lissalde, S. Moreira, F. Delmas, P. Mazzei, J.N. Huckins: Environ. Sci. Technol. 2010, 44, 1713-1719. For Diuron: N. Mazzella, J.-F. Dubern et, F. Delmas : Journal of Chromatography A 2007, 1154,) 42-51	Estimation of water calculation not used	please give a short description and relevant references	To obtain laboratory Rs: Plot of the concentration factor as a function of the time until the t1/2: $CF = C_s / C_w = (R_s * t) / (M_s)$. Use of this lab Rs in order to obtain in situ TWA concentrations using the equation $C_w = (C_s * M_s) / (R_s * t)$	please give a short description and relevant references	please give a short description and relevant references

Table AI -2 (continued) Provided passive samplers of polar pesticides: method information

LAB No.	17	18	19	21	23	30	32	36	37	39	40	42	43a	43	44	47	48	49	50a	50
Sampling rates used (literature value/ own calibration):	littérature	Lissalde et al. 2011	Literature (DA Alvarez et al, Tool for monitoring hydrophilic contaminants in water: polar organic chemical integrative sampler (POCIS), In Comprehensive Analytical Chemistry, D. Barcelo, Elsevier, 2007. p. 171-197). Atrazine=0.240, desethylatrazine=0.26	literature value	Mazzella 2007, Mazzella 2008			literature values for pesticides and pharmaceuticals	Mazzella 2007, Lissalde 2011	Sampling rates from Lissalde et al., 2011 were used	own calibration	0.253 (Mozzella and DIA-d5)	From calibration with SR results, Sampled volume = 3.0, 3.6, 3.4 L	From calibration with SR results, Sampled volume = 3.0, 3.6, 3.4 L	Rs[L/d] - literature values: Environ. Sci. Technol. - Rs (DEA)= 0,167, Rs (DET)= 0,205, Rs(Atrazine)= 0,239, Rs(S-Metolal chlor)= 0,225. J.Chromatography A: Rs (Diuron)=0.247. Rs for carben dazim not found.	N/A		Own calibration: ATRA= 0,1891 L/d; CARB= 0,2949 L/d; DIU=0,1976 L/d	Journal of Chromatography A, 1218 (2011) 1492-1502 and Water Research 43 (2009) 903-914	Journal of Chromatography A, 1218 (2011) 1492-1502
Ksw applied		No	No	log Ksw 3.85	No	no		NO	-	-	-		none	none		N/A		/		

Table AI -2 (continued) Provided passive samplers of polar pesticides: method information

LAB No.	17	18	19	21	23	30	32	36	37	39	40	42	43a	43	44	47	48	49	50a	50
Performance reference compounds applied (YES/NO):	YES	YES	NO	YES	NO	NO		NO	NO	NO	YES	NO	NO	NO	NO	NO		NO	NO	NO
Were the calibration data adjusted to reflect exposure conditions (temperature, flow, pH...?)	no	Yes	No	no	No	No		average flow was estimated with PFM: O'Brien et al., Chemosphere 83 (9), 2011	no	NO	PRC	No	Only an attempt to correct for flow	Only an attempt to correct for flow	No	N/A		No (laboratory calibration: temperature= 20,7°C ; pH=7,6 ; conductivity= 429 µS/cm; DOC=13,3 mg/L; flow=11 cm/s)		
REMARKS:								PRC not used for Ctwa-calculation	Amount of DIA-d5 (cell M12-P12) presented as % of initial concentration (G12-112).	-	-		Not very confident on sampling rate applied	Not very confident on sampling rate applied			No estimation of water concentration. Sampling rates were only available for triphasic POCIS.	/		

Annex II. Participant passive samplers of polar pesticides: method information

Table All- 1 Participant passive samplers of polar pesticides: method information

LAB No.	17	18	19	21	23a	23	30	36	37	39	40	43a	43	44	47	48	49
PS type :	POCIS pharmaceutical version	POCIS, pharmaceutical version	Empore Disk	POCIS	POCIS, pharmaceutical version	POCIS, pesticide version	CFIS (Continuous Flow Integrative Sampler)	Chemcatc her (3rd generation) polar configuration	POCIS	POCIS, pharmaceutical version	POCIS	Altesil translucent silicone rubber (4 sheets of 100cm ² each)	Speedisks (2 disks form one sampler)	POCIS, pharmaceutical version	POCIS	Empore SDB-RPS with PES-Membrane (0.1um)	POCIS, pharmaceutical version
Home made or commercial PS :	Commercial	Home made	Commercial	home made	commercial	commercial	Home made	homemade	home made	Home made	Home made	Home made	J.T. Baker, Bakerbond Speedisk, H2O Philic DVB, Art.nr.: 8072-07	commercial	Home made		Home made
							Home made	Chemcatc her bodies: University of Portsmouth (UK)		-	Home made						Home made
Supplier :	Exposmeter		Phenomenex		EST	EST	LABAQUA S.A.	Empore disk: VWR, Dresden (D); LDPE: University of Portsmouth		-	-	Altecweb.com	JT Baker	ExposMeter AB, Sweden		Infochroma	/

Table All- 1 (continued) Participant passive samplers of polar pesticides: method information

LAB No.	17	18	19	21	23 a	23	30	36	37	39	40	43a	43	44	47	48	49
Receiving phase material:	OASIS HLB	sorbent Oasis HLB, 60 µm	SDB-RPS Reverse Phase Sulfonated	Sepra ZT, Phenomenex, 30 µm, 85A	Oasis HLB	Biobeads, Ambersorb and Iolute ENV+	Sorbent Oasis HLB 60 µm	Varian Empore SDB-RPS extraction disk 47 mm	Oasis HLB	Oasis HLB sorbent, 60 µm	Oasis HLB 60µm custom Bulk WAT106068	AlteSilTM translucent material, 0.5±0.05 mm thickness	DVB		OASIS HLB	Styrene -divinylbenzene modified with sulfonic acid groups (SDB-RPS)	sorbent Oasis HLB, 60 µm
Receiving phase mass (g):	0,2 g approximately	0.200 g; mass of sorbent separated from samplers after exposure is given on each SPE cartridge	0.398	300	0.22	0.22	0.2458	0.327	0.1	0.2	200 mg	14	0.95	0,200 g	227mg	0.331	0.2
Receiving phase volume (cm³)			1.73494				unknown	0.344			-	12					/

Table All- 1 (continued) Participant passive samplers of polar pesticides: method information

LAB No.	17	18	19	21	23a	23	30	36	37	39	40	43a	43	44	47	48	49
Membrane material :	PE S	Polyethersulphone; SUPOR 100 Membrane Disc Filters (0.1 µm, 90 mm diameter)	Polyether sulfone (0.45µm) SUPOR 450 filters PALL Life Sciences	polyethersulfone, Pall corporation	Polyethersulphone	Polyethersulphone	no membrane	Pall Supor 200 polyether sulfone	polyethersulphone STERLITEC H 0.45µm	Polyethersulphone; SUPOR 100 Membrane Disc Filters (0.1 µm, 90 mm diameter)	PES Supor-100, 0,1 µm, 90mm, 100/PK Product# 60311	Silicon rubber	Glass fibre Filter ±0.5 mm		Pall Polyether sulfone Supor 100, 0.10µm	Polyether sulfone (PES)	Polyethersulphone; SUPOR 100 Membrane Disc Filters (0,1 µm, 90 mm diameter)
Active sampler surface area (or membrane area) (cm²):	45.8	41 cm2	16	45.80442089	47.5	47.5	not apply	15.9	14-Jan	42.47	45,78 cm²	400	35	45,8 cm2	45.8cm2	12.6	45.8
Performance Reference Compounds (PRC)																	
Commercial passive samplers with PRC:	no	Deisopropyl atrazine (DIA) d5			No	No				NO	no		No PRCs	No			No
or home made PS spiked with PRC:	no	concentration cca. 4ug/g sorbent		deisopropyl atrazine d5			The receiving phase material does not contain PRC	Pirimicarb -D6; Diuron-D6, Alachlor-D13, Atrazine-D5 (each 500 ng/disk)	no	NO	Home made PRC : DIA-d3, Salbutamol-d3, Caffeine-C13 (10µg/g)	Home spiked, D10-biphenyl, PCBs: CB001, CB002, CB003, CB010, CB014, CB021, CB030, CB050, CB055, CB078, CB104, CB145, CB204	No PRCs		None used		No

Table All- 1 (continued) Participant passive samplers of polar pesticides: method information

LAB No.	17	18	19	21	23a	23	30	36	37	39	40	43a	43	44	47	48	49
Transport and storage																	
Date of receipt by the study organiser :	26,04,2011		14 May 2011 (Handover at conference)	16-May-11			13/05/2011			16.05.2011	16/05/2011	~13/05/2011	~13/05/2011	5/26/11		11/05/2011	19/05/2011
Storage conditions before deployment (°C):	- 20 °C		Fridge (4 degrees C)	- 20 degrees celsius			4°C			room temperature	-20°C	4°C immersed in water	4°C immersed in water	freezer		4	Storage in fridge at 4°C
Storage conditions after sampler recovery (°C):	- 20 °C		Fridge (4 degrees C)	- 20 degrees celsius			4°C			-20	-20°C	minus 20°C	minus 20°C	freezer			Storage in freezer at -20°C
Date of return shipment from the organiser to the participant laboratory:		26.07.2011	21/07/2011	13-Jul-11			15/06/2011			15.06.2011	15/06/2011	~31/8/2011	~31/8/2011	6/23/11		15/06/2011	07/07/2011
Date of receipt by the participant laboratory:	24/06/2011	28.07.2011	26/07/2011	15-Jul-11	21/06/2011	21/06/2011	16/06/2011			16.06.2011	16/06/2011	~2/9/2011	~2/9/2011	6/23/11	03/08/2011	16/06/2011	08/07/2011
REMARKS :										-	-	Dates are approximate	Dates are approximate				/

Table All- 1 (continued) Participant passive samplers of polar pesticides: method information

LAB No.	17	18	19	21	23a	23	30	36	37	39	40	43a	43	44	47	48	49
Sampler deployment and recovery																	
Date and hour of the deployment:	30/05/11 15h55		30/05/2011 ; 19:50	30/05/2011 17:40	30.5.2011 , 16:15	30.5.2011 , 16:15	5/30/11 11:50			30.05.2011 15:10	30/05/2011 15:10	30/05/2011	30/05/2011	5/30/11 , 14:30		30/05/2011 20:20	30/05/2011 at 16:28
Air Temp on deployment (°C)	23		21	21	23	23	14			23	23			23°C		20	23.5
Duration of the deployment (exposure to air for field control)	25 minutes		27 min	30 minutes	00:15	00:15	50 min			20 min	00:35			25 min		30 min	29 min
Air Temp on recovery (°C)	23		23	23	22	22	15			22	23			23°C		23	22
Duration of the recovery (exposure to air for field control)	50 minutes		20 min	24 minutes	00:40	00:40	0 min			30 min	00:23			18 min		11 min	32 min
Date and hour of the recovery:	13/06/2011 14h40		13/06/2011 : 15:28	13/06/2011 13:55	13.6.2011 , 12:42	13.6.2011 , 12:42	6/13/11 12:25			13.06.2011 13:22	13/06/2011 13:22	13/06/2011	13/06/2011	6/13/11 , 14:17		13/06/2011 17:37	13/06/2011 at 12:43
Comment on fouling:				no fouling						Exposed membranes were spotted and darker than unexposed ones	-						Not much

Table All- 1 (continued) Participant passive samplers of polar pesticides: method information

LAB No.	17	18	19	21	23a	23	30	36	37	39	40	43a	43	44	47	48	49
Field deployment device used:	canister (exposmeter)	standard POCIS deployment cage for 3 samplers	Teflon Chemcatcher case	big cage provided by WRI	standard big cage	standard big cage	CFIS device	Small SPMD deployment cage	standard POCIS cage	Standard POCIS deployment cage for 3 samplers	standard small cage for 3 samplers	Wet mounted on open cage	Wet mounted on open cage	standard POCIS deployment cage	standard POCIS deployment cage for 3 samplers	Big cage (provided by WRI)	standard POCIS deployment cage for 6 samplers
Extraction technique:	elution methanol	SPE, 3 mL of MeOH and 3 mL MeOH:ethyl acetate, 75:25	sonication disk in 5 mL Acetone followed by 5 mL methanol at room temperature. Extracts combined.	sorbent rinsed with +/- 10 ml milli Q into empty glass column with PTFE frit, drying 10 minutes (-50 kPa), elution with 3x 4ml methanol	liquid extraction (2x 15ml MeOH)	liquid extraction	Solvent extraction (MeOH)	3 x 15 min ultrasonic extraction with 5 ml in 1.acetone 2.MeOH 3.mixture of both (1:1)	2 x 10mL 90% methanol (15 min in ultrasonic bath), then evaporation of solvent, reconstitution and analysis	5 mL MeOH - 5 mL MeOH/DCM (50/50) - 5 mL DCM	elution with Methanol and dichloromethane	Extraction by soxhlet with acetonitrile	Elution with 15 ml methyltertiarybutylether followed by 20 ml DCM and finally with 15 ml methanol	3x ultrasonic extraction (70%) MeOH	In column extraction with 80/20 Dichloromethane/IPA	7 mL Acetone, 7 mL Methanol	SPE
Date of extraction:	27/06/2011		22/08/2011	29-Sep-11			08/03/2011	05/07/2011	20/10/2011	12.09.2011	12/09/2011	20/10/2011	20/10/2011	13/12/2011	12/12/2011	19/08/2011	25/07/2011
Date of instrumental analysis:	23/08/2011		05/09/2011	18-Oct-11			08/03/2011	28/09/2011	21/10/2011	15.09.2011	24/09/2011	27/10/2011	27/10/2011	05/01/2012	10/01/2012	22/08/2011	23/09/2011

Table All- 1 (continued) Participant passive samplers of polar pesticides: method information

LAB No.	17	18	19	21	23a	23	30	36	37	39	40	43a	43	44	47	48	49
Cleanup method:	no	none	Filtration through PFTE filter (0.45µm)		no	no	Extrat filtered with 0.2 µm PVDF membrane	NaSO4, 0.45 µm cellulose acetate membrane	no	No cleanup	no	none	No		No clean up		/
Instrumental method:	UPLC/MS/MS	HPLC-MS/MS	LCMS	LC-MS	LC/MS/MS	LC/MS/MS	HPLC-MS/MS	LC-MS/MS	LC-MS/MS	LC-MS-MS	LC-MS/MS	LC-MSMS	LC-MSMS	LC/MS/MS, ESI+, column: Betasil C18, Mobile phase: gradient water 5mM NH4COOH, MeOH 5mM NH4COOH	LCMS QQQ and GCMS (for Atrazine)	online SPE (Oasis HLB) HPLC-MS/MS	LC-MS/MS
Injection solvent:	MEOH	Water:MeCN, 90:10	50% methanol/water	milli Q	MeOH/water	MeOH/water	Methanol/Water	MeOH	75% methanol/25% 5mM ammonium acetate	MeOH	Methanol	Acetonitrile water	Acetonitrile-water	methanol: water 5mM NH4COOH (1:1)	In mobile phase except for Atrazine which was in Hexane	HPLC grade Water, Methanol	Water
Recovery and internal standards used:	Simazine d10	No correction with recoveries, use of internal standards	IS: 25ng d-simazine, RS: 12ng d-atrazine		IS = C13 labelled Simazin, RS not used	IS = C13 labelled Simazin, RS not used	Atrazine-D5	Acenaphtene-D10; HCB-13C6	yes	Simazine d10, Hexazine d6, Diuron d6, Atrazine d5, Terbutylazine d5, Irgarol d9	alachlor-d13, atrazine-d5, hydroxyatrazine-d5, carbofuran-d3, cyanazine-d5, dea-d7, diuron-d6, hexazinone-d6, irgarol-d9, isoproturon-d6, simazine-d10, terbutylazine-d5	Diverse standards but not targets, recoveries vary	Several standards used but generally not the target compounds, Therefore no corrections were made.	internal standards: Atrazine D5, Isoproturon D6, Simazine D5, Terbutryn D5	YES - Deuterated (D5) Atrazine, (D6) Diuron and (D3)Carbendazim	Labeled IS used for every compound analysed	/

Table All- 1 (continued) Participant passive samplers of polar pesticides: method information

LAB No.	17	18	19	21	23a	23	30	36	37	39	40	43a	43	44	47	48	49
REMARKS:							The extracts obtained were diluted to analyze. Dilutions were performed: 1:2, 1:10 and 1:20.			-	-	No corrections for suppression made	No corrections for suppression made		Matrix interference made quantification of Atrazine problematic		/

Table All- 1 (continued) Participant passive samplers of polar pesticides: method information

LAB No.	17	18	19	21	23a	23	30	36	37	39	40	43a	43	44	47	48	49
Data evaluation aspects																	
Method for estimation of water concentration from passive sampler:	Data in ng/g, determination of TWA concentrations with application of k_u (Lissalde et al. 2011) and PRC (Mazzella et al. 2010) data	Eds were deployed in association with PFMs. Water concentrations of identified chemicals were estimated from the mass accumulated in the sampler using laboratory derived sampling rates adjusted in situ with the calibrated loss of plaster from the PFMs	according to Mazzella et al. ES&T, vol. 44, no5, 2010 eq 2 and 6, DIA5 PRC Log K_{sw} 3.85				One the pesticide amount in the receiving phase, determined in the analysis, % recoverie and sample volume (determined by meas of data in the electronic board) is applied to calculate the TWAC.	flow-dependent regression on over literature values (if R_s not available)	TWA calculated according to Alvarez 2004	Calculation with following formula : $C_s \times 0,2 = C_w \times R_s \times t$ (Vrana et al., 2005)	PRC approach using Salbutamol-d3, Caffeine-C13 and DIA-d5	Fitting PRC dissipation with model and a flowfactor or as adjustable parameter. Then this flow factor is applied to calculate the C_w	Uptake of Clotrimazole, Carbamezapine, Thiabendazole and Fluoranthene transferred to sampled volume using C_w from SR sampling	N.Mazzella, S. Lissalde, S. Moreira, F. Delmas, P. Mazellier, J.N. Huckins: Environ. Sci. Technol. 2010, 44, 1713-1719. For Diuron: N. Mazzella, J.-F. Dubernet, F. Delmas: Journal of Chromatography A 2007, 1154,) 42-51	Estimation of water calculation not used		To obtain laboratory R_s : Plot of the concentration factor as a function of the time until the $t_{1/2}$: $CF = C_s / C_w = (R_s \times t) / (M_s)$. Use of this lab R_s in order to obtain in situ TWA concentrations using the equation $C_w = (C_s \times M_s) / (R_s \times t)$

Table All- 1 (continued) Participant passive samplers of polar pesticides: method information

LAB No.	17	18	19	21	23 a	23	30	36	37	39	40	43a	43	44	47	48	49
Sampling rates used (literature value/own calibration):	literature	Lissalde et al. 2011	own calibration	literature value	Mazzeffa 2007, Mazzeffa 2008	Alvarez et al. 2007	Analyte recovery: Atrazine (97%), Diuron (94%) and Terbutylazine (92%). Sample volume 2 L.	literature values for pesticides and pharmaceuticals	own calibration	Sampling rates from Lissalde et al., 2011 were used	own calibration	From PRCs using Rusina Est 2010 and Booi and Smedes EST 2010	From calibration with SR results Sampled volume 2.2, 2.8 and 3.1 L	Rs[L/d]- literature values: Environ.Sci. Technol.- Rs (DEA)=0,167, Rs (DET)=0,205, Rs(Atrazine)=0,239, Rs(S-Metolalchlor)=0,225. J.Chromatography A: Rs (Diuron)=0.247. Rs for carbendazim not found.	N/A	own, unpublished data (between 0.078 and 0.094)	Own calibration: ATRA=0,1891 L/d; CARB=0,2949 L/d; DIU=0,1976 L/d
Ksw used:		No	no	log Ksw 3.85	No	No	no necessary.	NO	-	-	-	Smedes et al EST 2009	none		N/A		/
PRCs applied (YES/NO):	no	YES	no	yes	No	No	No	NO	no	NO	YES	Yes	NO	No	NO		NO
Were the calibration data adjusted to reflect exposure conditions (temperature, flow, pH...?)	no	Yes	flow/salinity through the use of the PFM	no	No	No	No	average flow was estimated with PFM: O'Brien et al., Chemosphere 83 (9), 2011	no	NO	PRC	Flow corrected (not Temperature)	Only an attempt to correct for flow	No	N/A		No (laboratory calibration: temperature=20,7°C; pH=7,6; conductivity=429 µS/cm; DOC=13,3 mg/L; flow=11 cm/s)
REMARKS:					Results of instrument control and of samplers provided by the organizer are in the first report form.		Only 2 CFIS devices have been analyzed because one broken and stoped in the sampling .	PRC not used for Ctwacalculation		concentrations in sorbent were calculated with a nominal mass of 0,2g	-	Preliminary Kpw used, some estimated some determined	Not very confident on sampling rate applied				/

Annex III. Provided passive samplers of pharmaceuticals: method information

TableAIII-1 Provided passive samplers of pharmaceuticals: method information

LAB No.	17	19	23a	23	29	31	32	36	39	40	43a	43	44	47	48	49	50a	50
Passive sampler (PS)																		
PS type :	POCIS, pharmaceutical version																	
Receiving phase material:	sorbent Oasis HLB, 60 um																	
Receiving phase mass (g):	0.200 g; mass of sorbent separated from samplers after exposure is given on each SPE cartridge																	
Membrane material :	Polyethersulphone; SUPOR 100 Membrane Disc Filters (0.1 um, 90 mm diameter)																	
Active sampler surface area (or membrane area) (cm2):	45.8 cm2																	
Performance and Reference Compound (PRC) *																		
Passive samplers with PRC :	Deisopropylatrazine (DIA) d5																	
	concentration cca. 4ug/g sorbent																	
Transport and storage																		
Storage conditions before deployment (°C)**:	Fridge (4 degrees C)																	

TableAIII- 2 Provided passive samplers of pharmaceuticals: method information

LAB No.	17	19	23 a	23	29	31	32	36	39	40	43a	43	44	47	48	49	50 a	50
Storage conditions after sampler recovery (°C)**:		Fridge (4 degrees C)							-20	-20°C			freezer			Storage in freezer at -20°C		
Date of return shipment from the organiser to the participant laboratory: **		21/07/2011							18.07.2011	18/07/2011	~31/8/2011	~31/8/2011				07/07/2011		
Date of receipt by the participant laboratory ** :	29/07/2011	26/07/2011		21/06/2011					19.07.2011	19/07/2011	~2/9/2011	~2/9/2011	10/25/11	03/08/2011	22/07/2011	08/07/2011	August, 5th	August, 5th
REMARKS:									-	-	Dates are approximate	Dates are approximate				/		

TableAIII- 2 (continued) Provided passive samplers of pharmaceuticals: method information

LAB No.	17	19	23a	23	29	31	32	36	39	40	43a	43	44	47	48	49	50a	50
Sampler deployment and recovery																		
Date and hour of the deployment ** :	30/05/2011	30/5/2011; 11:10am, 11:10am, 11:50am		30.5.2011, 10:35					30.05.2011 11:30	samplers 88, 83 : 30/05/2011 12:25 ; sampler 53 : 30/05/2011 11:50	20/06/2011	20/06/2011	(16) 5/30/11, 10:35 (20) 5/30/11, 10:35 (59) 5/30/11, 11:50		Sampler 43: 30.05.2011 11:10 Sampler 54: 30.05.2011 11:50 Sampler 75: 30.05.2011 12:25	Sample 67: 30/05/2011 at 11:50; sample 84: 30/05/2011 at 12:25; sample 95: 30/05/2011 at 12:25		
Air Temp on deployment (°C)**		21-22		00:00					00:00:00	samplers 88, 83 : 22 ; sampler 53 : 22			(16) 20°C (20) 20°C (59) 21°C		Sampler 43: 21; Sampler 54, 75: 22	Sample 67: 22°C; sample 84: 22,5°C; sample 95: 22,5°C		
Duration of the deployment (exposure to air for field control)**		35mins, 35mins, 40mins		00:45:00					30 min	samplers 88, 83 : 00:35 ; sampler 53 : 00:40			(16) 45 min (20) 45 min (59) 40 min		Sampler 43: 35min Sampler 54: 30min Sampler 75: 35min	Sample 67: 40 min; sample 84: 35 min; sample 95: 35 min		
Air Temp on recovery (°C)**		20-21		00:00					00:00:00	samplers 88, 83 : 21 ; sampler 53 : 20			(16) 18°C (20) 18°C (59) 20°C		Sampler 43, 54: 21; Sampler 75: 22	Sample 67: 21°C; sample 84: 21,5°C; sample 95: 21,5°C		
Duration of the recovery (exposure to air for field control)**		9, 9, 16 mins		00:40:00					30 min	samplers 88, 83 : 00:30 ; sampler 53 : 00:17			(16) 39 min (20) 39 min (59) 17 min		Sampler 43: 9min Sampler 54: 17min Sampler 75: 30min	Sample 67: 17 min; sample 84: 30 min; sample 95: 30 min		

TableAIII- 2 (continued) Provided passive samplers of pharmaceuticals: method information

LAB No.	17	19	23a	23	29	31	32	36	39	40	43a	43	44	47	48	49	50a	50
Date and hour of the recovery ** :	13/06/2011	13/6/2011 ; 10:34, 10:34, 10:43am		13.6.2011, 9:16					13.06.2011 10:00	samples 88, 83 : 13/06/2011 11:30 ; sampler 53 : 13/06/2011 10:43	04/07/2011	04/07/2011	(16) 6/13/11, 9:16 (20) 6/13/11, 9:16 (59) 6/13/11, 10:43		Sampler 43: 13.06.2011 10:34 Sampler 54: 13.06.2011 10:43 Sampler 75: 13.06.2011 11:30	Sample 67: 13/06/2011 at 10:43; sample 84: 13/06/2011 at 11:30; sample 95: 13/06/2011 at 11:30		
Comment on fouling*:									Exposed membranes were spotted and darker than unexposed ones	-						Not much		
Field deployment device used																		
Type of deployment device (canister, cage...):	standard POCIS deployment cage for 6 samplers																	
Analytical aspects																		
Extraction technique:	elution MeOH	Elution of cartridges with 3mL methanol, 2 ml acetonitrile, 2 ml acetone	liquid extraction	same as NIVA samplers		SPE	3 x 15 min ultrasonic extraction with MeOH	5 mL MeOH - 5 mL MeOH/DCM (50/50) - 5 mL DCM	elution with Methanol and dichloromethane	Elution with 4 ml methyltertiarybutylether followed by 8 ml methanol	Elution with 4 ml methyltertiarybutylether followed by 8 ml methanol	3x5 ml 100% MeOH	SPE column extraction with 80/20/0.1 (Dichloromethane/IPA/TFA)	5 mL Methanol	SPE	SPE	SPE	

TableAIII- 2 (continued) Provided passive samplers of pharmaceuticals: method information

LAB No.	17	19	23a	23	29	31	32	36	39	40	43a	43	44	47	48	49	50a	50
Date of extraction:	08/08/2011	29/08/2011					17/08/2011	15/11/2011	12.09.2011	12/09/2011	20/10/2011	20/10/2011	13/12/2011	09/12/2011	19/08/2011	25/07/2011	october, 13th	october, 13th
Date of instrumental analysis:	11/08/2011	05/09/2011							19.09.2011	12/09/2011	27/10/2011	27/10/2011	06/01/2012	07/01/2012	22.08.2011 (29.11.2011 for DIA)	23/09/2011 for all the pharmaceuticals except for atenolol: 09/09/2011	november, 11th	november, 11th
Cleanup method:	no			no			no cleanup	NaSO4, 0.45 µm cellulose acetate membrane	No cleanup	no	No	No		No cleanup		/	-	-
Instrumental method:	uplc/msms	LCMS		LC/MS/MS			HPLC-MS/MS	LC-MS/MS	LC-MS-MS (ESI+ and -)	LC-MS/MS	LC-MSMS	LC-MSMS	LC/MS/MS,ESI+/-/ESI-, column: Zorbax Eclipse XDB C18, Mobile phase: gradient: water 0,2% CH3COOH, MeOH 0,2% CH3COOH	LCMS QQQ	online SPE (Oasis HLB) HPLC-MS/MS	LC-MS/MS	HPLC-MS/MS	HPLC-MS
Injection solvent:	MEOH	50% methanol/water		MeOH/water			MeOH: H2O	MeOH	Milli-Q Water (ESI+) or ACN (ESI-)	Methanol	Acetonitrile-water	Acetonitrile-water	MeOH:water 0,2% CH3COOH (1:1)	In mobile phase	HPLC grade Water, Methanol	Water for all the pharmaceuticals except for atenolol: Water/Acetone nitrile (99/1) + metoprolol impurity A	methanol	methanol
Recovery and internal standard	oxazepam d5	No recovery correctly		IS = C13 labelled Sulfamethoxazole, RS			none		Carbamazepine d10, Diazepam	diazepam-d5, diclofenac-d4,	Several standards used but	Several standards used but	Int.stand.: Diclofenac D4, Ibuprofen D3,Carbamaz	YES - Deuterated (D7)Atenolol	Labeled IS used for every	/	only check on internal standard	only check on internal standard

s used:		on		not used					d5, Atenolol d7, Nordiazepam d5, Ketoprofen d3, Naproxen d3, Ibuprofen d3, Diclofenac d4	ibuprofen-d3, ketoprofen-d3, naproxen-d3, nordiazepam-d5	generally not the target compounds, Therefore no corrections were made.	generally not the target compounds, Therefore no corrections were made.	epine D10	lol, (D10) Carbamazepine, (D5) Diclofenac, (D3) Ibuprofen	compound analysed		s	s
REMARKS:									-	-	No corrections for suppression made	No corrections for suppression made		Matrix interference made quantification of Atenolol problematic. Ibuprofen was not present above our detection limits		/	DIA-d5 is not used for quantification	DIA-d5 is not used for quantification

TableAIII- 2 (continued) Provided passive samplers of pharmaceuticals: method information

LAB No.	17	19	23a	23	29	31	32	36	39	40	43a	43	44	47	48	49	50a	50
Data evaluation aspects																		
Method for estimation of water concentration from passive sampler:	m/R st	$C_w = N_s / (R_s * t)$	please give a short description and relevant references	please give a short description and relevant references	Same as for POCIS from NIVA	please give a short description and relevant references	The rough estimation of 4,2 L is based upon a report by Roberts & Balaam . Roberts , P.H., Balaam , J.L., 2006. Offline extraction and passive sampling. Modelk ey progress report SSP1-CT-2003-511237-2. They found water extractions between 50 and 300 ml	Literature values	Calculation with following formula : $C_s \times 0,2 = C_w R_s t$ (Vrana et al., 2005)	PRC approach using Salbutamol-d3, Caffeine-C13 and DIA-d5	Uptake of Clotrimazole, Carbamezapine, Thiabendazole, transferred to sampled volume using C_w from SR sampling	Uptake of Clotrimazole, Carbamezapine, Thiabendazole, transferred to sampled volume using C_w from SR sampling	S.L. Bartelt-Hunt, D.D.Snow, T. Damon-Powel at all:Environmental Toxicology and Chemistry, Vol. 30, No. 6, pp. 1412-1420, 2011. For diclofenac was used R_s from: S.L. MacLeod, E.L. McClure, Ch.S. Wong: Environmental Toxicology and Chemistry, Vol. 26, No	Estimation of water calculation not used	please give a short description and relevant references	To obtain laboratory R_s : Plot of the concentration factor as a function of the time until the $t_{1/2}$: $CF = C_s / C_w = (R_s * t) / (M_s)$. Use of this lab R_s in order to obtain in situ TWA concentrations using the equation $C_w = (C_s * M_s) / (R_s * t)$	please give a short description and relevant references	please give a short description and relevant references

TableAIII- 2 (continued) Provided passive samplers of pharmaceuticals: method information

LAB No.	17	19	23 a	23	29	31	32	36	39	40	43a	43	44	47	48	49	50a	50
Sampling rates used (literature value/own calibration):	littérature	Literature (Li et al, 2010; MacLeod et al , 2007; Togola et al 2007). Atenolol = 0.094, carbamazepine= 0.561, diazepam=0.28 , diclofenac=0.166 , ibuprofen=0.348, Naproxen=0.392		MacLeod, McClure, Wong 2007, Rs just for Pharm. POCIS				literature values for pesticides and pharmaceuticals	Own calibration for Carbamazepine and Diclofenac, literature values (Togola and Budzinski, 2007- Li et al., 2009) for other compounds	own calibration	From calibration with SR results, Sampled volume = 3.0, 3.6, 3.4 L	From calibration with SR results, Sampled volume = 3.0, 3.6, 3.4 L	literature values Rs[L/d]: ibuprofen 0,400; carbamazepin 0,288 ;diclofenac 0,166 (flowing Rs)	N/A		Own calibration: ATE=0,0218 L/d; CARBA=0,1876 L/d; DICLOF=0,2248 L/d; KETO=0,1213 L/d; NAPRO=0,0838 L/d	Journal of Chromatography A, 1216 (2009) 623-630 and Environmental Toxicology and Chemistry, Vol. 29, No. 4, pp.751-762,2010 and Estuarine, Coastal and Shelf Science xxx (2011) 1-11 (article in press)	Journal of Chromatography A, 1216 (2009) 623-630 and Environmental Toxicology and Chemistry, Vol. 29, No. 4, pp.751-762,2010
Sampler/water partition (distribution) coefficients used:		No						NO	-	-	none	none		N/A		/		
Performance reference compounds applied (YES/NO):	no	No		No				NO	NO	YES	NO	NO	No	NO		NO		No
Were the calibration data adjusted to reflect exposure conditions (temperature, flow, pH...?):																		

Annex IV. Participant passive samplers of polar pharmaceuticals: method information

Table AIV- 1 Participant passive samplers of pharmaceuticals: method information

LAB No.	17	19	23a	23	29	31	36	39	40	43a	43	44	47	48	49
PS type :	POCIS pharmaceutical version	Empore Disk	POCIS, pharmaceutical version	POCIS, pesticide version	POCIS	POCIS Filled with OASIS HLB Material	Chemcatcher (3rd generation) polar configuration	POCIS, pharmaceutical version	POCIS	Altesil translucent silicone rubber (4 sheets of 100cm ² each)	Speedisks (2 disks form one sampler)	POCIS, pharmaceutical version	POCIS	Empore SDB-RPS with PES-Membrane (0.1µm)	POCIS, pharmaceutical version
Home made or commercial PS :	commercial	Commercial	commercial	commercial	home made	Home made with parts from Environmental Sampling Technologies	homemade	Home made	Home made	Home made	J.T. Baker, Bakerbond Speedisk, H ₂ O Philiic DVB, Art.nr.: 8072-07	commercial	Home made		Home made
							Chemcatcher bodies: University of Portsmouth (UK)	-	Home made						Home made
Supplier :	Exposmeter	Phenomenex	EST	EST		Environmental Sampling Technologies, St Joseph, MO, USA	Empore disk: VWR, Dresden (D); LDPE: University of Portsmouth	-	-	Altecweb.com	JT Baker	ExposMeter AB, Sweden		Infochroma	/

Table AIV- 1 (continued) Participant passive samplers of pharmaceuticals: method information

LAB No.	17	19	23a	23	29	31	36	39	40	43a	43	44	47	48	49
Receiving phase material:	OASIS HLB	SDB-RPS Reverse Phase Sulfonated	Oasis HLB	Biobeads, Ambersorb and Isolute ENV+	OASIS HLB	Waters OASIS HLB	Varian Empore SDB-RPS extraction disk 47 mm	Oasis HLB sorbent, 60 µm	Oasis HLB 60µm custom Bulk WAT106068	AlteSiIT M translucent material, 0.5±0.05 mm thickness	DVB	Oasis HLB	OASIS HLB	Styrene-divenylbenzene modified with sulfonic acid groups (SDB-RPS)	sorbent Oasis HLB, 60 µm
Receiving phase mass (g):	0,2 approximately	0.398	0.22	0.22	0.2	0.200	0.327	0.2	200 mg	14	0.95	0,200 g	227mg	0.331	0.2
Receiving phase volume (cm³)		1.73494					0.344		-	12					/
Membrane material :	PES	Polyethersulfone (0.45µm) SUPOR 450 filters PALL Life Sciences	Polyethersulfone	Polyethersulfone	polyethersulfone	Polyethersulfone	Pall Supor 200 polyethersulfone	Polyethersulfone; SUPOR 100 Membrane Disc Filters (0.1 µm, 90 mm diameter)	PES Supor-100, 0,1 µm, 90mm, 100/PK Product#60311	Silicon rubber	Glassfibre Filter ±0.5 mm		Pall Polyethersulfone Supor 100, 0.10µm pore size	Polyethersulfone (PES)	Polyethersulfone; SUPOR 100 Membrane Disc Filters (0,1 µm, 90 mm diameter)
Active sampler surface area (or membrane area) (cm²):	45.8	16	47.5	47.5	45.8	45.8 cm2	15.9	42.47	45,78 cm²	400	35	45,8cm2	45.8cm2	12.6	45.8

Table AIV- 1 (continued) Participant passive samplers of pharmaceuticals: method information

LAB No.	17	19	23a	23	29	31	36	39	40	43a	43	44	47	48	49
Performance Reference Compounds (PRC)															
Commercial passive samplers with PRC:	no		No	No	no	Atrazine desethylpropyl D5 provided by the organizer		NO	no		No PRCs	No			No
or home made PS spiked with PRC:	no				no prc		Diuron-D6; Carbamazepime-D10 (each 500 ng/disk)	NO	Home made PRC : DIA-d3, Salbutamol-d3, Caffeine-C13 (10µg/g)	Home spiked, D10-biphenyl, PCBs: CB001, CB002, CB003, CB010, CB014, CB021, CB030, CB050, CB055, CB078, CB104, CB145, CB204	No PRCs		None used		No
Transport and storage															
Date of shipment to the organiser :		approx 7 May 2011	07/06/2011	07/06/2011	?	End of May, 2011		13.05.2011	13/05/2011	~10/05/2011	~10/05/2011	5/26/11		10/05/2011	16/05/2011

Table AIV- 1 (continued) Participant passive samplers of pharmaceuticals: method information

LAB No.	17	19	23a	23	29	31	36	39	40	43a	43	44	47	48	49
Date of receipt by the study organiser :	26,04,11	14 May 2011 (Handover at conference)			?	End of May, 2011		16.05.2011	16/05/2011	~13/05/2011	~13/05/2011	5/26/11		11/05/2011	19/05/2011
Storage conditions before deployment (°C):	_20 °C	Fridge (4 degrees C)			-20	-20 C in a freezer		room temperature	-20°C	4°C immersed in water	4°C immersed in water	freezer		4	Storage in fridge at 4°C
Storage conditions after sampler recovery (°C):		Fridge (4 degrees C)			-20	-20 C in a freezer		-20	-20°C	minus 20°C	minus 20°C	freezer			Storage in freezer at -20°C
Date of return shipment from the organiser to the participant laboratory:		21/07/2011				July 14th, 2011		15.06.2011	15/06/2011	~31/8/2011	~31/8/2011	6/23/11		15/06/2011	07/07/2011
Date of receipt by the participant laboratory:		26/07/2011	21/06/2011	21/06/2011		July 16th, 2011		16.06.2011	16/06/2011	~2/9/2011	~2/9/2011	6/23/11	03/08/2011	16/06/2011	08/07/2011

Table AIV- 1 (continued) Participant passive samplers of pharmaceuticals: method information

LAB No.	17	19	23a	23	29	31	36	39	40	43a	43	44	47	48	49
Sampler deployment and recovery															
Date and hour of the deployment:	30/05/2011 15h55	30/05/2011; 19:50	30.5.2011, 16:15	30.5.2011, 16:15		June 13th, 2011 12:43 PM		30.05.2011 15:10	30/05/2011 15:10	30/05/2011	30/05/2011	5/30/11, 14:30		30/05/2011 20:20	30/05/2011 at 16:28
Air Temp on deployment (°C)	23	21	23	23		22		23	23			23°C		20	23.5
Duration of the deployment	25 minutes	27 min	00:15	00:15		13.844 days		20 min	00:35:00			25min		30 min	29 min
Air Temp on recovery (°C)	23	23	22	22		17		22	23			23°C		23	22
Duration of the recovery	50 minutes	20 min	00:40	00:40				30 min	00:23:00			18 min		11 min	32 min
Date and hour of the recovery:	13/06/2011 14h40	13/06/2011: 15:28	13.6.2011, 12:42	13.6.2011, 12:42		June 13th, 2011 8:58 AM		13.06.2011 13:22	13/06/2011 13:22	13/06/2011	13/06/2011	6/13/11, 14:17		13/06/2011 17:37	13/06/2011 at 12:43
Comment on fouling:								Exposed membranes were spotted and darker than unexposed ones	-						Not much
Field deployment device used:	canister	Teflon Chemcatc her case	standard big cage	standard big cage	canister?	Prepared stainless steel cages	Small SPMD deployment cage	Standard POCIS deployment cage for 3 samplers	standard small cage for 3 samplers	Wet mounted on open cage	Wet mounted on open cage	standard POCIS deployment cage	standard POCIS deployment cage for 3 samplers	Big cage (provided by WRI)	standard POCIS deployment cage for 6 samplers

Table AIV- 1 (continued) Participant passive samplers of pharmaceuticals: method information

LAB No.	17	19	23a	23	29	31	36	39	40	43a	43	44	47	48	49
Extraction technique:	elution MeOH	5 mL Acetone followed by 5 mL methanol; sonication; at room temperature	liquid extraction	liquid extraction	Elution with MeOH (acidic and basic MeOH too)	Extraction with methanol, rotovap, N-evap, place in MeOH/H ₂ O	3 x 15 min ultrasonic extraction with 5 ml in 1. acetone 2. MeOH 3. mixture of both (1:1)	5 mL MeOH - 5 mL MeOH/DCM (50/50) - 5 mL DCM	elution with Methanol and dichloromethane	Extraction by soxhlet with acetonitrile	Elution with 15 ml methyl tertiary butyl ether followed by 20 ml DCM and finally with 15 ml methanol	3x ultrasonic extraction (70% MeOH)	SPE column extraction with 80/20/0.1 (Dichloromethane/IPA/TFA)	7 mL Acetone, 7 mL Methanol	SPE
Extraction:	27/06/2011	22/08/2011			06.01.2012	10.12.2011	05/07/2011	12.09.2011	12/09/2011	20/10/2011	20/10/2011	13/12/2011	09/12/2011	19/08/2011	25/07/2011
Date of instrumental analysis:	11/08/2011	05/09/2011			10.01.2012	December 13th, 2011	28/09/2011	19.09.2011	26/09/2011	27/10/2011	27/10/2011	06/01/2012	07/01/2012	22/08/2011	23/09/2011 atenolol: 09/09/2011
Cleanup method:	no	Filtration through PTFE filter (0.45um)	no	no	None	Included in separate File	NaSO ₄ , 0.45 µm cellulose acetate membrane	No cleanup	no	none	No		No cleanup		/
Instrumental method:	uplc/msms	LCMS	LC/MS/MS	LC/MS/MS	LC/MS	Included in separate File	LC-MS/MS	LC-MS-MS (ESI + and -)	LC-MS/MS	LC-MSMS	LC-MSMS	LC/MS/MS, ESI+/ESI-, Zorbax Eclipse XDB C18, Mobile phase: gradient: water 0,2% CH ₃ COOH, MeOH 0,2% CH ₃ COOH	LCMS QQQ	online SPE (Oasis HLB) HPLC-MS/MS	LC-MS/MS
Injection solvent:	MEOH	50% methanol/water	MeOH/water	MeOH/water	MeOH/water 50:50	10:90 Methanol: Water	MeOH	Milli-Q Water (ESI+) or ACN (ESI-)	Methanol	Acetonitrile water	Acetonitrile-water	MeOH:water 0,2% CH ₃ COOH (1:1)	In mobile phase	HPLC grade Water, Methanol	Water except for atenolol: Water/Acetonitrile (99/1)

Table AIV- 1 (continued) Participant passive samplers of pharmaceuticals: method information

LAB No.	17	19	23a	23	29	31	36	39	40	43a	43	44	47	48	49
Recovery and internal standards used:	oxazepam d5	No recovery correction	IS = C13 labelled Sulfamethoxazol, RS not used	IS = C13 labelled Sulfamethoxazol, RS not used	YES	Included in separate File	Acenaphtene-D10; HCB-13C6	Carbamazepine d10, Diazepam d5, Atenolol d7, Nordiazepam d5, Ketoprofen d3, Naproxen d3, Ibuprofen d3, Diclofenac d4	diazepam-d5, diclofenac-d4, ibuprofen-d3, ketoprofen-d3, naproxen-d3, nordiazepam-d5	Diverse standard standards but not targets, recoveries vary	Several standards used but generally not the target compounds, Therefore no corrections were made.	Int.stand.: Diclofenac D4, Ibuprofen D3, Carbamazepine D10	YES - Deuterated (D7)Atenolol, (D10) Carbamazepine, (D5) Diclofenac, (D3) Ibuprofen	Labeled IS used for every compound analysed	/
REMARKS :						Methods included in separate file.		-	-	No corrections for suppression made	No corrections for suppression made		Matrix interference made quantification of Atenolol problematic. Ibuprofen was not present above our detection limits		/

Table AIV- 1 (continued) Participant passive samplers of pharmaceuticals: method information

LAB No.	17	19	23a	23	29	31	36	39	40	43a	43	44	47	48	49
Data evaluation aspects															
Method for estimation of water concentration from passive sampler:	m/Rst	$C_w = N_s / (R_s * t)$	please give a short description and relevant references	please give a short description and relevant references	Use of mean of literature R_s values available for each compound, assuming linear uptake over 14 days	Please see separate file "NORMAN Report.doc x".	flow-dependent regression over literature values (if R_s not available)	Calculation with following formula : $C_s \times 0,2 = C_w R_s t$ (Vrana et al., 2005)	PRC approach using Salbutamol-d3, Caffein-C13 and DIA-d5	Fitting PRC dissipation with model and a flowfactor as adjustable parameter. Then this flow factor is applied to calculate the C_w	Uptake of Clotrimazole, Carbamezpine, Thiabendazol and Fluoranthene transferred to sampled volume using C_w from SR sampling	S.L. Bartelt-Hunt, D.D.Snow, T. Damon-Powel at all: Environmental Toxicology and Chemistry, Vol. 30, No. 6, pp. 1412-1420, 2011. For diclofenac was used R_s from: S.L. MacLeod, E.L. Mc Clure, Ch.S. Wong: Environmental Toxicology and Chemistry, Vol. 26, No	Estimation of water calculation not used	please give a short description and relevant references	To obtain laboratory R_s : Plot of the concentration factor as a function of the time until the $t_{1/2}$: $CF = C_s / C_w = (R_s * t) / (M_s)$. Use of this lab R_s in order to obtain in situ TWA concentrations using the equation $C_w = (C_s * M_s) / (R_s * t)$
Sampling rates used (literature value/own calibration):	literature	Own calibration .Own calibration Atrazine is used as a reference point. Other PPCPs are assigned a relative to atrazine ratio based on their sampling rates			Mean of literature values	Sampling rates in separate file "NORMAN report.doc x"	literature values for pesticides and pharmaceuticals	Own calibration for Carbamazepine and Diclofenac, literature values (Togola and Budzinski, 2007- Li et al., 2009) for other compounds	own calibration	From PRCs using Rusina Est 2010 and Booij and Smedes EST 2010	From calibration with SR results Sampled volume 2.2, 2.8 and 3.1 L	literature values: ibuprofen 0,400; carbamazepine 0,288 ; diclofenac 0,166 (flowing R_s)	N/A	own, unpublished data Carbamazepine: 0.100 L/d Diclofenac : 0.056 L/d	Own calibration : ATE=0,02 18 L/d; CARBA=0, 1876 L/d; DICLOF=0 ,2248 L/d; KETO=0,1 213 L/d; NAPRO=0, 0838 L/d

		(RsPPCP/Rs Atr) from our own calibration study. The laboratory Rs of atrazine is adjusted using the													
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Table AIV- 1 (continued) Participant passive samplers of pharmaceuticals: method information

LAB No.	17	19	23a	23	29	31	36	39	40	43a	43	44	47	48	49
Sampler/water partition (distribution) coefficients used:		No			No		NO	-	-	Smedes et al EST 2009	none		N/A		/
Performance reference compounds applied (YES/NO):	no	No			NO	No	NO	NO	YES	Yes	NO	No	NO		NO
Were the calibration data adjusted to reflect exposure conditions (temperature, flow, pH...?)	no	Flow and salinity through the PFM			not really		average flow was estimated with PFM: O'Brien et al., Chemosphere 83 (9), 2011	NO	PRC	Flow corrected (not Temperature)	Only an attempt to correct for flow	No	N/A		No (laboratory calibration : temperature=20,7°C ; pH=7,6; conductivity y=429 µS/cm; DOC=13,3 mg/L; flow=11 cm/s)

Annex V. Provided passive samplers of steroids: method information

Table AV- 1 Provided passive samplers of steroids: method information

LAB No.	19	20	23	26	33	36	37	39	43a	43	44	45	49	51
PS type :	POCIS, pharmaceutical version													
Receiving phase material:	sorbent Oasis HLB, 60 µm													
Receiving phase mass (g):	0.200 g; mass of sorbent separated from samplers after exposure is given on each SPE cartridge													
Membrane material :	Polyethersulphone; SUPOR 100 Membrane Disc Filters (0.1 µm, 90 mm diameter)													
Active sampler surface area (or membrane area) (cm ²):	45.8 cm ²													
Performance and Reference Compound (PRC) *														
Passive samplers with PRC :	NO													

Table AV- 2 Provided passive samplers of steroids: method information

LAB No.	19	20	23	26	33	36	37	39	43a	43	44	45	49	51
Transport and storage														
Storage conditions before deployment (°C)**:	Fridge 4 degrees C	4	-20					4					Storage in fridge at 4°C	
Storage conditions after sampler recovery (°C)**:	Fridge 4 degrees C	-20	-20		-20			-20			freezer		Storage in freezer at -20°C	
Return shipment	21/07/2011	September 5 2011	20/07/2011		13/07/2011			18/07/2011	~31/8/2011	~31/8/2011			07/07/2011	

Table AV- 2 (continued) Provided passive samplers of steroids: method information

LAB No.	19	20	23	26	33	36	37	39	43a	43	44	45	49	51
Date of receipt by the participant laboratory ** :	26/07/2011	September 11 2011	20/07/2011		15/07/2011			19/07/2011	~2/9/2011	~2/9/2011	10/25/11		08/07/2011	
REMARKS:		Samples stored at 4C upon receipt			none				Dates are approximate	Dates are approximate			/	
Sampler deployment and recovery														
Date and hour of the deployment ** :	20/6/2011; 10:34, 11:44, 12:00	6/20/2011 approx. 11:00	20.6.2011, 12:00	20/062011 10.34 (sampl.4) and 11.03 (sampl 9)	PS [27] and [33]: 20/06/2011 10:34; PS [77]: 20/06/2011 11:44	20/06/11-04/07/2012		20.06.2011 11:03	20/06/2011	20/06/2011	(57) 6/20/11 11:03 (64) 6/20/11 11:03 (111) 6/20/11 12:00	Sampler 1, 2 and 11: 20.06.2011 09:55:00	Sample 25: 20/06/2011 at 10:34; sample 72: 20/06/2011 at 11:44; sample 97: 20/06/2011 at 12:00	
Air Temp on deployment (°C)**	17,17, 20	22	20	17	PS [27] and [33]: 17 °C ; PS [77]: 20 °C			17			(57) 17°C (64) 17°C (111) 20°C	Sampler 1, 2 and 11: 15 °C	Sample 25: 17°C; sample 72: 20°C; sample 97: 20°C	
Duration of the deployment (exposure to air for field control)**	39, 44, 30	approx. 35 minutes	0.020833333	25 min (sampl 4) and 46 min (sampl 9)	PS [27] and [33]: 39 min; PS [77]: 44 min			30 min			(57) 46 min (64) 46 min (111) 30 min	Sampler 1, 2 and 11: 13.990	Sample 25: 39 min; sample 72: 44 min; sample 97: 30 min	
Air Temp on recovery (°C)**	17-19	21	19	18	PS [27] and [33]: 17 °C; PS [77]: 19 °C			17			(57) 18°C (64) 18°C (111) 17°C	Sampler 1, 2 and 11: 17 °C	Sample 25: 17°C; sample 72: 18,5°C; sample 97: 19°C	

Table AV- 2 (continued) Provided passive samplers of steroids: method information

LAB No.	19	20	23	26	33	36	37	39	43a	43	44	45	49	51
Duration of the recovery (exposure to air for field control)**	40, 30, 55 mins	approx. 45 minutes	0.03819444 4	20 min (sampl 4) and 30 min (sampl 9)	PS [27] and [33]: 40 min; PS [77]: 30 min			30 min			(57) 30 min (64) 30 min (111) 55 min		Sample 25: 40 min; sample 72: 30 min; sample 97: 55 min	
Date and hour of the recovery ** :	4/7/2011; 10:15, 11:30, 12:00	7/4/2011 approx. 11:30	4.7.2011, 12:00	4//2011 9,40 (sampl 4) and 11,00 (sampl 9)	PS [27] and [33]: 04/07/2011 10:15; PS [77]: 04/06/2011 11:30			04.07.2011 11:00	04/07/2011	04/07/2011	(57) 7/4/11 11:00 (64) 7/4/11 11:00 (111) 7/4/11 12:00	Sampler 1, 2 and 11: 04.07.2011 09:40:00	Sample 25: 04/07/2011 at 10:15; sample 72: 04/07/2011 at 11:30; sample 97: 04/07/2011 at 12:00	
Comment on fouling**:		None visible						Exposed membranes were spotted and darker than unexposed ones				-	Not much	

Table AV- 2 (continued) Provided passive samplers of steroids: method information

LAB No.	19	20	23	26	33	36	37	39	43a	43	44	45	49	51
Analytical aspects														
Extraction technique:	Elution of cartridges with 3 mL methanol, 2 mL 50:50 acetone hexane	Cold Benchtop with Dichloromethane	liquid extraction	Solvent elution	Extraction with acetone 50 ml	SPE	50 mL 8:1:1 DCM:toluene:methanol	5 mL MeOH - 5 mL MeOH/DCM (50/50) - 5 mL DCM	Elution with 4 mL methyltertiarybutylether followed by 8 mL methanol	Elution with 4 mL methyltertiarybutylether followed by 8 mL methanol	3x5ml acetonitrile	MeOH, 40 ml	SPE	Solid phase extraction
Date of extraction :	01/09/2011	November 4 2011		07/12/2011	13/10/2011	09/07/2011	July 18, 2011	23.08.2011	20/10/2011	20/10/2011	09/12/2011	25/07/2011	25/07/2011	October 5 2011
Date of instrumental analysis:	16/09/2011	December 6 2011		03/01/2012	14-15,17/10/2011	10/09/2011	July 19, 2011	30.09.2011	27/10/2011	27/10/2011	12/12/2011	04/08/2011	30/08/2011	November 11 2011
Cleanup method:	Liquid-liquid extraction with water to remove derivatising agent	None	SPE, florisil, dansylation	No cleanup	none	1-g Florisil@ cartridge SPE cleanup + derivatisation	C.Liscio et al: Environmental Pollution, 2009, 157, 2716	No cleanup	No	No	florisil (elution with 1% acetone in CH2Cl2)	no	/	None
Instrumental method:	GCMS	GC/MS	LC/MS/MS	GC/MS/SIS ion trap	LC-MS-MS	GC-MS	LC-ESI-MS/MS	LC-MS-MS	LC-MSMS	LC-MSMS	LC/MS/MS, ESI-, Column: Synergi Hydro-RP, Mobile phase: gradient: water, acetonitrile	LC-MS/MS	LC-MS/MS	Liquid chromatography-Tandem mass spectrometry
Injection solvent:	50% hexane/acetone	Methanol	MeOH/H2O	MSTFA	50% CH3OH 50% H2O	Hexane	MeCN	MeOH/ultra pure water (50/50)	Acetonitrile -water	Acetonitrile -water	Acetonitrile	EtOH	Water/Acetonitrile (60/40) + estradiol acetate	Methanol

Table AV- 2 (continued) Provided passive samplers of steroids: method information

LAB No.	19	20	23	26	33	36	37	39	43a	43	44	45	49	51
Recovery and internal standards used:	Derivatised with silyating agent (BSTFA + TMCS)	d4 17a Ethynylestradiol, Tribromobiphenyl	IS=deuterated beta-estradiol	Bisphenol-d16	Estrone d4 as internal std	PG-d and BPA-d	E2-D, EE2-D	E2 d5, EE2 d4, E1 d4	Several standards used but generally not the target compounds, Therefore no corrections were made.	Several standards used but generally not the target compounds, Therefore no corrections were made.	Int. stand. Estrone D4, 17b-Estradiol D5, 17a-Ethynylestradiol D4	D4-Estrone 13C2-17-beta-Estradiol D4-17-alpha-Ethynylestradiol	/	13C-sulfamethazine (positive) and bisphenol A (Negative)
REMARKS:						The long storage of derivatised extracts at -20°C could partly have caused degradation			No corrections for suppression made	No corrections for suppression made			/	No recovery standard was used
Data evaluation aspects														
Method for estimation of water concentration from passive sampler:	please give a short description and relevant references	Li, Helm, and Metcalfe ETC 2010	please give a short description and relevant references	Ardisoglou et al. Environmental Pollution 156 (2008) 316-324	Alvarez et al, Environ, Toxicol. Chem. 23 (2004) 1640-1648	please give a short description and relevant references		Calculation with following formula : $C_s \times 0,2 = C_w \times R_s \times t$ (Vrana et al., 2005)	Uptake of Clotrimazole, Carbamezapine, Thiabendazole, transferred to sampled volume using C_w from SR sampling	Uptake of Clotrimazole, Carbamezapine, Thiabendazole, transferred to sampled volume using C_w from SR sampling	S.L. Bartelt-Hunt, D.D.Snow, T. Damon-Powel at all:Environmental Toxicology and Chemistry, Vol. 30, No. 6, pp. 1412-1420, 2011.	Averaged sampling rate from 2 publications was used: 1. Z. Zhang et al., Anal Chim Acta 607, 37-44 2. A. Ardisoglou et al, Env Pollution 156, 316-324	To obtain laboratory Rs: Plot of the concentration factor as a function of the time until the $t_{1/2}$: $CF=C_s/C_w=(R_s \times t)/(M_s)$. Use of this lab Rs in order to obtain in situ TWA concentrations using the equation $C_w=(C_s \times M_s)/(R_s \times t)$	Not available

Table AV- 2 Provided passive samplers of steroids: method information

LAB No.	19	20	23	26	33	36	37	39	43a	43	44	45	49	51
Sampling rates used (literature value/own calibration):		Rs=0.853(17a-Ethynylestradiol), 0.699(Estrone), 0.693(17B-Estradiol)	Arditsoglou, Voutsas 2008	Literature Valur	Arditsoglou et al. Environmental Pollution 156 (2008) 316-324 (for E1 Rs 0.1199)	Arditsoglou, A., Voutsas, D., 2008, Environ Pollut 156:316-324. Averaged	T. Rujiralai, I.D Bull, neville Llewellyn R.P Evershed. J. Environ. Monit., 13, 2011, 13, 1427.	Own calibration	From calibration with SR results	From calibration with SR results, Sampled volumes on line 10 in result sheet.	Literature values:Rs(17beta estradiol) = 0,406[L/d]; Rs (estrone)= 0,394[L/d]; Rs (Ethynylestradiol) = 0,335[L/d]	Estrone: 17-beta-Estradiol: 17-alpha-Ethynylestradiol:	Own calibration: E1=0.2296 L/d, a-E2=0.2394 L/d, b-E2=0.2208 L/d, E3=0.1854 L/d, EE2=0.2605 L/d	
Sampler/ water partition (distribution) coefficients used:			No	Literature value				-	none	none			/	
Performance reference compounds applied (YES/NO):			No	NO	NO			NO	NO	NO	No	no	NO	
Were the calibration data adjusted to reflect exposure conditions (temperature, flow, pH...?)		No	No	NO	no		no	NO	Only an attempt to correct for flow	Only an attempt to correct for flow	No	no	No (laboratory calibration: temperature=20.7°C, pH=7.6, conductivity =429 µS/cm, DOC=13.3 mg/L, flow=11 cm/s)	
REMARKS:		Cw=ng(total)/(Rs*total days)							Not very confident on sampling rate applied	Not very confident on sampling rate applied			/	

Annex VI. Participant passive samplers of steroids: method information

Table A VI- 1 Participant passive samplers of steroids: method information

LAB No.	19	20	23	26	33	36	39	43a	43	49
PS type :	Empore Disk	Polyoxymethylene	POCIS, pharmaceutical version	POCIS, Pharmaceutical version	POCIS, pesticide version	POCIS	POCIS, pharmaceutical version	Altesil translucent silicone rubber (4 sheets of 100cm ² each)	Speedisks (2 disks form one sampler)	POCIS, pharmaceutical version
Home made or commercial PS :	Commercial	Home made	commercial	Commercial PS	commercial	Home made	Home made	Home made	J.T. Baker, Bakerbond Speedisk, H2O Philic DVB, Art.nr.: 8072-07	Home made
Supplier :	Phenomenex	N/A	EST	Exposmeter AB	EST (St. Joseph, USA).	no	-	Altecweb.com	JT Baker	/
Receiving phase material:	SDB-RPS Reverse Phase Sulfonated	Polyoxymethylene	sorbent Oasis HLB	sorbent Oasis HLB, µm	triphasic admixture	Isolute ENV+polystyrene divinylbenzene+ambersorb 1500 carbon dispersed on S-X3 Biobeads	Oasis HLB sorbent, 60 µm	AlteSiITM translucent material, 0.5±0.05 mm thickness	DVB	sorbent Oasis HLB, 60 µm
Receiving phase mass (g):	0.398	about 2	0.22	0,200g:	0.200 g	m1-m6 = 0.0951; 0.0966; 0.1011; 0.1002; 0.0998; 0.1017 g	0.200	14	0.95	0.2
Receiving phase volume (cm³)	1.73494	about 1.7				30 cm ³ (mL) DCM:EtAc:MeOH (2:2:1)	-	12		/
Membrane material :	Polyethersulfone (0.45µm) SUPOR 450 filters PALL Life Sciences	Polyoxymethylene	Polyethersulphon e	Polyethersulphon e	Polyethersulphon e ; 0.1 µm	Polyethersulfone 0.1 µm	Polyethersulphon e ; SUPOR 100 Membrane Disc Filters (0.1 µm, 90 mm diameter)	Silicon rubber	Glassfibre Filter ±0.5 mm	Polyethersulphon e ; SUPOR 100 Membrane Disc Filters (0.1 µm, 90 mm diameter)

Table A VI- 1 (continued) Participant passive samplers of steroids: method information

LAB No.	19	20	23	26	33	36	39	43a	43	49	
Active sampler surface area (or membrane area) (cm²):	16	about 620	47.5 cm ²	45,8 cm ²	45.8	1734 cm ² (d=47 mm)	42.47	400	35	45.8	
Performance Reference Compounds (PRC)											
Commercial passive samplers with PRC:		N/A	No	NO	NO		NO		No PRCs	No	
or home made PS spiked with PRC:		d4 17B Estradiol			NO	Home made PS spiked with PRC (E2-d3, EQ-d4 and NP-d4)	NO	Home spiked, D10-biphenyl, PCBs: CB001, CB002, CB003, CB010, CB014, CB021, CB030, CB050, CB055, CB078, CB104, CB145, CB204	No PRCs	No	
Transport and storage											
Date of shipment to the study organiser:	approx 7 May 2011	June 2 2011	07/06/2011	15/04/2011	31/05/2011			13.05.2011	~10/05/2011	~10/05/2011	16/05/2011
Date of receipt by the study organiser:	14 May 2011 (Handover at conference)	June 8 2011	07/06/2011		02/06/2011			16.05.2011	~13/05/2011	~13/05/2011	19/05/2011
Storage conditions before deployment (°C):	Fridge 4 degrees C	4	-20		4			room temperature	minus 20°C	4°C immersed in water	Storage in fridge at 4°C
Storage conditions after sampler recovery (°C):	Fridge 4 degrees C	-20	-20		-20			-20	minus 20°C	minus 20°C	Storage in freezer at -20°C
Date of return shipment from the organiser to the participant laboratory:	21/07/2011	September 5 2011	20/07/2011		13/07/2011			18.07.2011	~31/8/2011	~31/8/2011	07/07/2011
Date of receipt by the participant laboratory:	26/07/2011	September 11 2011	20/07/2011		15/07/2011			19.07.2011	~2/9/2011	~2/9/2011	08/07/2011
REMARKS:		Samples stored at 4C upon receipt				none		-	Dates are approximate	Dates are approximate	/

LAB No.	19	20	23	26	33	36	39	43a	43	49
Date and hour of the deployment:	20/6/2011; 15:45	20/06/2011	20.6.2011, 14:30	20/06/2012 13,25	20/06/2011	20/06/11- 04/07/11	20.06.2011 13:50	20/06/2011	20/06/2011	20/06/2011 at 13:00
Air Temp on deployment (°C)	20	22	20	20	20		20			20
Duration of the deployment (exposure to air for field control)	14:20-15:45	25 minutes	0.020833333	15 min	30 minutes		30 min			30 min
Air Temp on recovery (°C)	21	21	18	18	22		18			18
Duration of the recovery (exposure to air for field control)	15:17 - 16:15	10 minutes	0.020833333	20 min	20 minutes		20 min			30 min
Date and hour of the recovery:	4/7/2011; 15:17	04/07/2011	4.7.2011, 14:40	04/07/2011	04/07/2011		04.07.2011 14:30	04/07/2011	04/07/2011	04/07/2011 at 13:30
Comment on fouling:		None visible	all POCISes were cracked on the arrival				Exposed membranes were spotted and darker than unexposed ones			Not much
Field deployment device used:	Teflon chemcatcher case	Copper case	big cage	Canister	small cage	canister	Standard POCIS deployment cage for 3 samplers	Wet mounted on open cage	Wet mounted on open cage	standard POCIS deployment cage for 6 samplers

Annex VII. Provided passive samplers of BDEs: method information

Table A VII- 1 Provided passive samplers of BDEs: method information

LAB No.	19	20	21	23	25	26	29	30	36b	37	38	43	44	50
Passive sampler (PS)														
PS type :							Silicone rubber sheets; (1 sampler = 3 x sheet 90x55 mm)							
Receiving phase material:							AlteSiITM translucent material, 0.5±0.05 mm thickness							
Receiving phase mass (g):							8.91 g (Altesil density = 1.2 g/cm ³)							
Receiving phase volume (cm³)							7.43 cm ³							
Sampler surface area (or membrane area) (cm²):							297 cm ²							
Performance and Reference Compound (PRC) *														
Passive samplers with PRC :							D10-biphenyl, PCBs: CB001, CB002, CB003, CB010, CB014, CB021, CB030, CB050, CB055, CB078, CB104, CB145, CB204							
Transport and storage														
Date of shipment to the study organiser:			05/05/2011		Provided by the organiser. We didn't ship them.	15/04/2011				23/06/2011				
Date of receipt by the study organiser ** :			16/05/2011		See above.									
Storage conditions before deployment (°C)**:	Fridge 4 degrees C		- 20 degrees celsius		~5									
Storage conditions	Fridge 4 °C		- 20°C		~5			4°C		-18	4°C		freezer	

Table A VII- 1(continued) Provided passive samplers of BDEs: method information

LAB No.	19	20	21	23	25	26	29	30	36b	37	38	43	44	50
Date of return shipment from the organiser to the participant laboratory **: **	02/09/2011		13/07/2011		13/09/2011			31/08/2011		31.8.2011	September 6th, 2011	~31/8/2011		
Date of receipt by the participant laboratory **: **	07/09/2011		15/07/2011	29/09/2011	20/09/2011			01/09/2011	06/09/2011	2.9.2011	September 7th, 2011	~2/9/2011	10/25/11	september, 20th
REMARKS:												Dates are approximate		Standard solution didn't contain the 1 ml solution (it was empty). We put 1 ml hexaan in the empty vial for the solution of the standard.
Sampler deployment and recovery														
Date and hour of the deployment **: **	11/07/2011		7-July-2011 between 10:40 and 11:38	11.7.2011, 11:00	11/07/2011			11/07/2011			July 11st, 2011 at 10:48	11/07/2011	11/07/2011	
Air Temp on deployment (°C)**	22		22	22	22			22°C			22°C		19°C	

Table A VII- 1 (continued) Provided passive samplers of BDEs: method information

LAB No.	19	20	21	23	25	26	29	30	36b	37	38	43	44	50
Duration of the deployment (exposure to air for field control)**	between 16 and 25 mins		+/- 15 minutes	0.0104166 67	20mins			20 min			18 min	0	17min	
Air Temp on recovery (°C)**	between 26 and 29 degrees C		29	30	29			26°C			24°C	0	24°C	
Duration of the recovery (exposure to air for field control)**	between 25 and 65 mins		+/- 40 minutes	1h	40mins			1 hour			65 min	0	65min	
Date and hour of the recovery ** :	22/08/2011		22-August-2011 between 9:55 and 12.50	22.8.2011, 13:55	22/08/2011			22/08/2012			August 22nd, 2011 at 9:55	22/08/2011	8/22/11 11:10	
Comment on fouling**:			less fouling, cleaned with milli Q water and scourer											
Field deployment device used														
Type of deployment device (canister, cage...):				holder	Cage			Holder			Holder 1	Open cage		

Table A VII- 1(continued) Provided passive samplers of BDEs: method information

LAB No.	19	20	21	23	25	26	29	30	36b	37	38	43	44	50
Extraction technique:	2 x 200mL hexane; shaken at room temp for 2 x 24hrs. Extracts combined		Soxhlet extraction with hexane:acetone (3:1) 85 degrees 16 hours	Soxhlet	Hot Soxhlet extraction Acetonitrile /Methanol 2:1 mix	Solvent Dialysis	Same as for NIVA samplers	cold extraction with solvent	3 x 15 min with Cyclohexan :Acetone (90:10) in an ultrasonic bath	Soxhlet, Methanol	soxhlet Methanol	Soxhlet with acetonitril	liquid extraction, hexan	solvent extraction
Date of extraction :	26/10/2011		07/09/2011		08/11/2011	29/11/2012		17/10/2011	05/10/2011	16.1.2012	November 17-18, 2011	20/10/2011	16/12/2011	december, 6th
Date of instrumental analysis:	08/01/2012		13/09/2011		21/11/2011	12/01/2012		November - December	23/01/2012	19.1.2012	January, 2012	27/10/2011	20/12/2011	december, 8th
Cleanup method:	GPC followed by acid silica treatment		1 gram 40% sulfuric acid-silica, rinse with 4x 1ml hexane:dichloromethane (4:1), add extract, elute with total 3 ml hexane:dichloromethane (4:1)	silicagel, alumina and active carbon columns	C8 bonded silica (for the oligomers); 3% deactivated silica after solvent exchange to isohexane	No cleanup		no used	NaSO ₄ , 0.45 μm cellulose acetate membrane	H ₂ SO ₄ modified silica, column chromatography	Solvent transfer, copper	elution with hexane/diethyl ether over Florisil	SPE silicagel	
Instrumental method:	HR-GCMS		GC-MS	GC/MS/MS	GC-MS for the PBDEs, GC-ECD for the PCB PRCs	GC/MS/MS ion trap		GC-MS/MS	Agilent 6890N GC with 5973 MS and Gerstel TDU (MPS 2 autosampler)	GC-HRMS (PBDEs, isotope dilution), GC-MS/MS (PRCs)	GC/MS-SIM	GC-MS	GC-MS-NCI	GCMS-NCI

Table A VII- 1 Provided passive samplers of BDEs: method information

LAB No.	19	20	21	23	25	26	29	30	36b	37	38	43	44	50
Injection solvent:	hexane		isooctane	nonane	iso-hexane	Nonane		Hexane	cyclohexane (desorption of 1 µL from glass wool)	nonane	n-hexane	Hexane	hexan	hexane
Recovery and internal standards used:	IS for PBDEs: MBDE-MXE(Wellington), IS for PCBs: PCB 153		BDE58	C13 labelled IS (28,47,99,153,154); RS=1234T CDD, 123789HxCDD	Fluorinated BDE160 and C13 BDE 209	PCB 209 - 13C-PCB15		no used	Anthracene -D10	13C PBDEs (28, 47, 99, 100, 153, 154, 183, 209), Syringe std 13C (BDE 77, 138)	Acenaphtene D10, PCBs: CB 29, CB 112, CB 209.	95% of PCB209	none	
REMARKS:			PRC reported as peak area (no concentrations calculated)						glass liner for injection into GC was filled with SiO2 to block oligomers			0		We received standard solution PBDE; 3 cups with field blank BDE and 3 cups with spiked blank BDE. We didn't receive the 3 samples PS BDE, so we can not report the results of those samples.

Table A VII- 1 Provided passive samplers of BDEs: method information

LAB No.	19	20	21	23	25	26	29	30	36b	37	38	43	44	50
Method for estimation of water concentration from passive sampler:	$C_w = \frac{N_s}{(R_s \cdot t)}$		Kees Booij and Foppe Smedes: Environ. Sci. Technol., 2010, 44 (17), pp 6789-6794		Water concentrations estimated with PRC calibration and model based on Booij, K. et al. Environ. Sci. Technol. 44, 6789-6794.		No PRC data, Ratio = $\frac{m-pah(org)/m-pah(niva) \times t(niva)}{t(org)}$ is diff in R_s for PAHs with $\log K_{ow} > 6$	calculated with sampling rates calculated with PRCs release.	$C_{twa} = \frac{ms}{(K_{sw} \cdot V \cdot k_e \cdot t)}$; k_e obtained with logistic regression	$N = R_s \cdot C_{wt}$	Booij and Smedes, Environ. Sci. Technol. 2010, 44, 6789-6794.	Fitting PRC dissipation with model and a flow factor as adjustable parameter. Then this flow factor is applied to calculate the C_w	I used the method from Alvarez D.A., 2010: Guidelines for the use of the semipermeable membrane device (SPMD) and the polar organic chemical integrative sampler (POCIS) in environmental monitoring studies. U.S. Geological Survey, Techniques and Methods 1-	
Sampling rates used (literature value/own calibration):	average R_s (approx 15L/day) calculated from PCB030 $R_s = \frac{ke \cdot K_{sw} \cdot V_s}{ke \cdot K_{sw} \cdot V_s}$		own calculation		Sampling rates based on own calibration using PRCs (PCB1,2,3,10,14,21,30,50,55,78,104,145&204) based on: Rusina, T.P et al. Environ. Sci. Technol. 44, 362-367.		BDE- $R_s(niva) \times$ Ratio (ratio = 0.94 sd 0.12)	calculated with PRCs release in a lineal uptake zone	NO		calculated from PRC release with literature values distribution coefficients	From PRCs using Rusina Est 2010 and Booij and Smedes EST 2010	For water concentration estimation I used Excel sheet accessible from website http://www.cerc.usgs.gov/Branches.aspx?BranchId=8 (see publication above)	

Table A VII- 1 Provided passive samplers of BDEs: method information

LAB No.	19	20	21	23	25	26	29	30	36b	37	38	43	44	50
Sampler/ water partition (distribution) coefficients used:	log Ksw = 0.0128*MW +2.09 (from Booji & Smedes, ES&T, 2010)		Foppe Smedes, BDE Log Kws = log Kow		Partitionin coefficients based on: Smedes, F et al. Environ. Sci. Technol. 43, 7047- 7054		Ksw from extrapolate d from Ksw-Kow values from Smedes et al 2010	partition coefficients used in previous projects and works	Smedes et al. EST 43, 7047-7054, 2009		KPDMS/Wat er	Smedes et al EST 2009		

Table A VII- 1 Provided passive samplers of BDEs: method information

LAB No.	19	20	21	23	25	26	29	30	36b	37	38	43	44	50
Performance reference compounds applied (YES/NO):	yes		yes		YES	NO	No prcs	yes	YES	No	yes	Yes	Yes	
Were the calibration data adjusted to reflect exposure conditions (temperature, flow, pH...?)			no		No, only based upon the loss of the PRCs compared to the undeployed .	NO		no	NO			Flow corrected (not Temperature)	No	
REMARKS:	The sampling rate (approx 15L/d) was estimated from PCB 30, the most nonpolar PCB with a measurable ke. We found also some reproducible loss for the higher PCBs, such as PCB055, but less than 10%. Using the PCB055 data we estimate a sampling rate of approx		PRC reported as peak area (no concentrations calculated)						PRCs not quantified, retained fraction was obtained from peak areas, Altesil values valid for all following data sheets					

Annex VIII. Participant passive samplers of BDEs: method information

Table A VIII- 1 Participant passive samplers of BDEs: method information

LAB No.	19	20	21	23	26	29	30	36a	36b	36c	36d	36	38	43
PS type :	Polydimethylsiloxane (PDMS)	Polyethylene	silicone rubber sheets (3 sheets = 1 sampler, 9.5x5.5 cm)	standard SPMD (length 1 m)	SPMD	AlteSil Altec silicone 0.5 mm thick	CFIS	low-density polyethylene strips	membrane enclosed silicone collector (MESCO)	80 mm bare silicone rod (SR 80/15)	non-polar Chemcatcher (3rd generation)	Silicone rubber sheets; (1 sampler = 3 x sheet 90x55 mm)	MESCO	AlteSil translucent silicone rubber (6 sheets of 100cm ² each)
Home made or commercial PS :	Commercial	Home made	commercial	commercial	commercial	home made	Home made	homemade	homemade	homemade	homemade PS with commercial body		PDMS Stir Bar (Twister)	Home made
		-	Foppe Smedes, Deltares, The Netherlands				Home made		Silicone rod: Goodfellow, Bad Nauheim (D)		Chemcatcher body: University Portsmouth (UK)			
Supplier :	Purple Pig Australia	-	Foppe Smedes, Deltares, The Netherlands	Exposmeter AB	Exposmeter AB		LABAQUA	Polymersynthesewerk Rheinberg (D)	LDPE: Polymersynthesewerk Rheinberg (D)	Silicone rod: Goodfellow, Bad Nauheim (D)	Empore disk: VWR, Dresden (D); LDPE: University Portsmouth	Bundesamt für Seeschifffahrt und Hydrographie (BSH), Hamburg (D)	RIC - Lille, France	Altecweb.com
Receiving phase material:	Polydimethylsiloxane (PDMS)	Polyethylene	AlteSiITM translucent material	triolein	Triolein	Silicone/PDMS	Gerstel Twister 20x0.5 mm thickness	low-density polyethylene (100 µm * 1 m * 2.8 cm)	PVNQ-poly(dimethyl)siloxane (PDMS)	PVNQ-poly(dimethyl)siloxane (PDMS)	Varian Empore C18 extraction disk 47 mm & Oktanol	AlteSiITM translucent material, 0.5±0.05 mm thickness	PDMS	AlteSiITM translucent material, 0.5±0.05 mm thickness

Table A VIII- 1 (continued) Participant passive samplers of BDEs: method information

LAB No.	19	20	21	23	26	29	30	36a	36b	36c	36d	36	38	43
Receiving phase mass (g):	Average = 13.712	2	10.2			8.5	0.1213	1.75 g	~ 50 mg	~ 50 mg (15 mm piece used for analysis)	Oktanol: 0.3735; C18:	8.91 g (Altesil density = 1.2 g/cm3)	44 mg	20
Receiving phase volume (cm³)	92 cm x 2.5 cm x 0.05 cm = 11.5	2.2			1 mL	7.1	0.049	2.8 cm ³	47 µL	47 µL (15 mm piece used for analysis)	450 µL Oktanol; 144 µL C18	7.43 cm ³	47.10-3	16
Membrane material :	None	Polyethylene			LDPE		No membrane	none	50 µm low-density polyethylene tubing	-	40 µm LDPE membrane	-	Regenerated cellulose (Spectra/Por 6 cutoff 1000 Da)	Silicon rubber
Active sampler surface area (or membrane area) (cm²):	469.45	800	313		460	284	4.61	280 cm ²	Silicone rod: 1.005; LDPE over single silicone rod: 18	1.005	17.35	297 cm ²	5.4	600
Commercial passive samplers with PRC:		-	D10-biphenyl, PCBs: CB001, CB002, CB003, CB010, CB014, CB021, CB030, CB050, CB055, CB078, CB104, CB145, CB204	deuterated PAHs	13C-PCB1 - 13C-PCB8 - 13CPCB54 - 13CPCB-37	no	No						PCBs: CB 30, CB 78, CB 104, CB 145, CB 204.	

Table A VIII- 1 (continued) Participant passive samplers of BDEs: method information

LAB No.	19	20	21	23	26	29	30	36a	36b	36c	36d		36	38	43
Performance Reference Compounds (PRC)															
Home made PS spiked with PRC:		2-bromobiphenyl, 4-BB, 5-BB					YES	home made PS, electronic and analytical QC of the PS.	YES	YES	YES	YES			Home spiked, D10-biphenyl, PCBs: CB001, CB002, CB003, CB010, CB014, CB021, CB030, CB050, CB055, CB078, CB104, CB145, CB204
Date of shipment to the study organiser:	08/06/2011	02-Jun-11	05-May-11	07/06/2011	15/04/11				23/06/2011	23/06/2011	23/06/2011	23/06/2011	23/06/2011	July 1st, 2011	~10/05/2011
Date of receipt by organiser:	09/06/2011	08-Jun-11	16-May-11	07/06/2011										July 5th, 2011	~13/05/2011
Storage before deployment (°C):	Fridge 4 degrees C	4	- 20 degrees celsius	-20			-20	4 °C						4°C	minus 20°C
Storage conditions:	Fridge 4 degrees C	-20	- 20 degrees celsius	-20			-20	4 °C						4°C	minus 20°C
Date of return:	02/09/2011	05-Sep-11	13-Jul-11	29/09/2011				31/08/2011						September 6th, 2011	~31/8/2011
Date of return shipment from the organiser to the participant laboratory:	02/09/2011	05-Sep-11	13-Jul-11	29/09/2011				31/08/2011						September 6th, 2011	~31/8/2011

Table A VIII- 1 (continued) Participant passive samplers of BDEs: method information

LAB No.	19	20	21	23	26	29	30	36a	36b	36c	36d	36	38	43
Date of receipt by the participant laboratory:	07/09/2011	11-Sep-11	15-Jul-11	29/09/2011			01/09/2011	06/09/2011	06/09/2011	06/09/2011	06/09/2011	06/09/2011	September 7th, 2011	~2/9/2011
REMARKS:		Organizer PBDE samplers not received											The membrane material was completely damaged.	Dates are approximate
Sampler deployment and recovery														
Date and hour of the deployment:	11/7/2011; 13:40	11-Jul-11	11/07/2011 12:25	11.7.2011, 12:25	11/07/11 13:56		11/07/2011 11:23						July 11st, 2011 at 14:25	11/07/2011
Air Temp on deployment (°C)	24	24	24	24	24		22						24°C	
Duration of the deployment (exposure to air for field control)	16 mins	2.25 hours	25 minutes	00:15	26 min		01:15						20 min	
Air Temp on recovery (°C)	31	31	30	30	30		31						31°C	
Duration of the recovery (exposure to air for field control)	37 mins	7 minutes	40 minutes	00:20	15		00:12						11 min	
Date and hour of the recovery:	22/8/2011; 14:35	22-Aug-11	22/08/2011 13:30	22.8.2011, 13:55	22/08/11 14:30		22/08/2011 15:48						August 22nd, 2011 at 15:37	22/08/2011

Table A VIII- 1 (continued) Participant passive samplers of BDEs: method information

LAB No.	19	20	21	23	26	29	30	36a	36b	36c	36d	36	38	43
Comment on fouling:		-	less fouling, cleaned with milli Q water and scourer			less sticky fouling than on the organisers sampler								
Field deployment device used:	Stainless steel marine cage	Wire - no cage	standard SPMD deployment cage	big cage	canister	canister/spider holder	CFIS device, cage A4		10 x 60 cm stainless steel mesh wrapped to 10 x 30 cm	10 x 60 cm stainless steel mesh wrapped to 10 x 30 cm	Small SPMD deployment cage		conical fishing basket (mesh wire cage)	Open cage
Extraction technique :	2 x 200mL hexane; shaken at room temp for 2 x 24hrs. Extracts combined	Cold Benchtop Extraction	Soxhlet extraction with hexane:acetone (3:1) 85 degrees 16 hours	dialysis	Solvent dialysis	Pentane dialysis	thermal desorption	3 x 15 min with Cyclohexan:Acetone (90:10) in an ultrasonic bath	direct analysis with thermal desorption unit (TDU)	direct analysis with thermal desorption unit (TDU)	1 x 15 min Acetone, 2 x 15 min ethylacetate:isooctane (1:1) in ultrasonic bath	3 x 15 min with Cyclohexan:Acetone (90:10) in an ultrasonic bath	Sonication in 1,6 mL of solvents mixture (nC6:CH2Cl2, 1:1)	Soxhlet with acetonitril
Date of extraction:	26/08/2011	09-Oct-11	07-Sep-11		29/11/11	Dec-11	November - December	05/10/2011	-	-	06/10/2011	05/10/2011	January 3, 2011	20/10/2011
Date of instrumental analysis:	08/01/2012	05-Dec-11	13-Sep-11		12/01/12	Jan-12	November - December	19/01/2012	04/01/2012	04/01/2012	13/01/2012	19/01/2012	January, 2012	27/10/2011
Cleanup method:	GPC followed by acid silica treatment	-	1 gram 40% sulfuric acid-silica, rinse with 4x 1ml hexane:dichloromethane (4:1), add extract, elute with total 3 ml hexane:dichloromethane (4:1)	silicagel, alumina and active carbon columns	SFE with Silca deactivated 6%H2O	H2SO4 and GPC for d-PAH PRCs	none	NaSO4, 0.45 µm cellulose acetate membrane	none	none	NaSO4, 0.45 µm cellulose acetate membrane	NaSO4, 0.45 µm cellulose acetate membrane	None	elution with hexane/diethyl ether over Florisil

Table A VIII- 1 (continued) Participant passive samplers of BDEs: method information

LAB No.	19	20	21	23	26	29	30	36a	36b	36c	36d	36	38	43
Instrumental method:	HR-GCMS	GCMSMS	GC-MS	GC/MS/MS	GC/MS/MS ion trap	GC/MS	TD-GC-MS	Agilent 6890N GC with 5973 MS and Gerstel TDU (MPS 2 autosampler)	Agilent 6890N GC with 5973 MS and Gerstel TDU (MPS 2 autosampler)	Agilent 6890N GC with 5973 MS and Gerstel TDU (MPS 2 autosampler)	Agilent 7890C GC with Agilent 5975C MS; 15 m x 0.25 mm x 0.25 µm HP 5 ultra inert	Agilent 6890N GC with 5973 MS and Gerstel TDU (MPS 2 autosampler)	GC/MS - SIM	GC-MS
Injection solvent:	hexane	Ethyl Acetate	isooctane	nonane	Nonane		solventless method (TD)	200 µL cyclohexane (desorption of 1 µL from glass wool)	none	none	500 µL n-Octanol	200 µL cyclohexane (desorption of 1 µL from glass wool)	n-hexane	Hexane
Recovery and internal standards used:	IS: MBDE-MXE (Wellington Laboratories)	p-terphenyl, 13C12 PBDE28, 13C12 PBDE47, 13C12 PBDE99, 13C12 PBDE153, 13C12 PBDE183, 13C12 PBDE209	BDE58	C13 labelled IS (28,47,99,153,154); RS=1234TCDD, 123789HxCDD	PCB 209 - 13C-PCB15	YES	Chrysened12, Fluorend10	Anthracene-D10	recovery obtained with blank silicone rods spiked with PBDEs	recovery obtained with blank silicone rods spiked with PBDEs	Anthracene-D10	Anthracene-D10	PCBs: CB 29, CB 112, CB 209.	95% of PCB209
REMARKS:	For the Entox samplers: PDMS were deployed in pairs and combined into one sample. The weight of PDMS and surface area is the sum of the two strips together	-	PRC reported as peak area (no concentrations calculated)					glass liner for injection into GC was filled with SiO2 to block oligomers	1 MESCO = 3 silicone rods			glass liner for injection into GC was filled with SiO2 to block oligomers		

Table A VIII- 1 (continued) Participant passive samplers of BDEs: method information

LAB No.	19	20	21	23	26	29	30	36a	36b	36c	36d	36	38	43
Data evaluation aspects														
Method for estimation of water concentration from passive sampler:		Lohmann 2011	Kees Booij and Foppe Smedes : Environ. Sci. Technol., 2010, 44 (17), pp 6789-6794	please give a short description and relevant references	semiempirical methods (Huckins et al 2006)	Rusina et al method, Ksw values from Smedes et al 2009	calculation with calibrated sampling rate	$C_{twa} = ms / (K_{sw} * V * k_e * t)$; k_e obtained with logistic regression	$C_{twa} = ms / (K_{sw} * V * k_e * t)$; k_e obtained with logistic regression	$C_{twa} = ms / (K_{sw} * V * k_e * t)$; k_e obtained with logistic regression	$C_{twa} = ms / (K_{sw} * V * k_e * t)$; k_e obtained with logistic regression	$C_{twa} = ms / (K_{sw} * V * k_e * t)$; k_e obtained with logistic regression	Booij and Smedes, Environ. Sci. Technol. 2010, 44, 6789-6794.	Fitting PRC dissipation with model and a flowfactor as adjustable parameter. Then this flow factor is applied to calculate the C_w
Sampling rates used (literature value/own calibration):			own calculation	literature: Huckins, Petty, Booij	literature value	Rs from NLS method (Booij et al)	own calibration	NO					calculated from PRC release with literature values distribution coefficients	From PRCs using Rusina Est 2010 and Booij and Smedes EST 2010

Table A VIII- 1 (continued) Participant passive samplers of BDEs: method information

LAB No.	19	20	21	23	26	29	30	36a	36b	36c	36d	36	38	43
Performance reference compounds applied (YES/NO):		Yes	yes	YES D 10 phenantrene	Yes	YES, deuterated PAHs	NO	YES	YES	YES	YES	YES	yes	Yes
Were the calibration data adjusted to reflect exposure conditions (temperature, flow, pH...?)		Temperature corrected following Lohmann 2011 (using dH = 25 kJ/mol; Average water temperature = 18.71 degrees C)	no	no	No		YES	NO						Flow corrected (not Temperature)
REMARKS:		-	PRC reported as peak area (no concentrations calculated)					PRCs not quantified, retained fraction was obtained from peak areas	PRCs not quantified, ke-values were obtained from peak areas, Standard solution valid for all following data sheets	PRCs not quantified, ke-values were obtained from peak areas	PRCs not quantified, ke-values were obtained from peak areas	PRCs not quantified, retained fraction was obtained from peak areas		

Annex IX. Provided passive samplers of bisphenol A: method information

Table A IX- 1 Provided passive samplers of bisphenol A: method information

LAB No.	19	20	23	26	39	19	20	23	26	39				
PS type :	POCIS, pharmaceutical version													
Receiving phase material:	sorbent Oasis HLB, 60 µm													
Receiving phase mass (g):	0.200 g; mass of sorbent separated from samplers after exposure is given on each SPE cartridge													
Membrane material :	Polyethersulphone; SUPOR 100 Membrane Disc Filters (0.1 µm, 90 mm diameter)													
Active sampler surface area (or membrane area) (cm ²):	45.8 cm ²													
Performance and Reference Compound (PRC) *														
Passive samplers with PRC :	NO													

Table A IX- 2 Provided passive samplers of bisphenol A: method information

LAB No.	19	20	23	26	39
Transport and storage					
Date of shipment to the study organiser:		June 2 2011		15/04/2011	-
Date of receipt by the study organiser ** :		June 8 2011			-
Storage conditions before deployment (°C)**:	Fridge 4 degrees C	4			4
Storage conditions after sampler recovery (°C)**:	Fridge 4 degrees C	-20			-20

LAB No.	19	20	23	26	39
Date of return shipment from the organiser to the participant laboratory:**	21/07/2011	September 5 2011			18/07/2011
Date of receipt by the participant laboratory ** :	26/07/2011	September 11 2011	20/07/2011		19/07/2011
REMARKS:		Samples stored at 4C upon receipt			The extract from steroid samplers was used because there was not enough samplers to send triplicates for both compound classes

Table A IX- 3 Provided passive samplers of bisphenol A: method information

LAB No.	19	20	23	26	39
Sampler deployment and recovery					
Date and hour of the deployment ** :	20/6/2011; 10:34, 11:03	6/20/2011 approx. 10:30	20.6.2011, 12:00	20/06/2011 10.34 (sampl 4) and 11.03 (sampl 9)	20.06.2011 11:03
Air Temp on deployment (°C)**	17	17	20	17	17
Duration of the deployment (exposure to air for field control)**	39 mins, 46 mins	approx. 30 minutes	0.020833333	25 min (sampl 4) and 46 min (sampl 9)	30 min
Air Temp on recovery (°C)**	17,18	18	19	18	17
Duration of the recovery (exposure to air for field control)**	40 mins, 30 mins	approx. 30 minutes	0.038194444	20 min (sampl 4) and 30 min (sampl 9)	30 min
Date and hour of the recovery ** :	4/7/2011; 10:15, 11:00am	7/4/2011 approx. 11:00	4.7.2011, 12:00	4/7/2011 9,40 (sampl 4) and 11,00 (sampl 9)	04.07.2011 11:00
Comment on fouling**:		None visible			Exposed membranes were spotted and darker than unexposed ones
Field deployment device used					

LAB No.	19	20	23	26	39
Type of deployment device (canister, cage...):	standard POCIS deployment cage for 6 samplers	standard POCIS deployment cage for 6 samplers	standard POCIS deployment cage for 6 samplers	standard POCIS deployment cage for 6 samplers	standard POCIS deployment cage for 6 samplers
Analytical aspects					
Extraction technique:	Elution of cartridges under gentle vacuum with 3 mL methanol, 2 mL acetone/ hexane 50:50	Cold benchtop extraction with Dichloromethane	liquid extraction	Solvent elution	5 mL MeOH - 5 mL MeOH/DCM (50/50) - 5 mL DCM
Date of extraction:	01/09/2011	November 22 2011		07/12/2011	23.08.2011
Date of instrumental analysis:	05/09/2011	December 6 2011		03/01/2012	30.08.2011
Cleanup method:	Liquid-liquid extraction with water to remove derivatising agent	None	no	No cleanup	No cleanup
Instrumental method:	GCMS	GC/MS	GC/MS/MS	GC/MS/SIS ion trap	Derivatization - GC/MS
Injection solvent:	50% hexane/ acetone	Dichloromethane and Methanol	heptane	MSTFA	Acetone
Recovery and internal standards used:	Derivatized using silylating agent (BFTSA + TMCS). Analysis with external calibration	¹³ C ¹² Bisphenol A, Tribromobiphenyl	IS = C ¹³ labelled BPA, RS not used	Bisphenol - d ¹⁶	BPA d ⁴
REMARKS:					The extract from steroid samplers was used because there was not enough samplers to send triplicates for both compound classes

Table A IX- 4 Provided passive samplers of bisphenol A: method information

LAB No.	19	20	23	26	39
Data evaluation aspects					
Method for estimation of water concentration from passive sampler:	$C_w = N_s / (R_s * t)$	Li, Helm, and Metcalfe ETC 2010	please give a short description and relevant references	Arditsoglou et al Environmental Pollution 156 (2008)	Calculation with following formula : $C_s \times 0,2 = C_w R_s t$ (Vrana et al., 2005)
Sampling rates used (literature value/own calibration):	Literature: (Li et al, 2010). BPA = 0.835	$R_s = 0.835$		Literature value	Own calibration
Sampler/water partition coefficients used:	No			Literature value	-
Performance reference compounds applied (YES/NO):	No			NO	NO
Were the calibration data adjusted to reflect exposure conditions (temperature, flow, pH...?)	No	No		NO	NO
REMARKS:		$C_w = ng(\text{total}) / (R_s * \text{total days})$			

Annex X. Participant passive samplers of bisphenol A: method information

Table A X- 1 Participant passive samplers of bisphenol A: method information

LAB No.	19	20	23	26	39	45
PS type :	Empore Disk	Polyoxymethylene	standard SPMD (length 1m)	POCIS Pharmaceutical Version	POCIS, pharmaceutical version	POCIS, pharmaceutical version
Home made or commercial PS :	Commercial	Home made	commercial	Commercial PS	Home made	
Supplier :	Phenomenex	N/A	Exposmeter AB	Exposmeter AB	-	
Receiving phase material:	SDB-RPS Reverse Phase Sulfonated	Polyoxymethylene	triolein	Oasis HLB 60 µ	Oasis HLB sorbent, 60 µm	sorbent Oasis HLB, 60 µm
Receiving phase mass (g):	0.398	about 2		0.2	0.200	0.200 g; mass of sorbent separated from samplers after exposure is given on each SPE cartridge
Receiving phase volume (cm³)	1.73494	about 1.7			-	
Membrane material :	Polyethersulfone (0.45µm) SUPOR 450 filters PALL Life Sciences	Polyoxymethylene		Polyethersulphone	Polyethersulphone; SUPOR 100 Membrane Disc Filters (0.1 µm, 90 mm diameter)	Polyethersulphone; SUPOR 100 Membrane Disc Filters (0.1 µm, 90 mm diameter)
Active sampler surface area (or membrane area) (cm²):	16	about 620		45.8	42.47	45.8 cm ²
Performance Reference Compounds (PRC)						
Commercial passive samplers with PRC:		N/A	No	NO	NO	NO
or home made PS spiked with PRC:		d6 Bisphenol A		NO	NO	
Transport and storage						
Date of shipment to the study organiser:	approx 7 May 2011	June 2 2011	07/06/2011	15/04/2011	13.05.2011	

Table A X- 1 (continued) Participant passive samplers of bisphenol A: method information

LAB No.	19	20	23	26	39	45
Date of receipt by the study organiser:	14 May 2011 (Handover at conference)	June 8 2011	07/06/2011		16.05.2011	
Storage conditions before deployment (°C):	4 degrees C	4	-20		room temperature	
Storage conditions after sampler recovery (°C):	4 degrees C	-20	-20		-20	
Date of return shipment from the organiser to the participant laboratory:	21/07/2011	September 5 2011	20/07/2011		18.07.2011	
Date of receipt by the participant laboratory:	26/07/2011	September 11 2011	20/07/2011		19.07.2011	
REMARKS:		Samples stored at 4C upon receipt			-	
Date and hour of the deployment:	20/6/2011; 15:45	20/06/2011	20.6.2011, 14:30	20/06/2011 13,25	20.06.2011 13:50	Sampler 21: 20.06.2011 09:55:00 Sampler 38: 20.06.2011 10:34:00 Sampler 86: 20.06.2011 11:44:00
Air Temp on deployment (°C)	20	22	20	20	20	Sampler 21: 15 °C Sampler 38: 17 °C Sampler 86: 17 °C
Duration of the deployment (exposure to air for field control)	1 hr 25 mins	25 minutes	0.020833333	15 min	30 min	Sampler 21: 13.990 Sampler 38: 13.987 Sampler 86: 13.990
Air Temp on recovery (°C)	22	21	18	18	18	Sampler 21: 17 °C Sampler 38: 17 °C Sampler 86: 18 °C
Duration of the recovery (exposure to air for field control)	58 mins	approx. 45 minutes	00:30:00	20 min	20 min	

Table A X- 1 (continued) Participant passive samplers of bisphenol A: method information

LAB No.	19	20	23	26	39	45
Date and hour of the recovery:	4/7/2077; 15:17	04/07/2011	4.7.2011, 14:40	04/07/2011	04.07.2011 14:30	Sampler 21: 04.07.2011 09:40:00 Sampler 38: 04.07.2011 10:15:00 Sampler 86: 04.07.2011 11:30:00
Comment on fouling:		None visible			Exposed membranes were spotted and darker than unexposed ones	-
Field deployment device used:	Teflon chemcatcher case	Copper case	big cage	canister	Standard POCIS deployment cage for 3 samplers	standard POCIS deployment cage for 6 samplers
Extraction technique:	5 mL Acetone followed by 5 mL methanol; sonication; at room temperature	Cold benchtop with Dichloromethane	dialysis	Solvent elution	5 mL MeOH - 5 mL MeOH/DCM (50/50) - 5 mL DCM	MeOH, 40 ml
Date of extraction:	25/08/2011	November 6 2011		07/12/2011	23.08.2011	02/08/2011
Date of instrumental analysis:	16/09/2011	December 6 2011		03/01/2012	30.08.2011	04/08/2011
Cleanup method:	Liquid-liquid extraction with water to remove derivatising agent	None	dialysis	No cleanup	No cleanup	no
Instrumental method:	GCMS	CG/MS	GC/MS/MS	GC/MS/SIS ion trap	Derivatization - GC/MS	LC-MS/MS
Injection solvent:	50% hexane/ acetone	Dichloromethane and Methanol	heptane	MSTFA	Acetone	EtOH
Recovery and internal standards used:	Derivatized using silylating agent (BFTSA + TMCS). Analysis with external calibration	13C12 Bisphenol A, Tribromobiphenyl	IS = C13 labelled BPA, RS not used	Bisphenol-d16	BPA d4	D16-Bisphenol A
Method for estimation of water concentration from passive sampler:		Experimental value from Endo et al., ES&T 2011		Arditsoglou et al. Environmental Pollution 156 (2008) 316-324	Calculation with following formula : $C_s \times 0,2 = C_w \times R_s \times t$ (Vrana et al., 2005)	Averaged sampling rate from 2 publications was used: 1. Z. Zhang et al., Anal Chim Acta 607, 37-44 2. A. Arditoglou et al, Env Pollution 156, 316-324

Table A X- 1 (continued) Participant passive samplers of bisphenol A: method information

LAB No.	19	20	23	26	39	45
Data evaluation aspects						
Sampling rates used (literature value/own calibration):				literature value	Own calibration	0.14 L/day. Literature, averaged
Sampler/water partition (distribution) coefficients used:		K _{pom/w} =2.63		literature value	-	
Performance reference compounds applied (YES/NO):		YES		NO	NO	no
Were the calibration data adjusted to reflect exposure conditions (temperature, flow, pH...?)		Yes, to reflect a pH of 7.66		NO	NO	no
REMARKS:		Adjusted for % equilibrium reached based on PRC			-	

Annex XI. Provided passive samplers of triclosan: method information

Table A XI- 1 Provided passive samplers of triclosan: method information

LAB No.	19	20	23											
PS type :	POCIS, pharmaceutical version													
Receiving phase material:	sorbent Oasis HLB, 60 µm													
Receiving phase mass (g):	0.200 g; mass of sorbent separated from samplers after exposure is given on each SPE cartridge													
Membrane material :	Polyethersulphone; SUPOR 100 Membrane Disc Filters (0.1 µm, 90 mm diameter)													
Active sampler surface area (or membrane area) (cm²):	45.8 cm ²													
Performance and Reference Compound (PRC) *														
Passive samplers with PRC :	NO													

Table A XI- 2 Provided passive samplers of triclosan: method information

LAB No.	19	20	23
Transport and storage			
Date of shipment to the study organiser:		June 2 2011	
Date of receipt by the study organiser ** :		June 8 2011	
Storage conditions before deployment (°C)**:	Fridge 4 degrees C	4	
Storage conditions after sampler recovery (°C)**:	Fridge 4 degrees C	-20	
Date of return shipment from the organiser to the participant laboratory:**	21/07/2011	September 5 2011	
Date of receipt by the participant laboratory ** :	26/07/2011	September 11 2011	20/07/2011
REMARKS:		Samples stored at 4C upon receipt	

Table A XI- 2 (continued) Provided passive samplers of triclosan: method information

LAB No.	19	20	23
Sampler deployment and recovery			
Date and hour of the deployment ** :	20/6/2011; 11:03	6/20/2011 approx. 10:30	20.6.2011, 12:00
Air Temp on deployment (°C)**	17	17	20
Duration of the deployment (exposure to air for field control)**	45mins	approx. 30 minutes	0.020833333
Air Temp on recovery (°C)**	18	18	19
Duration of the recovery (exposure to air for field control)**	30 mins	approx. 30 minutes	0.038194444
Date and hour of the recovery ** :	4/7/2011; 11:00am	7/4/2011 approx. 11:00	4.7.2011, 12:00
Comment on fouling**:		None visible	
Field deployment device used			
Type of deployment device (canister, cage...):	standard POCIS deployment cage for 6 samplers	standard POCIS deployment cage for 6 samplers	standard POCIS deployment cage for 6 samplers

Table A XI- 2 (continued) Provided passive samplers of triclosan: method information

LAB No.	19	20	23
Analytical aspects			
Extraction technique:	Elution of cartridges under gentle vacuum with 3 mL methanol, 2 mL acetone/ hexane 50:50	Cold benchtop extraction with Dichloromethane	liquid extraction
Date of extraction:	40787	November 22 2011	
Date of instrumental analysis:	40791	December 6 2011	
Cleanup method:	No clean up	None	no, derivatization - acetylation
Instrumental method:	LCMS	GC/MS	GC/MS/MS
Injection solvent:	50% methanol/ water	Dichloromethane	heptane
Recovery and internal standards used:	none	¹³ C ¹² Triclosan, d ¹⁴ -para Terphenyl	IS = C ¹³ labelled triclosan, RS not used
REMARKS:			

Table A XI- 2 (continued) Provided passive samplers of triclosan: method information

LAB No.	19	20	23
Data evaluation aspects			
Method for estimation of water concentration from passive sampler:	$C_w = N_s / (R_s * t)$	Li, Helm, and Metcalfe ETC 2010	please give a short description and relevant references
Sampling rates used (literature value/own calibration):	Literature (Li et al, 2010). Triclosan=1.929	$R_s = 2.150$	
Sampler/water partition (distribution) coefficients used:	No		
Performance reference compounds applied (YES/NO):	No		
Were the calibration data adjusted to reflect exposure conditions (temperature, flow, pH...?)	No	No	
REMARKS:		$C_w = n_g(\text{total}) / (R_s * \text{total days})$	

Annex XII. Participant passive samplers of triclosan: method information

Table A XII- 1 Participant passive samplers of triclosan: method information

LAB No.	19	20	23
PS type :			
Home made or commercial PS :	Empore Disk	Polyethylene	standard SPMD (length 1m)
	Commercial	Home made	commercial
Supplier :	Phenomenex	N/A	Exposmeter AB
Receiving phase material:	SDB-RPS Reverse Phase Sulfonated	Polyethylene	triolein
Receiving phase mass (g):	0.398	about 1.7	
Receiving phase volume (cm ³)	1.73494	about 2	
Membrane material :	Polyethersulfone (0.45um) SUPOR 450 filters PALL Life Sciences	Polyethylene	
Active sampler surface area (or membrane area) (cm ²):	16	about 700	
Performance Reference Compounds (PRC)			
Commercial passive samplers with PRC:		N/A	D10 Phenantrene
or home made PS spiked with PRC:		d6 Bisphenol A	
Transport and storage			
Date of shipment to the study organiser:	approx 7 May 2011	June 2 2011	07/06/2011
Date of receipt by the study organiser:	14 May 2011 (Handover at conference)	June 8 2011	07/06/2011
Storage conditions before deployment (°C):	Fridge 4 degrees C	4	-20
Storage conditions after sampler recovery (°C):	Fridge 4 degrees C	-20	-20
Date of return shipment from the organiser to the participant laboratory:	21/07/2011	September 5 2011	20/07/2011
Date of receipt by the participant laboratory:	26/07/2011	September 11 2011	20/07/2011

LAB No.	19	20	23
REMARKS:		Samples stored at 4C upon receipt	
Sampler deployment and recovery			
Date and hour of the deployment:	20/6/2011; 15:45	40714.70486	20.6.2011, 14:30
Air Temp on deployment (°C)	20	22	20
Duration of the deployment (exposure to air for field control)	1 hr 25 mins	25 minutes	00:30:00
Air Temp on recovery (°C)	22	21	18
Duration of the recovery (exposure to air for field control)	58 mins	10 minutes	00:30:00
Date and hour of the recovery:	4/7/2011; 15:17	04/07/2011	4.7.2011, 14:40
Comment on fouling:		None visible	

Table A XI- 1 Participant passive samplers of triclosan: method information

LAB No.	19	20	23
Field deployment device used:	Teflon Chemcatcher case	Wire, No cage	standard big cage for POCISes and SPMDs
Extraction technique:	5 mL Acetone followed by 5 mL methanol; sonication; at room temperature	Cold benchtop extraction with Ethyl Acetate	dialysis
Date of extraction:	01/09/2011	November 22 2011	
Date of instrumental analysis:	05/09/2011	December 6 2011	
Cleanup method:	no clean up	None	no, derivatization - acetylation
Instrumental method:	LCMS	CG/MS	GC/MS/MS
Injection solvent:	50% Methanol/ water	Dichloromethane and Methanol	heptane
Recovery and internal standards used:	None	13C12 Bisphenol A, 13C12 Triclosan	IS = C13 labelled triclosan, RS not used
REMARKS:			

Table A XI- 2 Participant passive samplers of triclosan: method information

LAB No.	19	20	23
Data evaluation aspects			
Method for estimation of water concentration from passive sampler:	No sampling rates available for triclosan in Empore Disks	Equation 5, as well as initial partitioning from Sacks and Lohmann, ES&T 2011	please give a short description and relevant references
Sampling rates used (literature value/own calibration):			literature: Huckins, Petty, Booij
Sampler/water partition (distribution) coefficients used:		K _{pe/w} = 3.14	calculated from K _{ow} and Le Bas V (Mackay et al.)
Performance reference compounds applied (YES/NO):		YES	YES D10 phenantrene
Were the calibration data adjusted to reflect exposure conditions (temperature, flow, pH...?)		Yes, to reflect a pH of 7.66	no
REMARKS:		Adjusted for % equilibrium reached based on d6 Bisphenol A PRC	

Annex XIII. Provided passive samplers of fluorinated surfactants: method information

Table XIII- 1 Provided passive samplers of fluorinated surfactants: method information

LAB No.	19	21	23	29	37	39	43	44	52					
PS type :	POCIS, pharmaceutical version													
Receiving phase material:	sorbent Oasis HLB, 60 µm													
Receiving phase mass (g):	0.200 g; mass of sorbent separated from samplers after exposure is given on each SPE cartridge													
Membrane material :	Polyethersulphone; SUPOR 100 Membrane Disc Filters (0.1 µm, 90 mm diameter)													
Active sampler surface area (or membrane area) (cm²):	45.8 cm ²													
Performance and Reference Compound (PRC) *														
Passive samplers with PRC :	NO													

Table XIII- 2 Provided passive samplers of fluorinated surfactants: method information

LAB No.	19	21	23	29	37	39	43	44	52
Transport and storage									
Storage conditions before deployment (°C)**:	4		-20			4			4°C
Storage conditions after sampler recovery (°C)**:		- 20 degrees celsius	-20			-20		freezer	-20°C
Date of return shipment from the organiser to the participant laboratory:*		13/07/2011	20/07/2011			18.07.2011	~31/8/2011		18.7.2011 via TNT; shipment GD 31269940 WW
Date of receipt by the participant laboratory ** :	13/07/2011	15/07/2011	20/07/2011			19.07.2011	~2/9/2011	10/25/11	19.7.2011
REMARKS:							Dates are approximate		

Table XIII- 2 (continued) Provided passive samplers of fluorinated surfactants: method information

LAB No.	19	21	23	29	37	39	43	44	52
Date and hour of the deployment** :	20/06/2011	20-June-2011 between 9:55 and 12:00	20.6.2011, 12:00			20.06.2011 11:03	20/06/2011	(15) 6/20/11, 9:55 (52) 6/20/11,10:17 (101) 6/20/11, 12:00	20.6.2011
Air Temp on deployment (°C)**	16	17	20			17		(15) 15°C (52) 17°C (101) 20°C	17
Duration of the deployment (exposure to air for field control)**	25 min	+/- 30 minutes	0.020833333			30 min		(15) 25 min (52) 46 min (101) 30 min	
Air Temp on recovery (°C)**	17	18	19			17		(15) 17°C (52) 18°C (101) 19°C	18
Duration of the recovery (exposure to air for field control)**	20 min	+/- 30 minutes	0.038194444			30 min		(15) 20 min (52) 30 min (101) 55 min	
Date and hour of the recovery** :	04/07/2011	4-July-2011 between 9:40 and 12:00	4.7.2011, 12:00			04.07.2011 11:00	04/06/2011	(15) 7/4/11, 9:40 (52) 7/4/11, 11:00 (101) 7/4/11, 12:00	4.7.2011
Comment on fouling**:		no fouling				Exposed membranes were spotted and darker than unexposed ones			

Table XIII- 2 (continued) Provided passive samplers of fluorinated surfactants: method information

LAB No.	19	21	23	29	37	39	43	44	52
Extraction technique:	placed in pre-cleaned 6 cc cartridges. Eluted 4 ml methanol + 0.1% ammonia followed 4 ml methanol.	sorbent rinsed with +/- 10 ml milli Q into empty glass column with PTFE frit, drying 10 minutes (-50 kPa), elution with 3x 4ml methanol	liquid extraction	Same as for NIVA samplers	according to Alvarez 2004	10 mL MeOH - 10 mL MeOH/DCM (50/50) - 10 mL DCM	Elution with 4 ml methyltertiary butylether followed by 8 ml methanol	3x5ml 70% MeOH	Elution with methanol (15 ml)
Date of extraction:	30/08/2011	13/09/2011			20/10/2011	18.08.2011	20/10/2011	13/12/2011	27/07/2011
Date of instrumental analysis:	31/09/11					24.08.2011			
Cleanup method:	none	100 mg Envicarb	No		no	No cleanup	No	Supelco Envi-Carb (6ml)	
Instrumental method:	LC MS	LC-MS	LC/MS/MS		LC-MS/MS	LC-MS-MS	LC-MSMS	LC/MS/MS, ESI-, Column: Zorbax Eclipse XDB-C18 RR, Mobile phase: gradient: water 0,2% CH3COOH, MeOH 0,2% CH3COOH	HPLC-MS-MS
Injection solvent:	50:50 methanol:water	methanol	MeOH/H2O		75% methanol/25% 5mM ammonium acetate	MeOH/ultrapure water (50/50)	Acetonitrile-water	MeOH	Methanol / Water (50/50)

Table XIII- 2 (continued) Provided passive samplers of fluorinated surfactants: method information

LAB No.	19	21	23	29	37	39	43	44	52
Recovery and internal standards used:	C labelled solution mixture (MPFAC MXA, Wellington Laboratories, Guelph, Ontario, Canada)	13C8PFOA, 13C8PFOS	IS=C13 labelled PFOS and PFOA		yes	13C4-PFOA, 13C4-PFOS	Several standards used but generally not the target compounds, Therefore no corrections were made.	Int.stand.: Perfluorooctanoic acid 4C13, Perfluorooctane sulfonic acid 4C13	PFOS 13C4 and PFOA 13C4
REMARKS:	M8PFOA used as instrument performance standard and to check recovery of Internal standards				sample PP PFOS 2 (provided sampler) lost		No corrections for suppression made		
Data evaluation aspects									
Method for estimation of water concentration from passive sampler:	please give a short description and relevant references	not calculated, uptake rate/sampling rate unknown	please give a short description and relevant references	No Cw calculated as no Rs available		-	Uptake of Clotrimazole, Carbamezapine, Thiabendazol, transferred to sampled volume using Cw from SR sampling	please give a short description and relevant references	please give a short description and relevant references

Table XIII- 2 (continued) Provided passive samplers of fluorinated surfactants: method information

LAB No.	19	21	23	29	37	39	43	44	52
Sampling rates used (literature value/own calibration):	N/A					No sampling rates were found in the literature	From calibration with SR results, see line 7		not available
Sampler/water partition (distribution) coefficients used:	N/A					-	none		
Performance reference compounds applied (YES/NO):	No	no			no	NO	NO		
Were the calibration data adjusted to reflect exposure conditions (temperature, flow, pH...?)	No	no			no	-	Only an attempt to correct for flow		
REMARKS:		not calculated, uptake rate/sampling rate unknown			bad recovery and calibration problems, TWA data not shown		Not very confident on sampling rate applied		

Annex XIV. Participant passive samplers of fluorinated surfactants: method information

Table XIV- 1 Participant passive samplers of fluorinated surfactants: method information

LAB No.	19	21	23	29	37	39	43
PS type :	Modified POCIS	POCIS	POCIS, pesticide version	POCIS	POCIS	POCIS, pharmaceutical version	Speedisks (2 disks form one sampler)
Home made or commercial PS :	Home made	home made	commercial	home made	home made	Home made	J.T. Baker, Bakerbond Speedisk, H2O Philic DVB, Art.nr.: 8072-07
			EST			-	JT Baker
Supplier :							
Receiving phase material:	Strata XAW sorbent (Phenomenex), 33 µm	Sepra ZT, Phenomenex, 30 µm, 85A	Biobeads, Amborsorb and Isolute ENV+	OASIS HLB	Oasis HLB	Oasis HLB sorbent, 60 µm	DVB
Receiving phase mass (g):	0.6	300	0.22	0.2	0.1	0.200	0.95
Receiving phase volume (cm³):						-	
Membrane material :	Polyethersulphone; SUPOR 100 Membrane Disc Filters (0.45 µm, 47 mm diameter)	polyethersulfone, Pall corporation	Polyethersulphone	polyethersulphone	polyethersulphone STERLITECH 0.45µm	Polyethersulphone; SUPOR 100 Membrane Disc Filters (0.1 µm, 90 mm diameter)	Glassfibre Filter ±0.5 mm
Active sampler surface area (or membrane area) (cm²):	16.0	45.8	47.5	45.8	14.1	42.5	35.0
Performance Reference Compounds (PRC)							
Commercial passive samplers with PRC:	None		No	no		NO	No PRCs

Table XIV- 1 (continued) Participant passive samplers of fluorinated surfactants: method information

LAB No.	19	21	23	29	37	39	43
or home made PS spiked with PRC:	None			no	no	NO	No PRCs
Transport and storage							
Date of shipment to the study organiser:	08/06/2011	05/05/2011	07/06/2011			13.05.2011	~10/05/2011
Date of receipt by the study organiser:		16-May-11	07/06/2011			16.05.2011	~13/05/2011
Storage conditions before deployment (°C):	4	- 20 degrees celsius	-20	-20		room temperature	4°C immersed in water
Storage conditions after sampler recovery (°C):		- 20 degrees celsius	-20	-20		-20	minus 20°C
Date of return shipment from the organiser to the participant laboratory:		13/07/2011	20/07/2011			18.07.2011	~31/8/2011
Date of receipt by the participant laboratory:	13/07/2011	15/07/2011	20/07/2011			19.07.2011	~2/9/2011
REMARKS:						-	Dates are approximate
Date and hour of the deployment:	20/06/2011	20/06/2011	20.6.2011, 14:30			20.06.2011 13:50	20/06/2011
Air Temp on deployment (°C)	20.5	20	20			20	
Duration of the deployment (exposure to air for field control)	85 min	25 minutes	00:30			30 min	
Air Temp on recovery (°C)	22	18	18			18	
Duration of the recovery (exposure to air for field control)	58 min	15 minutes	00:30			20 min	
Date and hour of the recovery:	04/07/2011	04/07/2011	4.7.2011, 14:40			04.07.2011 14:30	04/07/2011
Comment on fouling:		no fouling	2nd and 3rd POCISes were cracked on the arrival			Exposed membranes were spotted and darker than unexposed ones	

Table XIV- 1 (continued) Participant passive samplers of fluorinated surfactants: method information

LAB No.	19	21	23	29	37	39	43
Sampler deployment and recovery							
Field deployment device used:	Entox deployment cage, 3x POCIS per cage	big cage provided by WRI	big cage	canister/holder	standard POCIS cage	Standard POCIS deployment cage for 3 samplers	Wet mounted on open cage
Extraction technique:	placed in pre-cleaned 6 cc cartridges. Eluted 4 ml methanol + 0.1% ammonia followed 4 ml methanol.	sorbent rinsed with +/- 10 ml milli Q into empty glass column with PTFE frit, drying 10 minutes (-50 kPa), elution with 3x 4ml methanol	liquid extraction	Elution with MeOH	2 x 10mL 90% methanol (15 min in ultrasonic bath), then evaporation of solvent, reconstitution and analysis	10 mL MeOH - 10 mL MeOH/DCM (50/50) - 10 mL DCM	Elution with 15 ml methyltertiarybutylether followed by 20 ml DCM and finally with 15 ml methanol
Date of extraction:	30/08/2011	13/09/2011		01/09/2011	20/10/2011	18.08.2011	20/10/2011
Date of instrumental analysis:	31/09/11	21-Sep-11		Oct-11	21/10/2011	24.08.2011	27/10/2011
Cleanup method:	none	100 mg Envicarb	No	none	no	No cleanup	No
Instrumental method:	LC MS	LC-MS	LC/MS/MS	LC/MS	LC-MS/MS	LC-MS-MS	LC-MSMS
Injection solvent:	50:50 methanol:water	methanol	MeOH/H2O		75% methanol/25% 5mM ammonium acetate	MeOH/ultrapure water (50/50)	Acetonitrile-water
Recovery and internal standards used:	C labelled solution mixture (MPFAC MXA, Wellington Laboratories, Guelph, Ontario, Canada)	13C8PFOA, 13C8PFOS	IS=C13 labelled PFOS and PFOA	YES	yes	13C4-PFOA, 13C4-PFOS	Several standards used but generally not the target compounds, Therefore no corrections were made.
REMARKS:	M8PFOA used as instrument performance standard and to check recovery of Internal standards						No corrections for suppression made

Table XIV- 1 (continued) Participant passive samplers of fluorinated surfactants: method information

LAB No.	19	21	23	29	37	39	43
Data evaluation aspects							
Method for estimation of water concentration from passive sampler:	Huckins et al. ES&T 1999	not calculated, uptake rate/sampling rate unknown	please give a short description and relevant references	No Cw calculated as no Rs available	TWA calculated according to Alvarez 2004	-	Uptake of Clotrimazole, Carbamezapine, Thiabendazol and Fluoranthene transferred to sampled volume using Cw from SR sampling
Sampling rates used (literature value/own calibration):	Own calibration				own calibration	No sampling rates were found in the literature	From calibration with SR results, see line 7
Sampler/water partition coefficients used:	Own calibration				-	-	none
Performance compounds reference applied (YES/NO):	NO	no			no	NO	NO
Were the calibration data adjusted to reflect exposure conditions (temperature, flow, pH...?)	NO	no			no	-	Only an attempt to correct for flow
REMARKS:		not calculated, uptake rate/sampling rate unknown			bad recovery and calibration problems, TWA data not shown	Cartridges with HLB sorbent were not completely dry (mass of about 0,25 g) so concentrations in sorbent were calculated with a nominal mass of 0,2g	Not very confident on samplingrate applied

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