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An interlaboratory study on passive sampling of emerging water pollutants

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Highlights

- A collaborative trial was performed to assess the variability of passive sampling.
- The passive sampling process does not cause excessive data variability.
- Unsatisfactory accuracy of sampler analysis was the main source of variability.
- Translation from passive sampler to water concentration increases the variability.
- In future passive sampling and laboratory analysis should be assessed separately.

Abstract

An inter-laboratory study was organised for the monitoring of emerging aquatic pollutants (pharmaceuticals, pesticides, steroids, brominated diphenyl ethers and others) using passive samplers. Thirty laboratories participated in the sampler comparison exercise. Various samplers designs were exposed at a single sampling site to treated waste water. The organisers deployed in parallel multiple samplers of a single type, which were distributed for evaluation of the contribution of the different analytical procedures to the data variability. Between laboratory variation of results from passive samplers was about factor 5 larger than within laboratory variability. Similar results obtained for different passive samplers analysed by individual laboratories and also low within laboratory variability indicate that the passive sampling process is causing less variability than the analysis. Concentrations in composite water samples were within the range obtained by passive samplers. In future a significant improvement of analytical precision and calibration of adsorption based passive samplers is needed.

Keywords

brominated diphenyl ether, fluorinated surfactant, emerging pollutant, interlaboratory study, pharmaceutical, polar pesticide, passive sampling, steroid hormone, water analysis

1 Introduction

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). Chemical water analysis is done on routine basis in the Member States according to their national regulations and it is crucial that currently applied approaches will merge into a common strategy which results in comparable assessments throughout Europe. The recently issued Directive 2013/39/EU on Environmental Quality Standards under WFD [1] specifically recommends further development of passive sampling techniques as a promising tool for future application in compliance checking and trend monitoring of priority substances. The potential of passive samplers (PS) to support WFD monitoring requirements was first recognized in an ad hoc expert meeting organised by the NORMAN association in 2009 [2]. Other initiatives to investigate the application of PS in regulatory monitoring were the "Utrecht workshop" organized by Deltares [3], the SETAC Pellston workshop on PS methods in sediments, [4] and the ICES Workshop on Passive Sampling and Passive Dosing [5]. One of the outcomes of these workshops was that inter-laboratory trials are essential to further validate this sampling method and to increase the confidence of the technological approach for end users. A number of inter-laboratory studies addressing PS in the aquatic environment have been conducted so far, (Table 1) targeting mainly PS of hydrophobic persistent organic pollutants. Allan et al. [6] showed that free dissolved water concentration

values of nonpolar compounds obtained from LDPE strip samplers, SPMDs and silicone PSs deviated less than a factor of 2 from the average of six PSs. Similar results were reported by Miège et al. [7], who evaluated the measurement of selected polar pesticides, polycyclic aromatic hydrocarbons (PAHs) and metals by various available passive sampling techniques in freshwater and marine environments. Although the above mentioned studies assessed the current variability of the passive sampling method, the chosen study designs in most cases did not allow to assess the contribution of various steps of the passive sampling process (i.e. sampling, sample analysis and calculation of the water concentrations) to the observed variability. The ICES Passive Sampling Trial Survey identified chemical analysis (20-40%) and sampling rate estimation (30%) to be the main sources of interlaboratory variability of reported water concentration values of PAHs and polychlorinated biphenyls (PCBs) [8–10]. Most recently, QUASIMEME [11] organised a proficiency testing (PT) scheme on silicone rubber (SR) analysis (for PAHs, PCBs and brominated diphenyl ethers; BDEs) and on conversion of concentrations in SR into water concentrations. The PT scheme revealed that most of the participating laboratories were able to analyse PAHs, PCBs and PBDEs in SR with a satisfactory z-score (<2). Most laboratories also showed a good performance in application of existing models [12,13] available for translation of passive sampling data into water concentrations.

The inter-laboratory study presented here 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 as a follow-up of the above mentioned exercise. It was still a learning exercise with the objective to assess the current variability of passive sampling method for a range of emerging pollutants, but in comparison with the AQUAREF study a further step was made by including assessment of various sources of the method variability and to identify the current weak points and needs for future sampler development, and development of consistent procedures for future method validation, especially for the adsorption based passive samplers. 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 adsorption based samplers, which were dominantly evaluated in this study, is generally higher than that of partition based passive samplers [14]. The study addressed a relative 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 watch list [1]. 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.

2 Material and methods

2.1 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 passive sampling (PS) process, including analytical comparability and comparison of PS with composite water sampling. All samplers were exposed in parallel to water at a single site. The components in the study design were:

- 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 for analysis in parallel with the various sampler extracts.
- For each target analyte class, passive samplers of a single type (*provided samplers*) were exposed to water at the study site in parallel with participant samplers, and were consequently provided to each participant. These *provided samplers* were analysed together with the participant's own passive samplers. These components support the interpretation of the main activity of the exercise, which was to evaluate the present data variability from various passive samplers selected by the individual participating laboratories.
- Data from the passive samplers analysed by participant laboratories (with exception of BDEs) were compared with contaminant concentrations in composite water samples collected using an autosampler at the study site during sampler exposure and analysed by the organiser laboratories.

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, additional to that of sampler processing and analysis, can be attributed to the variability/differences between samplers.

2.2 Target compounds

The selection of the analytes included for investigation in this study was performed based on results of a questionnaire that was circulated during the study preparation to laboratories that have experience with application and analysis of passive samplers. Compounds were selected from the NORMAN list comprising the most frequently discussed emerging substances [15]. The availability of PS calibration data for target compounds was also considered as a selection criterion. The final analyte list consisted of 29 compounds and included

- 7 polar pesticides (atrazine, carbendazim, desethylatrazine, desethylterbutylazine, diuron, S-metolachlor, terbutylazine)
- 7 pharmaceuticals (alprazolam, atenolol, carbamazepine, diazepam, diclofenac, ibuprofen, naproxen)
- 5 steroid hormones (17-alpha-estradiol, 17-alpha-ethinylestradiol, 17-beta-estradiol, estriol, estrone)
- 6 brominated diphenyl ethers (BDE 28, BDE 47, BDE 99, BDE 100, BDE 153, BDE 154)
- 2 fluorinated surfactants (PFOA, PFOS)
- bisphenol A
- triclosan

Several of the selected compounds recently regulated as priority substances under the WFD and related Directives on Environmental Quality Standards [1,16] include: atrazine, diuron, PFOS and BDEs. Moreover, diclofenac, 17-alpha-ethinylestradiol and 17-beta-estradiol are compounds from the watch list established in Article 8b of Directive 2013/39/EU [1].

2.3 Standard solution

The standard solution of analytes in suitable solvents was prepared by the central laboratories, which also performed sample homogeneity tests before distribution to

participants. Distribution of standard solution to participants was performed in cooled polystyrene containers together with provided samplers by a fast courier service.

2.4 Participant passive sampler

For the study each participant supplied passive samplers (3 replicates + 1 field blank) that were deployed to sample the water phase at a single sampling site. Participating laboratories were free and encouraged to test all recently available types/designs of passive samplers that are suitable for sampling selected target analytes. For this step in the exercise participants were requested to report for each target compound the amount sampled by their sampler and the aqueous phase concentration they derived from the sampler uptake, using a calculation method of their choice.

A wide range of passive sampler designs has been applied. Table 2 lists the main categories of samplers that were applied and the abbreviations used to later label them in the data projection. Samplers were exposed in 3 subsequent sampling campaigns in summer 2011. Deployment of samplers for analysis of all substance classes with the exception of BDEs lasted 14 days. Deployment of samplers for BDEs lasted 42 days. Following exposure, each sampler was handled and stored according to participant instructions and sent to participant laboratory for analysis by courier in cooled containers.

2.5 Provided passive sampler

The *provided samplers* (3 replicates + field blank) and their analysis by participating laboratories allowed an inter-comparison of the analysis of passive samplers and an estimate of the contribution of the analytical (sampler extraction + analysis) component to total variability. Provided samplers were exposed to water at the study site in parallel with and for the same time periods as participant samplers.

2.5.1 Sampler for polar compounds

The *provided sampler,* applied for pesticides, pharmaceuticals, steroid hormones, fluorinated surfactants, bisphenol A and triclosan, was the Polar Organic Chemical Intergrative Sampler (POCIS) comprising of a standard configuration (200 mg of OASIS HLB sorbent fitted with poly-ethersulphone membrane with 0.1 µm pore size and 45.8 cm^2 surface area). For sampling of polar pesticides the adsorbent was spiked with app. 4 µg/g of D_5-desisopropylatrazine (D_5-DIA) according to the procedure described by Mazzella et al.[17] before sampler assembly and deployment. Mazzella et al. [17] suggested applicability of D_5-DIA as a suitable PRC for compensation of effects of environmental conditions (especially flow velocity) on performance of the applied variant of POCIS.

Following exposure at the organising laboratory, the adsorbent material from each sampler was transferred into a pre-weighted empty solid phase extraction (SPE) cartridge, dried and the sorbent mass was recorded. Each participant laboratory received sorbent material from 3 randomly chosen replicate samplers and one field blank. Samples were distributed to participants by courier in cooled containers. Participants were asked to report results in ng/g of sorbent. In case of pesticide analysis, participants were asked to additionally report the D_5-DIA amount ratio between the exposed and the unexposed sampler, i.e. between sample and the field blank, respectively, in order to test the practical suitability of D_5-DIA as a PRC. Participants alsohad to report their estimation of the freely dissolved concentration in the sampled water (C_w) in ng/L and provide a description of the method and modelling they

routinely apply for evaluation of data from POCIS, or to use relevant up-to-date information from scientific literature.

2.5.2 Sampler for BDEs

The *provided sampler* applied for BDEs was made of Altesil® silicone rubber. Each sampler consisted of 3 sheets (90 x 55 x 0.5 mm). The exact "post deployment" dry weight of each sampler was determined by participants after extraction. The samplers were spiked with 15 performance reference compounds (PRCs; D_{10}-biphenyl, PCBs: CB001, CB002, CB003, CB010, CB014, CB021, CB030, CB050, CB055, CB078, CB104, CB145, CB204) during preparation according to the procedure described by [18]. Participants were asked to estimate sampling rates from the dissipation rates of PRCs. *Provided samplers* were exposed to water at the sampling site for 42 days, together with *participant samplers*. Each participant laboratory received from the organiser 3 randomly selected replicate field exposed samplers + 1 field blank + 1 field blank spiked by a uniform concentration of BDEs. Samplers were distributed to participants stored in amber glass bottles closed by stainless steel lined screw caps by courier in cooled containers.

Participants were asked to report results in absolute ng/sampler and for individual PRCs the ratio between the PRC amount in exposed and unexposed samplers, i.e. between sample and the field blank, respectively.

Participants were also asked to report an estimation of the freely dissolved concentration in the sampled water in 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.

2.6 Composite water sample

The average value of concentration of analytes measured in collected 2 weekly composite samples of water (for all target analytes except BDEs) during entire sampler exposure provided the comparison of passive sampling with a conventional sampling approach. An automatic water sampler (Bühler 1029, Hach Lange, Germany) collected 24h composite water samples at the sampling site during the 14 day passive sampler deployment periods (not during sampling of BDEs). The sampling was time-proportional. The sampler was programmed to collect a total of 2.5 L of water (100 ml water every hour) that was separately collected for each day and kept at 4°C in the autosampler storage container. Every 24h the collected water sample was transported on ice to the laboratory, where it was 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). Details are given in the full study report [19]. Every day a prescribed aliquot was added to the storage bottles. Seven-day composite samples were obtained every week by applying this procedure. Water samples and procedural blank samples were shipped once per week by a fast courier service for analysis in selected expert laboratories.

Analysis of water samples was not performed for BDEs since comparative alternative methods (other than PS) for measurement of their dissolved concentrations in water are not available.

2.7 Participants

The study was open for participants from commercial, academic and regulatory laboratories. Altogether, 30 laboratories from 13 different countries registered for the study, with the numbers of participants registered to analyse individual contaminant classes in brackets: polar pesticides (19), pharmaceuticals (17), steroid hormones (15), triclosan (8), bisphenol A (11), PFOA, PFOS (8), BDEs (16). Not all laboratories delivered results for all registered compound classes and several laboratories failed to report any data.

2.8 Sampling site

The exercise addressed sampling in treated wastewater, which is a highly relevant matrix for future monitoring of priority substances, but also a complex matrix that presented a challenge for methods used for analysis. The exercise was performed at the discharge of treated wastewater from a large municipal WWTP in Brno, Czech Republic (capacity cca. 500 000 equivalent inhabitants). The sampling was conducted in an effluent basin that is used for measurement of flow and volume of discharged treated wastewater.
A test to assess the exposure homogeneity was performed before the actual study. For this purpose 5 standard POCIS deployment cages containing 3 POCIS samplers as described above) were deployed each at various positions (2 positions and 3 water depths) in the sampling basin and analsyed for 9 polar pesticides. The results revealed that the location in the outflow tank within the tested zones did not affect (increase) the subsequent variance of the sample analysis in the laboratory [19].
Data on several parameters including water discharge, temperature, suspended solids, pH, conductivity and TOC of sampled water were provided by the WWTP operator.

2.9 Data evaluation

The interlaboratory comparison was not intended to be a proficiency testing scheme, but a learning exercise. The median of participant`s data was used to compare the laboratories between each other without stating it as an assigned value. No attempts were made to derive assigned values since for the analysis of passive samplers the true concentration was not known. The study objective was to assess method variability (or between laboratory precision) at various procedural levels.
Collected participant data were $\log_2$ transformed for statistical treatment, assuming their log-normal distribution. For data presentation in graphs, results were back-transformed to original values. Box-and-whisker plots, bar graphs and bi-plot graphs were used to display participant data.

2.9.1 Box-and-whisker plots

For all tested compounds, groups of four box-and-whisker plots (Figure 1) were constructed, with a general view on the overall variability of all data. In these graphs, outliers were not excluded. The box in the plot (Figure 1) comprises the data between the 25^{th} and the 75^{th} percentile with the median of the data shown by the horizontal line inside the box. The ends of the whiskers represent the 10^{th} and the 90^{th} percentile. The crosses show the concentration declared as reference value by the central laboratory (top left) or concentration measured in composite water samples (bottom left). Crosses below bars (bottom left) denote limits of detection of compound in water samples.

An exemplary figure for pharmaceuticals (Figure 1) shows:

- The results obtained from the analyses of standard solution, showing also the concentration and uncertainty declared as reference value by the central laboratory.
- The data obtained from analyses of the *provided sampler* expressed as uptake per unit of surface. For *provided samplers* uptake was assumed to be integrative and thus proportional to the surface area.
- Aqueous phase concentrations derived from the participant`s passive samplers and their comparison with results from composite water samples.
- Ratios between aqueous concentrations derived from *provided* and *participant's* sampler.

2.9.2 Bar graphs

Three bar charts that compare results obtained by individual laboratories were constructed for every compound, as is shown in exemplary Figure 2 for carbamazepine and in Figure 3 for BDE 47, respectively. These represent 3 matrices analysed: the standard solution, the *provided sampler* (expressed as uptake per unit of sampler surface area) and the *participant sampler* (expressed as calculated water concentration), respectively.

Each laboratory is identified by a number on the x-axis in consistent order to allow an easy comparison of results obtained by the laboratory across different matrices (*standard solution*, *provided sampler*, *participant sampler*). There were cases when a laboratory analysed a *standard solution* and *provided samplers* but did not analyse any *participant samplers*. In such case a column was left empty in the bar chart dedicated to results from participant sampler; this projection should not be misunderstood as a reported false negative result.

Before plotting, identifying outliers, and calculation of the standard deviations the data were $\log_2$ transformed. Data on the y-axis is always centred to the median of all participant's data. The bars represent the mean value of the determinations (4 repeated measurements for the analysis of standards and for the analysis of 3 replicate samplers) in a particular matrix by an individual laboratory. Consequently, the height of the bar represents the deviation of the laboratory's mean from the median. Data reported by participants to be below their method detection limit were not included in the evaluation. The repeatability (within laboratory variability) of participant data is indicated by error bars. The error bars represent 2 times the standard deviation calculated from replicate determinations.

High outliers were identified as values larger than the sum of the 75% percentile and 1.5 times the inner quartile range. Values lower than the 25^{th} percentile subtracted by 1.5 times the inner quartile range were also marked as outliers. Outliers are filled darker 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, excluding outlier values.

In the graph showing results of the standard solution analysis Figure 1-3, reference values of concentrations (determined by central laboratories) are shown as a horizontal line. The dotted blue horizontal lines cover the interval of reference value ± 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 were displayed on the side of the bar graphs. These included the median of participant's data (*Median*), standard deviation of all data (*s*), geometric mean (*Geomean*), number of data points (*n*), number of outlier values (*Outliers*), and standard deviation of data excluding outlier values (*s excl. outl*), respectively. For the standard solution, reference value of concentration (*Refvalue*) and associated expanded combined uncertainty with coverage factor 2 (*Exp. unc.*) are displayed. Next to the participant 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 water sample detection limit (*LOD*), respectively.

2.9.3 Biplot graphs

For carbamazepine and BDE 47, Figure 2 and Figure 3, respectively, also contain scatter biplots (sometimes referred to as Youden plot) that compare results for analytes obtained by each laboratory in the 2 different samples: the *participant sampler* and the *provided sampler*. The plot visualises the between-laboratory variability. Data obtained by these two methods can be directly compared, assuming that certain simplifying criteria are fulfilled:

- Sampling should be integrative, i.e. the concentrations in the sampler far from the thermodynamic equilibrium with the sampled water. In other words, the mass of analyte found in the sampler should depend solely on the sampling rate (R_s) and not on the sampler uptake capacity. The *participant samplers* differed in the surface area and the mass of sorbent material applied. However, in most cases the sampler uptake capacity was high and an integrative uptake over the 2 weeks of exposure can be assumed.
- The sampling rate is a product of mass transfer coefficient and the active sampler surface area. In most samplers the main barrier to mass transfer is the water boundary layer and similar mass transfer coefficients are expected.

Thus, it was 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 (measured by central laboratories) are shown on the biplot as blue triangles and the limit of detection in water samples is plotted as a red square. A one to one reference line (the 45 degrees reference line) is drawn to show the equality of the 2 values. Labels of points identify the type of participant passive sampler according to Table 2. A label was omitted if the *participant sampler* had the same design as the *provided sampler* (POCIS for polar compounds or silicone rubber for BDEs, respectively).
The scatter biplots can be interpreted as follows: points that lie near the equality line (the 45 degrees reference line) confirm good repeatability, but on the line but far from other laboratories indicate systematic error. Points that lie far from the equality line indicate random error.

2.9.4 Expression of data variability

Variability of participant data at different procedural levels was 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 [20]:

$$CV = \ln 2 \; s_{\log 2} \qquad \text{Equation 1}$$

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 mean values reported by laboratories. Outlier values were identified according to the procedure described above and were excluded from the calculation of between laboratory coefficients of variation reported in Table 3 and 4.

2.9.5 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:

$$C_w = \frac{N_{PS}}{R_S \, t} \qquad \text{Equation 2}$$

For this model, the combined coefficient of variation can be expressed from the law of error propagation, which provides a formula to estimate the coefficient of variation of the sampling rates applied in calculation as:

$$CV_{R_s} = \sqrt{CV_{C_w}^2 - CV_{N_{PS}}^2} \qquad \text{Equation 3}$$

where individual terms express coefficients of variation of the water concentration estimate (CV_{Cw}), of the analyte amount accumulated by the *provided sampler* (CV_{Nps}) and of the sampling rate applied in calculation (CV_{Rs}), respectively. Results of the estimation of CV_{Rs} are shown in Tables 3 and 4.

3 Results and discussion

The detailed report containing study results for individual compounds have been published in a full study report [19]. Conclusions made during result evaluation for individual compound groups investigated in the collaborative trial can be generalised.

- With a few exceptions, an acceptable within laboratory precision and also between laboratory variability was observed for analysis of target compounds in standard solution (Tables 3 and 4). 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. In general, no systematic positive correlation was found between the deviation of the laboratory`s mean from the median (or the value assigned by the central laboratory) for the standard solution and the laboratory`s deviation from the median for other analysed matrices (provided sampler, participant sampler). Therefore, data sets from analysis of passive samplers were not excluded, even when an individual result was identified as an outlier according to procedure described in section 2.9.2.
- For most classes of polar compounds sampling with *provided samplers* (POCIS) was homogeneous, which was confirmed by the low within laboratory variability in the analysis of replicate samplers (see examples in Figure 4). This implies that the compound uptake by these samplers was not depending on the position of samplers in the sampled system. Higher within laboratory variability of steroids in *provided samplers* can be explained by the very low concentrations that were close to the method limit of detection (data not shown).
- With a very few exceptions, concentrations of analytes in field blank samplers of both types were low, in most cases less than 10% of the concentration found in field exposed samplers and close to method detection limits. Detailed information can be found in [19].
- In cases where *provided* and *participant sampler* uptake mechanisms were expected to be similar, the obtained within laboratory results for surface specific uptake (ng/cm^2) by the different passive samplers were well comparable (see examples in left biplots in Figure 2 and Figure 3). This indicates that the PS process is causing less variability than the between laboratory chemical analysis, and the subsequent data translation to water concentration.
- In most cases the between laboratory variability of results from passive samplers was roughly a factor 5 larger than the within laboratory variability (see examples in Figure 4). The generally 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 [21,22]. 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.
- An impression of the variability of sampling rates that participant laboratories applied for translation from provided sampler uptake to water concentration can be made when the amount of a compound reported by a laboratory in the provided sampler N_{PS} (ng) is divided by the water concentration reported by the same laboratory C_w (ng/L). When integrative uptake is assumed, a rearranged equation 2 gives the sampling rate $N_{PS}/C_w/t=R_S$ (L/d). The Figure 5 illustrates the variability of the

sampling rates for pharmaceuticals. The observed variability was similar to the variability of R_S values compiled from literature in the critical review by Harman et al. [22]. The estimated contribution of R_S to the overall variability of water concentration, evaluated according to section 2.9.5 is listed also in Tables 3 and 4.

- 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 (data not shown, but available in [19]).
- For BDEs, which were sampled by partitioning-based *provided samplers* (silicone rubber), the variability of applied calculation procedures is the main factor causing the elevated between laboratory variability for water concentration estimates from *provided sampler* data (see an example for BDE 47 in Figure 4). Besides difficulties the laboratories experienced in application of the sampler uptake models available in the literature, difficulties with the analysis of PRC compounds also significantly contributed to the total variability of reported water concentration.
- In most cases, discrepancies between water concentrations obtained by PS and water sampling were not observed (see an example in the lowest bar chart in Figure 2), however, the precision of the PS method needs a significant improvement. Note that the analysis of composite water samples was always performed by a single „expert" laboratory, which implies that some bias in reported values cannot be excluded. Therefore, results of composite water samples should not be misunderstood as an assigned reference values for the bias assessment of the passive sampling method. Still, it is useful to compare the passive sampling with results of a conventional method that is currently applied in water quality monitoring. 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 is repeatable 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.

4 Conclusions

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

4.1.1 Accuracy of analysis of complex samples using LC/MS methods

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 susceptible to ion suppression or also ion enhancement [23]. Such problem is not specific for analysis of extracts from adsorption-based passive samplers and occurs in extracts of other sample preparation techniques, such as SPE. The accuracy of sampler analysis can be improved by several approaches:

- Laboratories should validate their LC/MS methods specifically for extracts from passive samplers exposed in complex matrices such as wastewater.
- 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 the 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.
- Despite the broadly spread belief that LC/MS/MS techniques are selective and thus, sample cleanup is generally not required, we strongly recommend the sample dilution and/or cleanup or analyte derivatisation to reduce the potential matrix effects during sample analysis.
- Use of alternative ionisation techniques such as atmospheric pressure chemical ionisation (APCI) instead of ESI may help to reduce problems with ion suppression.

4.1.2 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 [24] 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 [25]. 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 PRCs 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.

- The understanding and monitoring (or control) of the contaminant uptake to adsorption based samplers is 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.
- PRCs still could be used as surrogates to monitor exposure conditions in time and space or link to calibration data (quality control).
- 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 with 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.

4.1.3 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:

- In case samplers reach equilibrium with sampled water, deriving the concentration of a chemical in the water phase from the amount accumulated in the sampler requires sampler-water partition coefficient (K_{sw}) [26–28]. Accurate values of K_{sw} should be available for target analytes, but also for applied PRCs required to confirm achievement of equilibrium.
- In case no equilibrium is attained, aqueous concentrations should be estimated by sampler/water exchange kinetics models that can be *in situ* calibrated from the release of PRCs dosed to the sampler prior to exposure [12]. Booij and Smedes [13] 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 [13].
- 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 [29]. 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 available guidelines for passive sampling of hydrophobic contaminants in water using silicone rubber samplers [30]. 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. We believe that training of laboratories in proper analysis of PRCs and application of published uptake models will help to significantly reduce variability of reported data.

4.1.4 Organisation of future inter-laboratory studies

In future inter-laboratory studies, it is necessary to clearly separate the issue of laboratory analysis from the passive sampling testing. We propose a two stage inter-laboratory study:

- In preparation of the inter-laboratory 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.
- The *first stage* of the study would be a **Proficiency Testing (PT) scheme**, where laboratories will analyse the reference material prepared in step 1. Only laboratories that demonstrate acceptable performance in the PT scheme will be admitted to participate in the main inter-laboratory study addressing the passive sampling inter-comparison. Alternatively, if the PT scheme is performed in parallel with the inter-

laboratory sampler comparison, passive sampling results of laboratories that fail in the PT scheme will be excluded from evaluation (or, depending on the achieved z-score, their result will have a lower weight). This approach will minimise the effect of laboratory analysis on the assessment of passive sampling results.

- The *second stage* of the study would be an **inter-laboratory passive sampler comparison**, with a similar design to the one demonstrated in our study. *Provided* and *participant samplers* will be again 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 will be assessed and compared to the criteria set for routine monitoring methods, e.g. under Water Framework Directives.
- Assessment of **trueness of water concentrations** calculated from the passive sampling data is the most important objective of future inter-laboratory 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 order to obtain an acceptable **reference value** of water concentration, several expert laboratories should 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.
- 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 passive sampling agreed upon by a group of expert laboratories.

Acknowledgments

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6 Figure captions

Figure 1 An example showing the overall variability 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.

Figure 2 Exemplary results of analysis of carbamazepine in treated wastewater by passive sampling in the interlaboratory study. Detailed graph explanation is given in sections *Bar graphs* and *Biplot graphs*.

Figure 3 Exemplary results of analysis of BDE47 in treated wastewater by passive sampling in the interlaboratory study. Detailed graph explanation is given in the section *Bar graphs* and *Biplot graphs*.

Figure 4 Variability of reported results at different procedure levels: example for carbamazepine and BDE47. Coefficients of variation (without outliers) for individual compounds are shown. NPS – provided passive sampler; PPS – participant passive sampler. (N) –amount; (C_w) – water concentration.

Figure 5 Variability of sampling rates that individual laboratories applied to convert uptake of pharmaceuticals by the provided passive sampler into aqueous concentrations.

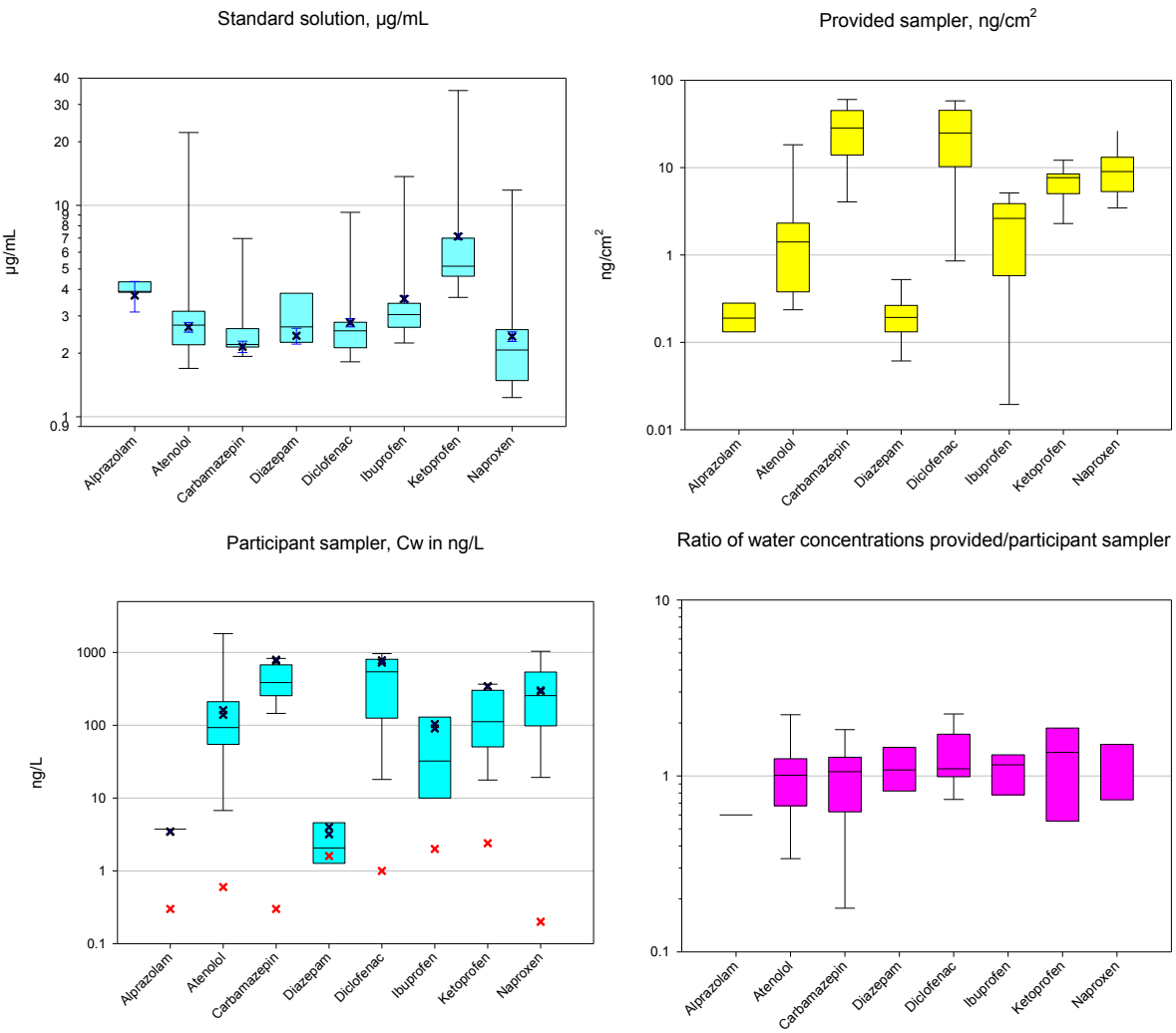

Figure 1

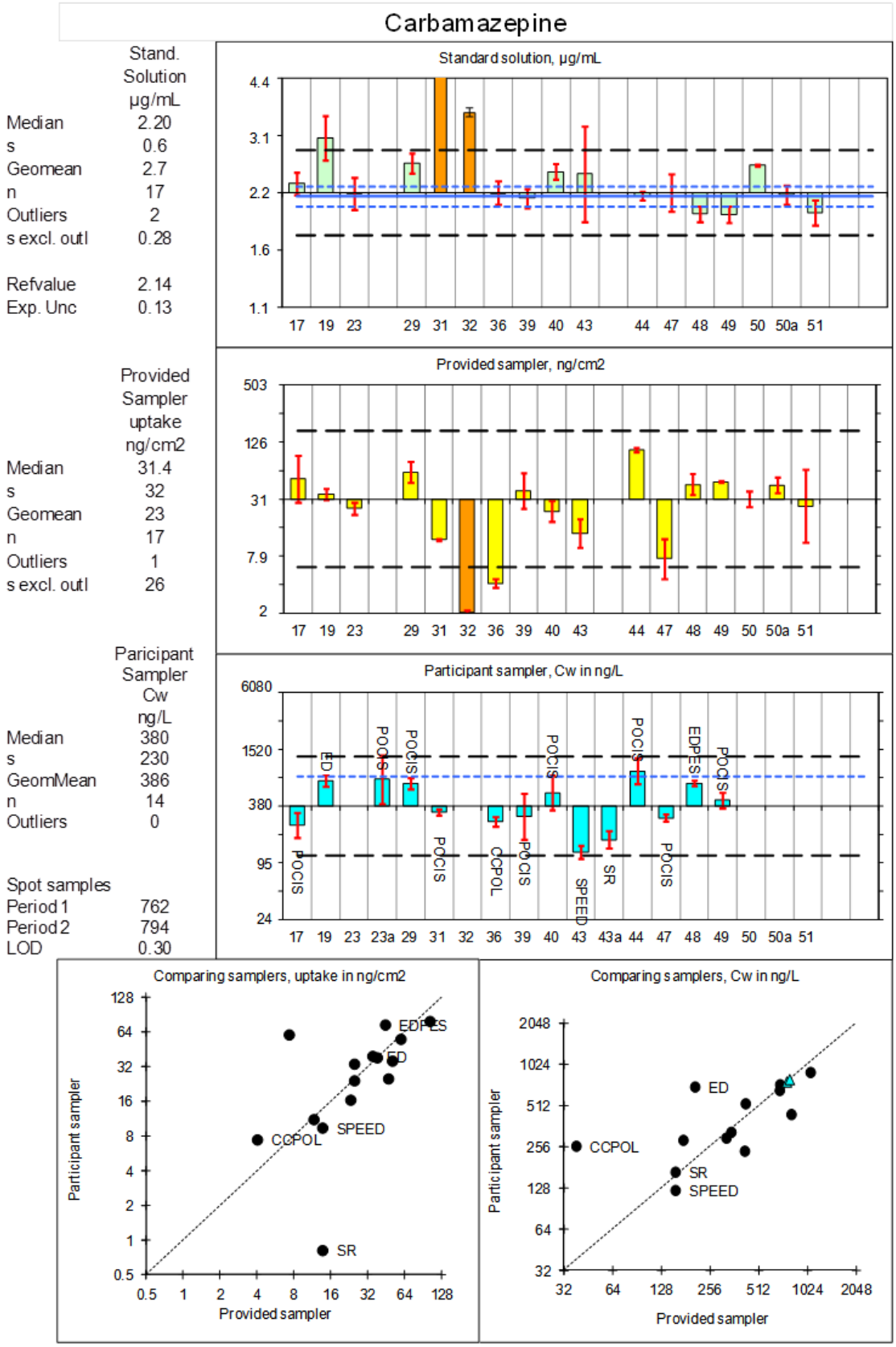

Figure 2

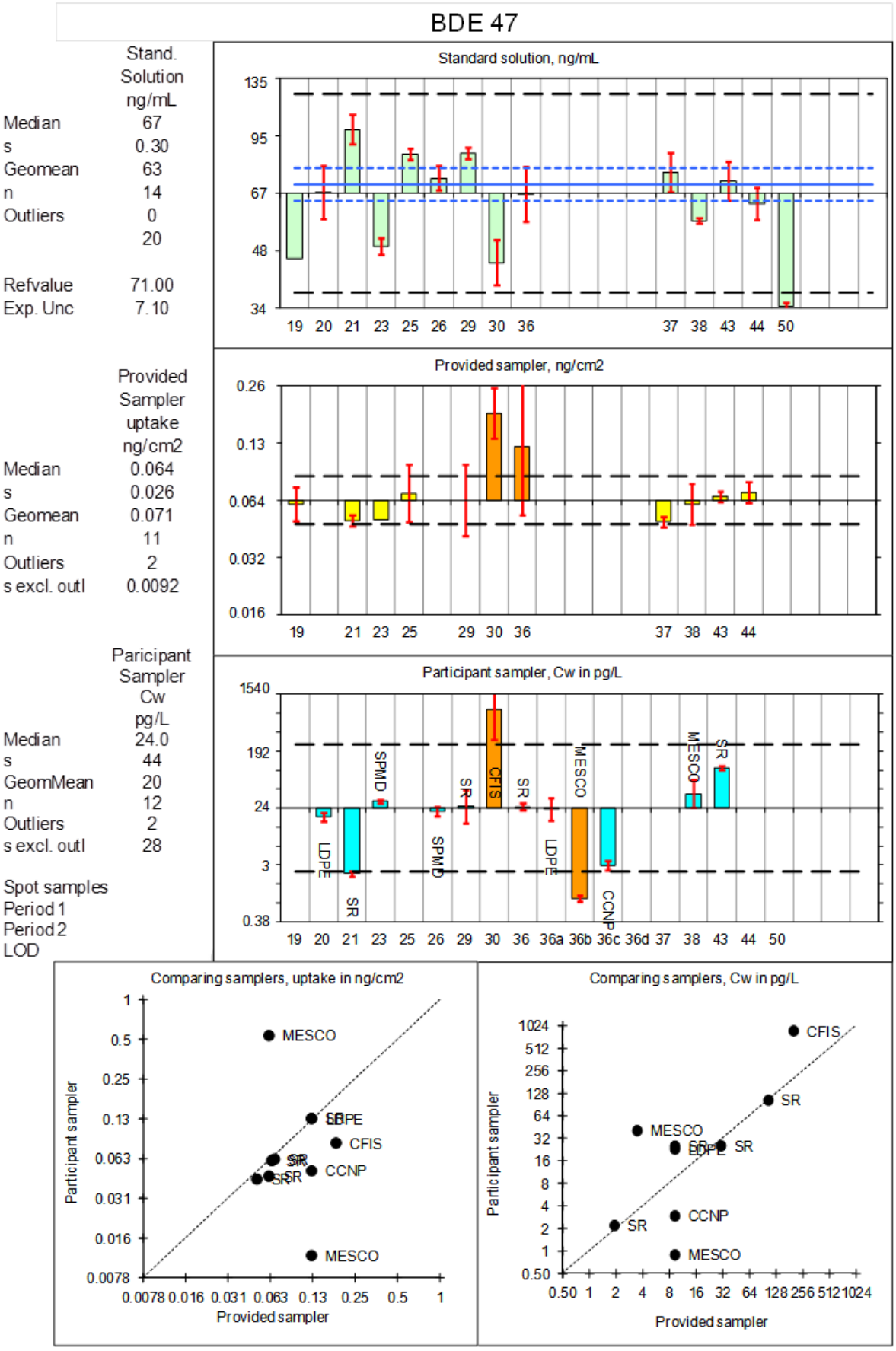

Figure 3

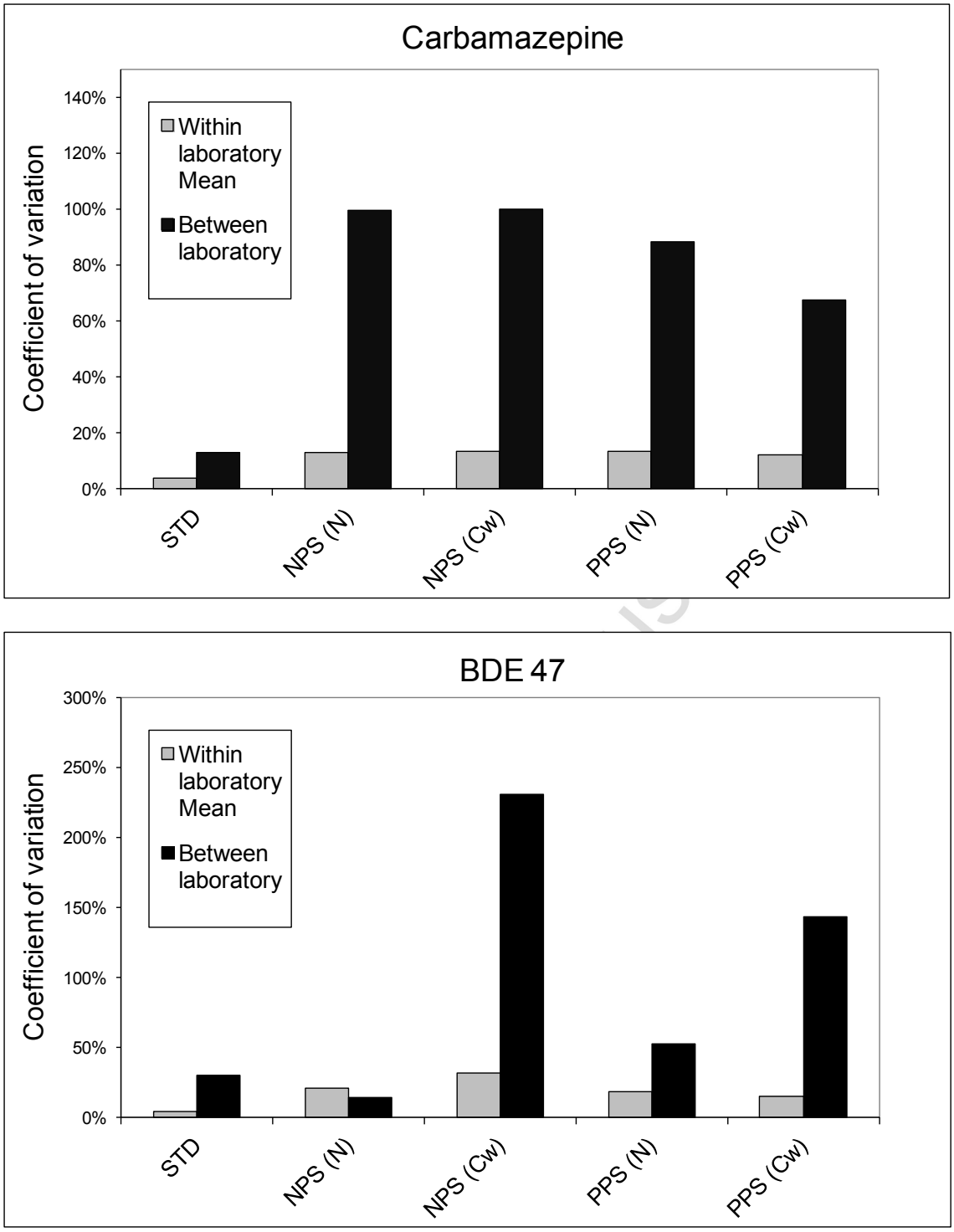

Figure 4

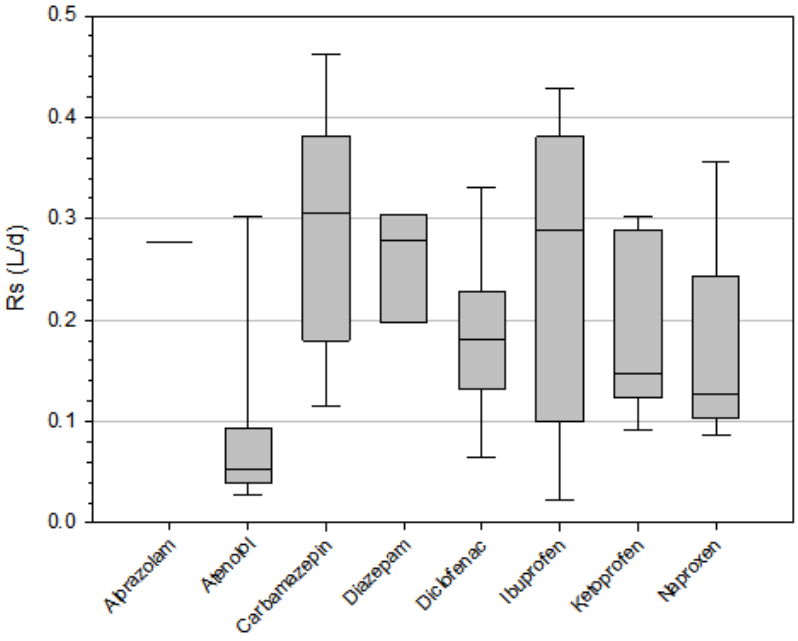

Figure 5

7 Tables

Table 1. Inter-laboratory studies addressing passive sampling of organic pollutants in aquatic environment

Inter-laboratory study	Study design	Sampler/s	Sampled matrix	Analytes	Reference
ICES Trial Survey and intercalibration on Passive Sampling	*In situ* laboratory inter-comparison exercise	Silicone rubber (SR) sheets	seawater and sediment	PAHs and PCBs	[8–10]
SWIFT-WFD studies	*In situ* sampler inter-comparison exercise	Chemcatcher, low density polyethylene membrane (LDPE), membrane-enclosed sorptive coating (MESCO), silicone rods, silicone strips and semipermeable membrane devices (SPMD)	river water and fortified river water	PAHs, PCBs, hexachlorobenzene, p,p`-DDE	[6,31]
ECLIPSE study	Laboratory sampler inter-comparison exercise	SPMD, SR, LDPE, Chemcatcher, CFIS sampler	fortified tap water	PCBs	[32]
AQUAREF study	*In situ* sampler inter-comparison exercise	Various passive samplers	river water and seawater	PAHs, currently used pesticides	[7]
Quasimeme Passive Sampling Development Exercise	Proficiency testing scheme on sampler analysis and conversion of concentrations in sampler into water concentrations	Silicone rubber sheets	seawater	PAHs, PCBs, PBDEs	[11]

Table 2. Various passive sampler designs applied in the inter-laboratory study

Sampler design category	Abbreviation
POCIS, pharmaceutical version	POCIS
Empore Disk	ED
POCIS, pesticide version	POCIP
Chemcatcher variant for sampling polar compounds	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
Semipermeable membrane device	SPMD
Low density polyethylene stripe	LDPE
Membrane enclosed silicone collector (MESCO)	MESCO
Chemcatcher variant for sampling non-polar compounds	CCNP

Table 3 Median concentration values and associated between laboratory variability's of reported results for polar pesticides and brominated flame retardants at different procedure levels.

Compound class	Compound	Standard solution				Provided sampler, compound uptake			Provided sampler, water concentration estimate				Participant sampler, water concentration estimate			Composite samples of water		
		n	c(ref) (ng/mL)	c (median) (ng/mL)	CV (%)	n	c (median) (ng/cm$^{2)}$)	CV (%)	n	c (median) (ng/L)	CV (%)	CV_{Rs}[1] (%)	n	c (median) (ng/L)	CV (%)	week 1 (ng/L)	week 2 (ng/L)	LOD (ng/L)
Pesticides	Atrazine	19	1.37	1.90	6	19	1.47	16	19	21	90	88	17	18.4	79	25	18	10
	Carbendazim	16	1.85	1.94	10	17	4.40	68	11	51	96	67	10	46	185	90	101	10
	Desethylatrazine	16	1.88	1.72	18	16	1.12	82	17	20	138	111	11	26.1	127	37	38	10
	Desethylterbutylazine	13	2.00	2.00	11	13	1.75	23	15	25	110	108	12	22.2	39	39	33	10
	Diuron	16	2.76	1.87	13	17	9.20	94	19	135	125	82	16	71	97	223	169	20
	S-metolachlor	16	1.91	1.96	11	16	0.20	59	14	4	93	72	12	2.96	84	21	20	20
	Terbutylazine	16	1.76	1.99	10	16	1.82	40	17	21	124	118	14	18.7	87	30	24	10
Brominated flame retardants	BDE 28	13	20.0	21.2	34	8	0.0035	62	7	$4.4x10^{-3}$	187	176	7	$2.0x10^{-3}$	103	n.a.[2]	n.a.	
	BDE 47	14	71.0	67.0	30	11	0.0640	14	14	$16.0x10^{-3}$	231	230	12	$24x10^{-3}$	143	n.a.	n.a.	
	BDE 99	14	100.0	88.0	25	11	0.0320	19	14	$4.8x10^{-3}$	549	548	11	$5.3x10^{-3}$	568	n.a.	n.a.	
	BDE 100	14	20.0	18.8	30	10	0.0098	74	13	$1.6x10^{-3}$	572	569	9	$1.4 x10^{-3}$	193	n.a.	n.a.	
	BDE 153	14	16.0	16.2	44	8	0.0009	53	5	$1.3x10^{-3}$	665	663	7	$0.5 x10^{-3}$	320	n.a.	n.a.	
	BDE 154	12	15.0	14.1	41	9	0.0008	13	7	$0.7x10^{-3}$	66	65	7	$0.1 x10^{-3}$	185	n.a.	n.a.	

[1]CV_{Rs} – estimated contribution of R_s to the overall variability of water concentration, using Equation 3; [2]n.a. - not analysed;

Table 4 Median concentration values and associated between laboratory variability's of reported results for bisphenol A, fluorinated surfactants, steroid hormones and pharmaceuticals at different procedure levels.

Compound class	Compound	Standard solution				Provided sampler, compound uptake			Provided sampler, water concentration estimate				Participant sampler, water concentration estimate			Composite samples of water		
		n	c(ref) (ng/mL)	c (median) (ng/mL)	CV (%)	n	c (median) ($ng/cm^{2)}$)	CV (%)	n	c (median) (ng/L)	CV (%)	CV_{Rs}[1] (%)	n	c (median) (ng/L)	CV (%)	week 1 (ng/L)	week 2 (ng/L)	LOD (ng/L)
	Bisphenol A	6	0.11	0.26	140	6	6.40	153	5	41.4	237	181	3	4.8	482	212	171	75
	Triclosan	3	0.11	0.21	78	3	0.83	91	3	3.0	55	n.e.	2	1.06	1194	nq	nq	50
Fluorinated surfactants	PFOA	9	0.05	0.05	28	9	0.83	36	1	10.8	[2]n.e.	n.e.	2	15.7	190	28	36	1.2
	PFOS	9	0.05	0.03	36	9	0.14	50	1	1.9	n.e.	n.e.	2	1.64	110	5.7	8.5	1
Steroid hormones	17-alpha-Estradiol	8	0.021	0.022	8	3	0.23	1428	3	16.5	1043	n.e.	2	11.6	63	<1.0	<1.0	1.0
	17-alpha-Ethinylestradiol	13	0.016	0.022	52	5	0.18	413	4	0.9	289	n.e.	3	2.74	1213	<13.4	<13.4	13.4
	17-beta-Estradiol	13	0.021	0.020	25	6	0.04	830	6	0.8	387	n.e.	4	1.33	2979	0.5	0.58	0.5
	Estriol	9	0.021	0.022	28	1	0.18	n.e	0			n.e.	1	7.8		<5.4	<5.4	5.4
	Estrone	13	0.021	0.022	25	10	0.05	169	11	3.0	170	23	8	5	348	<0.9	<0.9	0.9
Pharmaceuticals	Alprazolam	3	3.75	3.90	6	3	0.19	38	1	2.2	n.e.	n.e.	1	3.7		3.5	3.4	0.3
	Atenolol	12	2.65	2.71	22	12	1.45	76	13	92.9	73	n.e.	9	92	62	161	139	
	Carbamazepine	17	2.14	2.20	13	17	31.40	93	17	346.2	100	37	14	380	64	762	794	0.3
	Diazepam	8	2.41	2.65	28	8	0.20	58	7	2.6	88	66	4	1.95	72	3.2	4	1.6
	Diclofenac	17	2.79	2.54	18	17	29.10	74	17	612.9	256	245	12	536	112	778	725	1.0
	Ibuprofen	13	3.61	3.04	16	11	3.40	119	11	29.5	171	123	6	55	145	90	104	2.0
	Ketoprofen	13	7.13	5.10	26	12	7.70	35	13	164.4	73	64	9	111	126	344	341	2.4
	Naproxen	14	2.40	2.04	35	14	9.00	55	15	265.0	112	97	9	254	153	292	300	0.2

[1]CV_{Rs} – estimated contribution of R_s to the overall variability of water concentration, using Equation 3; [2]n.e. – not estimated