NORMAN

Network of reference laboratories and related organisations for monitoring and bio-monitoring of emerging environmental pollutants

Joint Programme of Activities

Workplan/actions for 2011

TOPIC: PASSIVE SAMPLING

Chemical Monitoring On Site (CM Onsite) organised by NORMAN Association and JRC in support of CIS WFD

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

Information for participants

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1 Design of the study

The design is organized stepwise with a sampler comparison exercise that will be extended to cover individual aspects in the passive sampling process, such as analytical comparability and comparison with spot sampling. The levels in the study design are:

1. The main network activity will evaluate the **present variability in data** by comparing results from various passive samplers sent by participating laboratories exposed to water at a single (reference) site. Participants are free to select the applied passive samplers. Target compounds are listed below (section 3).

2. Participating laboratories will analyse a standard solution of target analytes in parallel with step 1; the solutions are prepared for each tested family of compounds by reference laboratories.

3. The central organising lab will provide for each target analyte class a passive sampler of one type (exposed to water at the reference site in parallel with samplers sent by participating laboratories) to be analysed, if possible, by all participating labs and by the central laboratories.[1]

4. Data from the passive samplers will be compared with contaminant concentrations in several spot water samples. Water samples will be collected by the central organizing lab and sent for analysis to reference central laboratories. Water samples will NOT be analysed by participants.

Ideally, after Step 1, all labs will derive the identical aqueous phase concentrations from the sampler results, and those results will also be equal to those from the repetitive spot water sampling. If not ideal, the results will serve as a good illustration of the variability over different samplers. Steps 1, 2 and/or 3 will help to exclude sources of variability such as instrumental analytical bias (step 2) and the extraction component (step 3; sampler processing) to total variability by allowing the differences between samplers to be studied.

[1] POCIS sampler (filled with Oasis HLB sorbent; the « pharmaceutical » version) will be used as provided sampler for all substance classes excepting PBDEs. For PBDEs, Altesil silicone rubber sheets will be applied as provided samplers.

2 Study results

The study results obtained will allow a realistic evaluation of passive sampling of the selected compounds and give participating laboratories information about whether a particular passive sampling method provides comparable results within the variability of the exercise.

a) Passive samplers. The study will consist of passive samplers deployed to sample the water phase at a single reference site. Participating laboratories are free and encouraged to deploy all recently available types/designs of passive samplers (that are suitable for sampling selected target analytes) at the reference site. For this step in the exercise participants will be requested to supply for each target compound the amount sampled by their sampler and the aqueous phase concentration they derived from the uptake.

b) Standard solution. This will show the variability of applied instrumental methods and is a simple first step to allow correction of data for analytical deviations.

c) Passive sampler provided by the organiser. The reference samplers provided (three replicates + blank) and their analysis by both central and participating laboratories will allow an intercalibration of the analysis of passive samplers and an estimate to be made of the contribution of the analytical (sampler extraction + analysis) uncertainty component to total variability.[1]

d) Spot water sampling. The mean value of concentration of analytes measured in daily collected spot samples of water (for PFOA, PFOS and pharmaceuticals) or concentration in two composite week samples (pesticides, bisphenol A, triclosan) during sampler deployment will provide 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 spot sampling average is possible.[2]

[2] This step will not be performed for PBDEs.

3 Target compounds

3.1 Pesticides

1. Terbutylazine
2. Desethylatrazine
3. Desethylterbutylazine
4. Atrazine
5. Carbendazim
6. S-Metolachlor
7. Diuron

3.2 Pharmaceuticals

8. Carbamazepine
9. Diclofenac
10. Ibuprofen
11. Naproxen
12. Diazepam
13. Alprazolam
14. Ketoprofen
15. Atenolol

3.3 Steroid hormones

16. 17-alpha-Estradiol
17. 17-alpha-Ethinylestradiol
18. 17-beta-Estradiol
19. Estriol
20. Estrone

3.4 Bisphenol A and Triclosan

21. Bisphenol A
22. Triclosan

3.5 Brominated flame retardants

23. BDE 28
24. BDE 47
25. BDE 99
26. BDE 100
27. BDE 153
28. BDE 154

3.6 Fluorinated surfactants

29. PFOA
30. PFOS

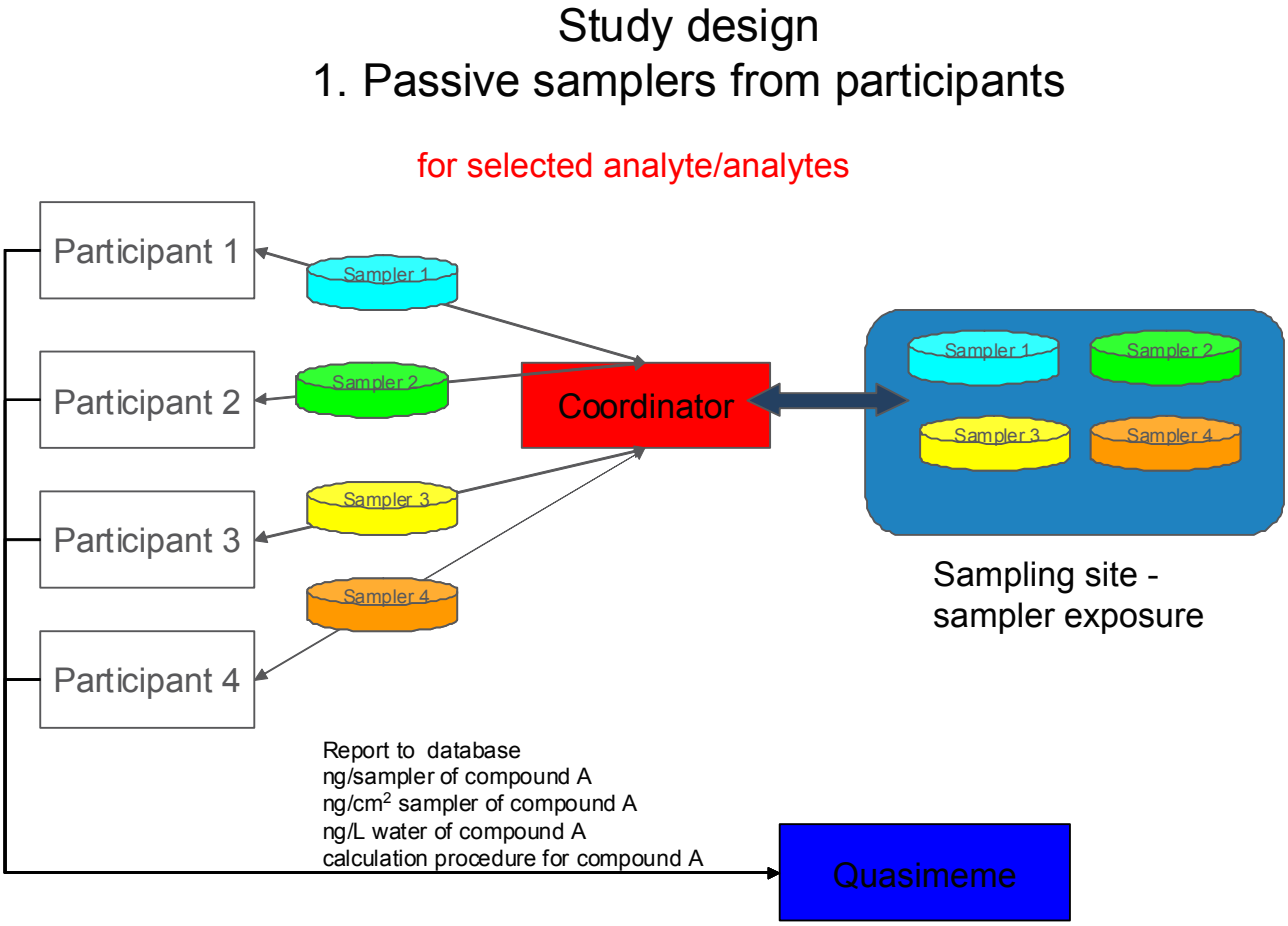

Figure 1. Passive samplers. The study will consist of passive samplers deployed to sample the water phase at a single reference site. Participating laboratories are free and encouraged to deploy all recently available types/designs of passive samplers (that are suitable for sampling selected target analytes) at the reference site

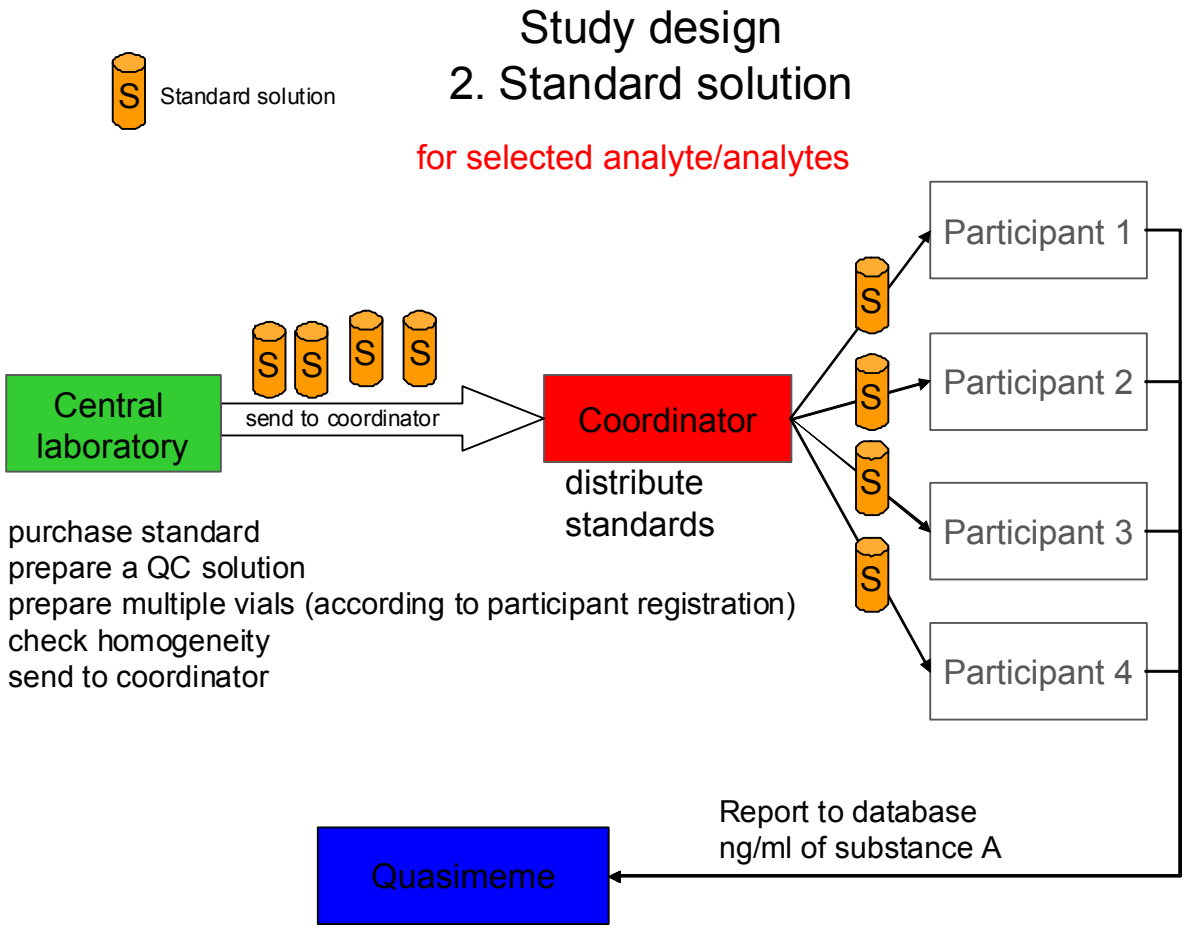

Figure 2. Standard solution. This will show the variability of applied instrumental methods and is a simple first step to allow correction of data for analytical deviations.

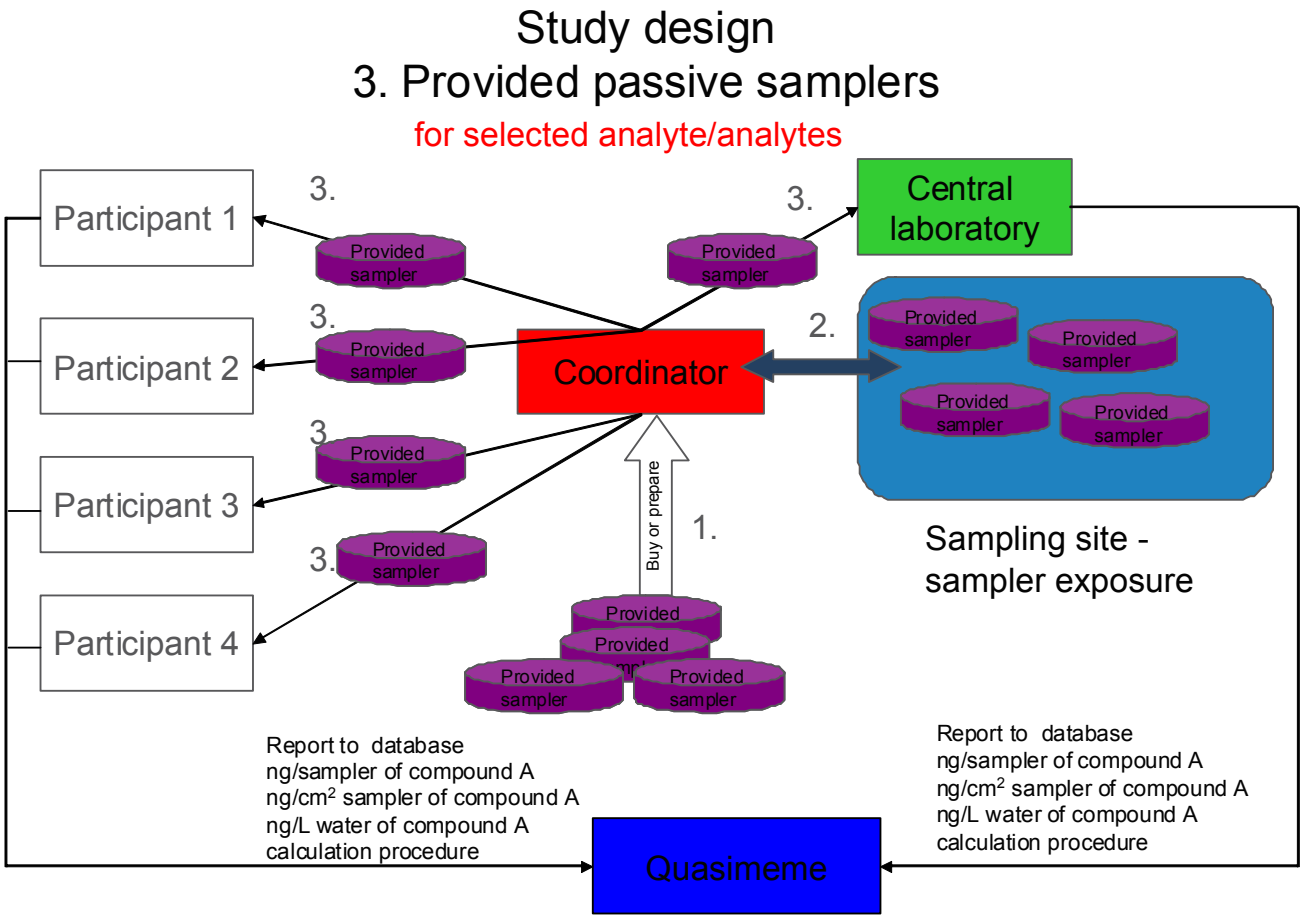

Figure 3. Provided passive sampler. The replicate (three replicates + blank) provided samplers and their analysis by both central and participating laboratory will allow an intercalibration of the analysis of passive samplers and an estimate to be made of the contribution of the analytical (sampler extraction + analysis) uncertainty component to total variability.

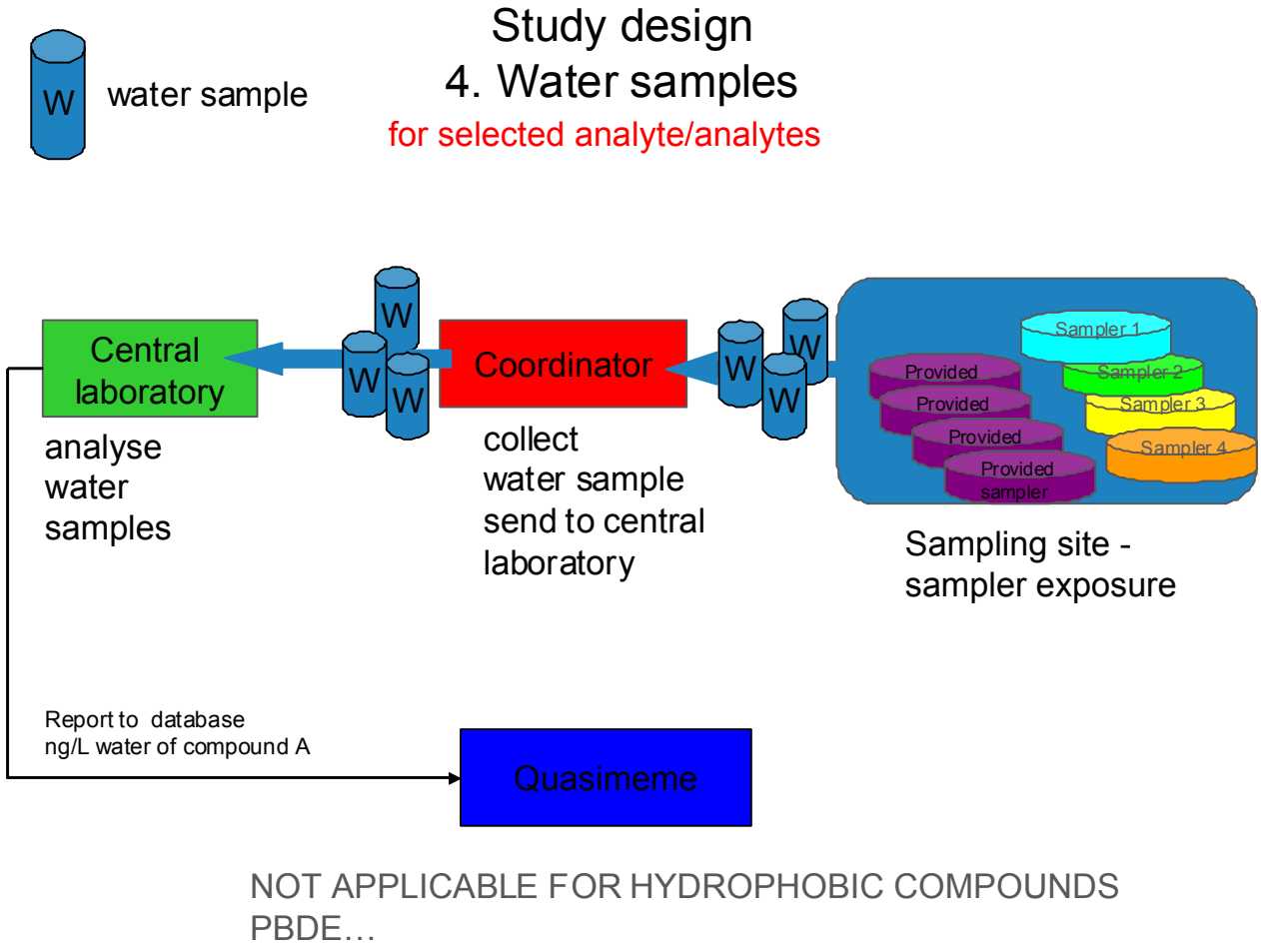

Figure 4. Spot water sampling. The mean value of concentration of analytes measured in spot samples of water (or concentration in one or two composite samples) during sampler deployment will provide the comparison with a conventional sampling approach.

4 Reported values

4.1 Participants

As a result of the study, participants will report to the organiser:

1. A detailed description of their applied passive sampler (name, producer, surface area, material of diffusion membrane, mass and nature of the sorbent applied, performance reference compounds spiked in the sampler, deployment device applied)

2. Amount of target compounds determined by the participant laboratory in their own passive samplers (the triplicate exposed samplers + one trip blank).

3. Amount of target compounds per unit of surface area and per unit of mass of sorbent, determined by the participant laboratory in their own passive samplers (the triplicate exposed + one trip blank).

4. A detailed description of the procedure applied for calculation of time weighted average (TWA) concentration in water from passive sampler data (blank correction, PRCs applied, conversion model, calculation procedure)

5. Concentration in water derived by the participant laboratory using their own passive samplers

6. Amount of target compounds determined in the provided standard solution (in micro grams per milliliter; triplicate determination)

7. Amount of target compounds in provided passive samplers (triplicate exposed + one trip blank).

8. Ratio of PRC amounts in exposed/blank provided passive sampler.[3]

[3] This step will not be compulsory, if participants indicate that they are not able to analyse PRCs in provided samplers. PRC-spiked provided samplers will be used only for these classes: polar pesticides (POCIS) and PBDE (silicone rubber Altesil)

4.2 Central laboratories

Central laboratories will confidentially report to the organiser:

1. Statement of a reference value and its uncertainty for the standard solution distributed to participants.

2. Amount of target compounds in passive sampler blanks provided by organiser.

3. Amount of target compounds in field exposed passive samplers provided by organiser .

4. Where applicable, ratio of PRCs in exposed/blank samplers provided by organiser

5. Concentration of target compounds in water samples collected during the sampler exposure

5 Participants

The study will be open for participants from commercial, academic and regulatory laboratories.

5.1 Participant registration

Registration of participants can be done until **31st March** on a website setup for participant registration http://www.recetox.muni.cz/index.php?pg=registrace-norman .

5.2 Registration fees.

Registration fee is 100,-EUR per compound group (pesticides, pharmaceuticals, steroid hormones, [bisphenol A + triclosan]; brominated flame retardants; fluorinated surfactants) but participants will have in their own charge to provide to the organizer the items:

5.3 Equipment to be provided by participants to the organiser

Participants have to provide to the organiser (VUVH) for each compound class of interest at least 2 weeks before the start of sampler deployment:

a) 4 passive samplers in air tight boxes (3 that will be exposed in triplicate + 1 as the field blank that will not be exposed in water),

b) The system to deploy their own passive samplers (holders and cages)

c) precise and clear instructions how the samplers are installed in the deployment system and how the sampling system should be deployed in water

d) Instruction for sampler storage following exposure

e) **a prepaid shipping coupon (WAYBILL)** for a courier service to get back their own passive samplers, deployment systems and samplers provided by the organiser. The cost of shipment to and from the sampling site will be covered by individual participating laboratories.

Remark : The costs for shipping the samplers following exposure back to the laboratories by an express courier service is expensive. A quick shipment is an alternatively to a refrigerated truck service, which may not be available (must be arranged for participants from outside Europe (Australia, USA…). Alternatively, deployment cages (do not need cooling) and samplers can be sent back separately using a slower mail.

5.4 Material to be received from the organiser

Following the sampler exposure each participant will receive for each target compound class of interest (according to registration) from the organiser:

a) standard solution (prepared by central lab) of each substance class in a suitable solvent.

b) 3 exposed passive samplers provided by the organiser

c) 1 blank passive sampler provided by the organiser

d) 3 exposed passive samplers provided by the participant*

e) 1 blank passive sampler provided by the participant*

* This step will be performed based on the participant feedback during registration (see 5.5)

5.5 Are participants able to analyse provided passive samplers?

During registration, participants are asked if they are able to process and analyse the passive samplers provided by the organiser:

For compound classes 3.1-3.4:
Is the participant laboratory able to:
a) extract and analyse their analytes of interest from Oasis HLB sorbent material?
b) in case of class 3.1 (pesticides), analyse desisopropylatrazine-d5 (DIA-d5)?
c) perform analysis of several analyte classes in the same extract from point a)?

For compound class 3.5:
Is the participant laboratory able to:

a) extract and analyse their analytes of interest + PRCs (D10-biphenyl + PCBs: CB001, CB002, CB003, CB010, CB014, CB021, CB030, CB050, CB055, CB078, CB104, CB145, CB204) from a list from Altesil silicone sheet material?

Table 2. Samplers provided by the organiser for individual studies.

Campaign number	Class number	Compound class	Sampler deployment period	Provided sampler
1	1 2	Pesticides Pharmaceuticals	14 days	POCIS with Oasis HLB, spiked with PRC[1]
2	3 4 5	Steroid hormones PFOA PFOS Bisfenol A, Triclosan	14 days	POCIS with Oasis HLB, no PRC
3	6	PBDE	42 days	Altesil silicone sheet spiked with PRCs[2]

[1] PRC: $^{3}D_{5}$-desisopropylatrazine
[2] PRCs: $^{4}D_{10}$-biphenyl, PCBs: CB001, CB002, CB003, CB010, CB014, CB021, CB030, CB050, CB055, CB078, CB104, CB145, CB204

6 Sampling station

6.1 Site description

The exercise will be performed at a single sampling site – the outflow of a large municipal WWTP in Brno-Modřice. The site is secured so that expensive onsite equipment such as the continuous water sampler can be used. Also, the WWTP can provide some of the necessary supporting measurements (continuous temperature, discharge, pH). Access to the sampling site is permitted by the WWTP operator. Details of the WWTP are given here:

http://www.bvk.cz/en/about-company/waste-water-treatment/brno-modrice-wwtp/

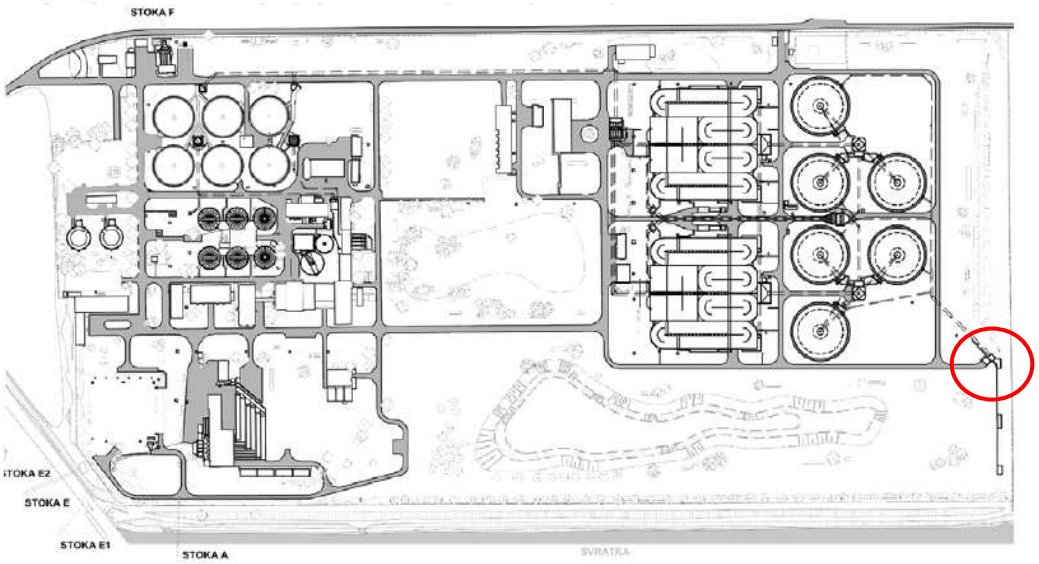

Fig. 6. Layout of the WWTP in Brno-Modřice. The sampling site is located at the outflow of treated wastewater and is marked with the red circle.

Fig. 7. View of the sampling site: the outflow of the WWTP in Brno-Modřice.

More photos of the sampling site, collected during an initial screening campaign, are available here:

http://www.flickr.com/photos/10155144@N00/tags/passivesamplerdeploymentatmodricewwtp/

http://www.flickr.com/photos/10155144@N00/sets/72157624293628185/

6.2 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 paraments fluvial environment with emphasis on the identification of endocrine substances*" (funded by the Czech The Ministry of Education, Youth and Sports MEYS, MŠMT in Czech) that was performed also at this sampling site, allowed preliminary identification of relevant substances. In 2010, a screening survey and homogeneity test was also performed.

7 Sampling campaigns

Organisers will:

a) **Deploy participant`s passive samplers** at the sampling site using deployment devices provided by participants according to participant instructions. Deployment devices will be suspended in water on ropes.

b) **Deploy provided passive samplers** at the sampling site. Deployment devices will be suspended in water on ropes.

c) **Operate the automatic water sampler** and visit the sampling site every day to collect water samples collected in last 24 hours, transport them to laboratory for processing (filtration, stabilisation) and storage.

d) **Collect the necessary supporting data** (discharge, temperature, TOC, particulate matter, conductivity, pH.)

8 Campaign timing: passive sampler deployment

Table 3. Time plan of passive sampler deployment.

Campaign number	Class number	Compound class	Registration deadline	Deadline for sending samplers + deployment equipment	Sampler exposure	Sampler deployment period
1	1 2	Pesticides Pharmaceuticals	31.3.2011	16.5.2011	**14 days**	**30.5.-13.6. 2011**
2	3 4 5	Steroid hormones PFOA PFOS Bisfenol A, Triclosan	31.3.2011	3.6.2011	**14 days**	**20.6.-4.7. 2011**
3	6	PBDE	31.3.2011	27.6.2011	**42 days**	**11.7.-22.8. 2011**

9 Submission of results

The result form will be available on a website setup by Quasimeme. Results will have to be reported electronically on this website with respect to the requested units and the number of digits.

The identity of participant will be kept confidential when processing data. The results from this intercalibration exercise will be published in a scientific report written in English and that mentions the list of the expert participating laboratories.

10 Dissemination

Results will be disseminated to the EU Member states as a Chemical Monitoring Activity Initiative in support to the Water Framework Directive implementation, the so called “CMA onsite” exercise.