Environmental Science
Processes & Impacts

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

rsc.li/process-impacts

Passive samplers will provide a cost effective tool for environmental monitoring if the amount of chemical accumulated to the sampler could be converted to concentration in aquatic phase as required by environmental legislation. Therefore the effect of prevailing environmental conditions on the passive sampling process should be understood more thoroughly. We studied the effect of the sampler orientation in respect of the main flow direction as well as the velocity of the surrounding water on the sampling efficiency both experimentally and numerically. Although the simulations illustrated differences in average pressure on the sampler surface as a function of its orientation which suggests the increase of accumulation, we were not able to verify this with our laboratory experiments.

Effect of the orientation and fluid flow on the accumulation of organotin compounds to Chemcatcher passive samplers

H. Ahkola[a], J. Juntunen[a], M. Laitinen[b], K. Krogerus[a], T. Huttula[a], S. Herve[a] and A. Witick[c]

[a] Finnish Environment Institute (SYKE), Survontie 9 A (Technopolis), 40500 Jyväskylä, Finland.
[b] Numerola Ltd P.O.Box 126, FI-40101 Jyväskylä, Finland.
[c] Institute for Environmental Research, P.O.Box 35, 40014 University of Jyväskylä, Finland.

Abstract

Monitoring of harmful substances in aquatic environment is based on spot sampling which is the only sampling technique accepted by environmental authorities in European Union. Still the implementation of European Union Water Framework Directive (WFD)[1] requires novel sampling tools for monitoring priority pollutants since their concentrations in natural waters can often remain below the limit of detection when using conventional spot sampling method. However, this does not necessary mean that the pollutant is not present in the aquatic environment. Many chemicals that are considered to be harmful are bioaccumulative and can effect on e.g. reproduction of aquatic organisms even at very low concentration levels. Also the timing is crucial since with spot sampling the pulse of harmful substances can easily be missed. Passive samplers collect the compounds for certain time which allow the concentrations in sampler to rise on the measurable level where they are easy to detect. Organotin compounds (OTCs) have been widely used as plastic stabilizers and antifouling agents in ship paints and in many industrial processes. Among the OTCs, tributyltin is listed as a WFD priority substance. In this study a small scale flow simulation around the Chemcatcher passive sampler was performed to visualize the flow streamlines in the vicinity of the sampler and to study the pressure faced by the receiving phase in different sampler positions. With laboratory experiments the sampling rates for each OTC was determined and effect of the flow velocity and sampler orientation on the accumulation of OTCs was discussed. The pressure changes were observed on the surface of the receiving phase in simulations with varying sampler orientations. Despite that, the laboratory experiments discovered no difference on the accumulation of compounds when varying the sampler orientation. The concentrations of OTCs in surrounding water calculated from the passive sampling results were equivalent to spot sampling ones. Hence, Chemcatcher passive sampler provides a practical tool for implementation of WFD.

1 Introduction

Monitoring of harmful substances in aquatic environment is based on spot sampling which is the only sampling technique accepted by environmental authorities of the European Union. With this sampling technique the concentration of harmful substances, such as organotin compounds (OTCs), often remain below the detection limit. For example in this study the detection limit of tributyltin (TBT) in water samples was the same as its environmental quality standard concentration (0.2 ng L^{-1}).[2] However, this does not necessary mean that the pollutant is not present in the aquatic environment. Many chemicals that are considered to be harmful are bioaccumulative and can effect on e.g. reproduction of aquatic organisms even at very low concentration levels.[3] Also the timing is crucial since with spot sampling the pulse of harmful substances can easily be missed. Their presence in aquatic environment can still be studied with passive samplers which concentrate the harmful substances into the measurable level and for this reason number of passive sampling methods has been developed in past decades.[4,5,6]

The passive sampling technique combines the sampling and the enrichment of the target compound.[6,7] The passive samplers are placed in the sampling site for a known time and during that time the sampler will collect the freely dissolved part of the analyte.[8,9] The passive sampling is based on the free flow of the analyte from the surrounding media to the receiving phase, which is caused by the difference between the chemical potentials of studied compound in these two media.[4] The sampling continues until the equilibrium between the analyte concentration in the receiving phase of the sampler and the surrounding aquatic media is reached or the sampling is stopped.[4]

The Chemcatcher passive sampler was first developed for monitoring organic pollutants in aquatic environments in a pan-European project called STAMPS (Standardized Aquatic Monitoring of Priority Pollutants by Passive Sampling).[8] The aim of that project was to develop a monitoring tool for implementation of European Union Water Framework Directive (2000/60/EC) (WFD).[1,10,11] The variation of the receiving phase material of the sampler enables to extend the group of substances which can be studied with Chemcatcher passive sampler, such as metals,[12-14] mercury,[9,15] organotin compounds,[15,16] PAHs[17] and nonylphenol ethoxylates[18].

The Chemcatcher passive sampler has become popular because it is simple to use and the receiving phase can be attached to various surfaces so it can be easily fitted in almost anywhere e.g. in ground water pipes. In Finland Chemcatcher samplers have been used for detecting harmful substances in surface and ground waters as well as in influents and effluents of a waste water treatment plant.[19,20] The sampler assembly is straightforward and it can be installed to the sampling site with several techniques. The most convenient manner in surface waters is to fix the samplers into a cage and the typical installation of the sampler is presented in Fig. 1. Plastic or metal cage, depending on the nature of the studied substances,

protects samplers from disturbances caused by fishes or birds and it also provides a good frame to deploy multiple samplers. The cage is attached to a rope connected to the surface buoy and anchor. Note that the samplers are fixed to a cage with cable tie only at one side which enables fairly free secondary movement (like rotation and flapping) of the sampler as the cage moves up and down with the waves.

Fig. 1. Typical deployment of Chemcatcher passive sampler in the natural water.

Although by using passive samplers the presence of studied substances in aquatic environment is revealed, this kind of information is not very informative when considering numerical modelling. Computational modelling has been considered as one of the alternative approaches to downsize the actual amount of laborious sampling.[21] Obviously, changing the point of view and testing alternative methodologies causes a new set of problems which have to be resolved. To be able to trust any computational model, it has to be calibrated and validated with the conventional measurements. In numerical modelling/simulation the concentration levels always differ from zero. To be able to calibrate and validate modelled dispersion of harmful substances based on passive sampling results the conceptual basis of the sampling procedure should be understood more thoroughly.

When using passive samplers for monitoring purposes many environmental characteristics of the surrounding media are often neglected simply because the data is not available. This applies especially to the physical environment and its variables like fluid velocities and pressure, their fluctuations and other properties such as sampler orientation and characteristics of its surface. In computational modelling it is just the opposite since many computational methods can provide exhaustive amount of information which could be used in interpreting passive sampling results. The advection by horizontal and vertical currents has been expected to be the main process responsible for the transportation of substances to the surface of the receiving phase. Previously the effect of the hydrodynamics on the Chemcatcher uptake has been studied with flow through tank equipped with rotating carousel.[17,22,23] Vermeirssen et al.[24] fixed the

Chemcatcher samplers to a water channel in parallel position. Still the orientation of the receiving phase of the sampler has not been studied in this detail described in this paper. Discussion of the results has been quite limited concentrating mostly on the impact of flow velocities. In this paper we aim to add some new aspects in this regards.

The OTCs were selected as test compounds in experiments described in this paper since it is closely related to the field and modelling studies concerning transportation and fate of OTCs in the Northern Lake Päijänne.[19,21] OTCs have been widely used as plastic stabilizers and antifouling agents in ship paints and in many industrial processes. In the aquatic environment OTCs accumulate into the sediment or organisms and are transformed to less substituted substances. TBT and triphenyltin (TPhT) are toxic to many organisms[25] and tributyltin (TBT) is listed as a WFD priority substance.

In this study a small scale flow simulation around the Chemcatcher passive sampler was performed by Numerola Ltd with a commercial software package. The aim was to visualize the flow streamlines in the vicinity of the sampler and to study the pressure faced to the receiving phase in different sampler orientations. The sampling rate R_S on Chemcatcher passive sampler was determined of each OTC in laboratory calibration test. Also the effect of water flow velocity and the orientation of the receiving phase of the sampler on the accumulation of OTCs were studied in a rotating ring-shaped flume test. The simulated and experimental results were applied to discuss the effect of sampler orientation and flow velocity on sampling procedure for assessing the optimal use to deploy samplers in natural waters.

2 Theory

The uptake kinetics of pollutants on passive samplers has been published by several authors.[6,8,26] The basic assumptions are that sampling rates are dependent on the rate of permeation of analyte through the surface of the exposed phase material. The rate of permeation is based on Fickian diffusion and on the receiving phase having a high affinity for the analyte, such that its concentration at the surface of the phase is zero. The rate of permeation depends on physico-chemical properties of the pollutant e.g. the molecular size and it is also inversely proportional to the length of the diffusion path.[22] Altogether the uptake kinetics of a studied compound on the sampler is controlled by the receiving phase, the aqueous boundary layers, the diffusion limiting membrane (if used) and a layer caused by biofouling (in field trials).[27] If the layer contributes more than 50% of the total resistance, it is considered as uptake rate-limiting.

The uptake of chemicals to the passive sampler has been described as an exponential process reaching steady state at some point of sampling.[8,28] In general it consists of three possible stages: linear, curvilinear and finally steady state, which is not assumed to be reached during the deployment. The thickness of the

aqueous boundary layer is decreased by turbulence, which increases the sampling rate R_S.[22] However, high sampling rate shorten the linear uptake phase of the sampler.[23] In this study the uptake was assumed to remain at the linear stage[29] where the following relationship applies:

$$M_S(t) = C_W R_S t \quad (1)$$

where $M_S(t)$ is the amount of substance (ng) measured in the receiving phase after the deployment time t (days), C_w is the average concentration of the substance in water during the trial and R_S is the sampling rate (L d^{-1}).[8] According to Kingston et al.,[8] the accumulation factor (AF) can be determined as:

$$AF(t) = \frac{M_S(t)}{C_W} \quad (2)$$

in which AF(t) is the accumulation factor (L) during the deployment time t (days). This description involves constant concentration of analyte in surrounding medium (C_w), constant water temperature and hydrodynamic conditions (mainly advection as well as the intensity of the turbulence). If analyte concentration fluctuates, C_w describes the time-averaged concentration of analyte during the trial.

Vrana et al.[30] studied the exchange kinetics and discussed the accumulation mechanisms for hydrophobic pollutants on the Chemcatcher passive sampler during the field trial. They also referred to Gale[31] and discussed the thickness of velocity boundary layer on top of the receiving phase. In our study the thickness of this boundary layer was calculated using well-known physical formulation of Prandtl[32]:

$$\delta = \sqrt{\frac{x\nu}{u}} \quad (3)$$

where x is distance from the leading edge (m) which in this case means the frame edge of the receiving phase, ν describes kinematic viscosity (m^2 s^{-1}), that depends on the water temperature and u is the flow velocity of medium (m s^{-1}).

The velocity boundary layer is not the only boundary layer emerging on the system when external obstacle is affecting the free flow. If the concentrations or temperatures of the free stream and the surface of the obstacle differ it causes the boundary layers for concentration and temperature. All these three boundary layers can be present simultaneously. In such cases the boundary layers rarely have equal growth rates. Since we are interested in mass transfer we will further consider only the concentration boundary layer.

Good approximation for the concentration boundary layer thickness δ_c is given by

$$\delta_c \approx \delta Sc^{-n} \quad (4)$$

in which Sc is the Schmidt number defined as a ratio of momentum and mass diffusivities $Sc \equiv \upsilon/D_{AB}$.[33] For most applications n=1/3 is assumed to be reasonable. Detailed calculations of mass fluxes in various situations can be found in the literature but usually the information is revealed from some non-dimensional number. For mass transfer the Sherwood number Sh defined as a dimensionless

concentration gradient at the surface gives a measure of the convection mass transfer occurring at the surface of the obstacle. Since thickness of the boundary layers increase as a function of distance from the leading edge also the mass transfer coefficients are local characteristics. Usually we are interested in total mass transfer that is given as:

$$\overline{Sh} = CRe_L^m Sc^n \qquad (5)$$

where C, m and n are constants and $Re_L \equiv uL/\upsilon$ is the Reynolds number. Above equation is general and it applies almost in every scenario. The actual values of C, m and n are usually measured. For most applications n=1/3 is assumed to be reasonable.

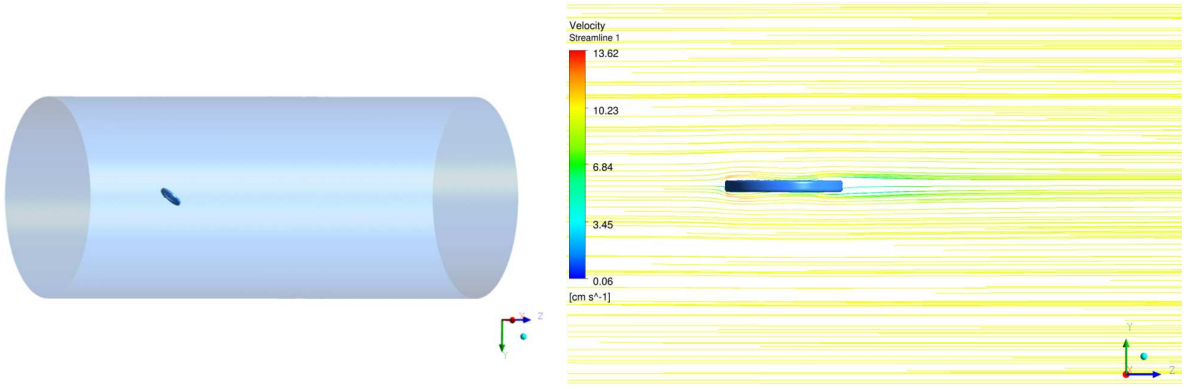

Fig. 2 Computational domain (left) and stream lines (right) in numerical flow simulations at velocity of 10 cm s^{-1}

The hydrodynamic conditions are often described as stagnant and implicitly expressed as a constant boundary layer over the sampler surface isolating it from the turbulent flow outside of the layer.[8,17,23] In this layer viscosity prevails over inertial forces and the uptake is based completely on the Fickian diffusion. In this respect there are many similarities to plankton dynamics or microbiological ecology and the nutrient exchange through the cells.[34] Reynolds stresses caused by the turbulent fluctuations and changes in boundary layer thickness has not been widely discussed in the literature concerning passive samplers. The discussion has mostly been limited on the advective currents whose effect has been studied by different tank or flume experiments[23,30] or using approximations e.g. based on river flow in the field studies.[18,35]

Lobpreis et al.[22] studied the effect of the sampler housing geometry on the calibration parameters of hydrophobic organic pollutants. They compared two Chemcatcher passive sampler types and in the first version the receiving phase was placed inside a 20 mm deep cavity. In the second housing type the cavity was only about 3 mm. The uptake and offload rate in sampler body with deeper cavity were twofold

lower than in sampler body with lower cavity. The housing geometry did not effect on the correlation of uptake and offload kinetics of studied compounds. Previous studies indicate that the properties of the aqueous boundary layer dominate the sampling rate R_S.[8,30] However, character of the boundary layer has not been specified unambiguously. Nevertheless, R_S is usually determined in a laboratory trial in which constant turbulent flows are generated with stirring the surrounding water or fixing the sampler to a rotating carousel. Although in field trials the samplers are usually deployed in a way that allows them to move freely at a certain level, the aquatic environment still differs from the laboratory conditions.

3 Experimental

3.1 Numerical simulations

Small scale flow simulation around the sampler was performed with ANSYS CFX 14.5 software assuming 3D laminar flow with control volume method. The aim of this work was to visualize the flow streamlines in surrounding medium caused by the sampler and study the pressure faced by the receiving phase in different sampler positions (Fig. 2). In simulations the water temperature was 18 °C and the flow velocities were 1, 3, 5, 7, 10, 15 and 20 cm s^{-1}. Non-slip condition on the sampler surface was used which means that at the surface velocity was set to zero. Due to laminar conditions the turbulence calculation was not included in these simulations.

3.2 Sample treatment and analysis

The purities of the solvents used in this study were at minimum HPLC-grade and the reagents were certified reference materials. The blank samples were measured to ensure the validity of the procedure. The laboratory tests were conducted using UHQ-water (internal resistance ≥ 18 MΩ cm^{-1} at 25 °C).

The Chemcatcher passive sampler consisted of a C-18 Empore disk receiving phase (47 mm diameter, 3M Agilent Technologies Finland Oy) supported by polycarbonate sampler housing (AlControl AB, Linköping, Sweden). The sampler housing was made of three pieces, two to attach the receiving phase and one to act as a transportation lid that protects the receiving phase. The sorbent in the C-18 Empore disk has an octadecylsilica phase, where the octadecyl group is bonded to the silica surface with an average particle size of 12 µm. Its retention mechanism is strongly non-polar and the average carbon percentage in the disk is 22.5 %. The C-18 Empore disks was first immersed in methanol for 20 min and placed in the filtration apparatus. 10 mL of methanol was passed through the disk, followed by 20 mL of UHQ water, and the disk was not allowed to dry in between. The sampler bodies had been kept in methanol overnight. The disk was fixed inside the sampler body and the cavity was filled with UHQ water. The lid was sealed and the sampler was placed in a zip-lock bag. Before deployment the samplers were stored in a fridge.

The Chemcatcher samplers were analysed within three days after retrieval. According to stability tests performed by Aguilar-Martinez et al.[16] no significant losses of OTCs were observed if the samplers were analysed within one week from the exposure. After the trial the samplers were diassembled and the receiving phase was placed into a glass tube. Tri-n-propyltin was added as an internal standard and the disk was extracted with acetic acid/methanol (3:1) in an ultrasonic bath. The extract was transferred to clean glass tube and 4 mL acetate buffer (1 M, pH 5.4) was added. The organotin compounds were derivatized with sodium tetraethylborate ($NaB(C_2H_5)_4$) and extracted with hexane. Finally, the hexane part was transferred to a sample vial. Laboratory blank was prepared with each sample batch.

The conventional spot water samples were measured immediately after sampling. In water samples tri-n-propyltin was added as an internal standard following acetate buffer (1 M, pH 5.4) and sodium tetraethylborate ($NaB(C_2H_5)_4$). The organotin compounds were extracted from the water phase with hexane. The volume of the hexane part was reduced by evaporating under a nitrogen stream and transferred to a sample vial. Laboratory blank was prepared with each sample batch.

Analysis of organotin compounds was performed by GC-ICP-MS (Agilent 6890N gas chromatograph coupled to Agilent 7500ce ICP-MS). GC and ICP-MS parameters for analysis of organotin compounds are presented in Table 1.

Table 1 Instrumental conditions for analysis of organotin compounds

	Value
GC parameters	
Column	HP 5 (30 m x 0.32 mm x 0.25 μm)
Injection mode	Splitless 1 μl
Oven program	60°C (1 min) to 300°C (5 min) at 30°C min^{-1}
Carrier gas	He at 2 ml min^{-1}
Transfer line temp.	300 °C
ICP-MS parameters	
Isotopes acquired	118, 119, 120
Dwell time	0.1 s
RF power	900 W
Carrier gas	1.05 l min^{-1}

3.3 Calibration trial

The sampling rate was determined with a laboratory test, where eight Chemcatcher samplers were deployed in a cylindrical water tank for 2, 5, 7 and 9 days expecting a linear uptake. The samplers operated in turbulent conditions since they were fixed to a stirrer bar with cable ties. The tank water (volume of 41 L) was spiked with 100 μL OTC mixture in ethanol/methanol and the concentration of each OTC is presented in Table 5. Two replicate samplers were retrieved at each occasion and the water was renewed with equally spiked UHQ-water. The OTC concentrations were measured in spot water

samples taken from old and renewly spiked water. The stirring speed was 90 rpm (33 cm s^{-1}) and the temperature 18 °C during the whole test. The trial was conducted in dark room.

3.4 Flume experiments

Further experiments were performed in a ring-shaped rotating flume with diameter of 2 m (Fig. 3). The width of the flume was 20 cm and the height of the water surface 14 cm which produced a total volume of 158 L. The flume was rotated to obtain a constant water flow. The length of the wake caused by samplers was first studied with placing a Chemcatcher sampler to the flume using different rotation speed, and spiking a small amount of food dye to the water in front of the sampler. The behavior and the dissolution of the dye were ocularly observed. The perpendicular Chemcatcher caused turbulence to the flume water but its effect was vanished after the flume had rotated about one eighth of the turn, which is equal to the length of 79 cm. With this test we could confirm that water flow had stabilized and the turbulence caused by sampler sets did not have an effect on the other samplers since they were placed at four places further than 79 cm from each other (Fig 3). The flume was filled with UHQ-water and spiked with 2.5 mL of solution containing MBT, DBT and TBT in ethanol/methanol. Their nominal concentrations are presented in Table 5. Since there were only eight samplers in the flume, the amount of OTCs was estimated to be high enough to be sufficient for the samplers without further addition. No solid matter was available for OTCs and they were mainly expected to remain in soluble form. The effect of rotation speed and the orientation of the passive sampler were studied on the accumulation of the compounds to the receiving phase.

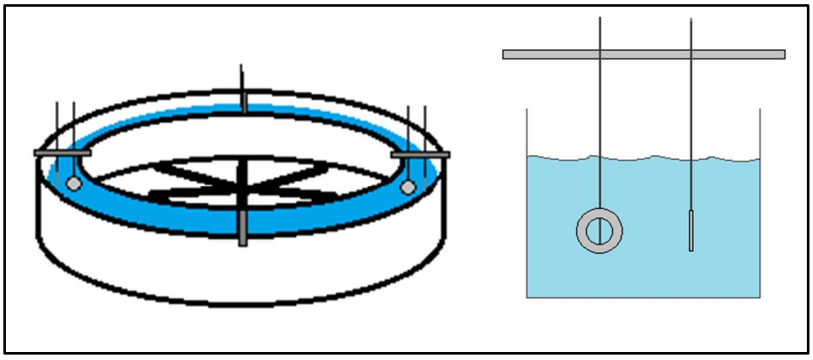

Fig. 3 Flume schematic (left) and a cross-section of the deployment of samplers (right)

Two tests were performed with different rotation speeds, generating a flow velocity of 7 cm s^{-1} (Experiment 1) and 12 cm s^{-1} (Experiment 2). The Experiment 2 was conducted five weeks after the Experiment 1 and the tank was emptied and cleaned with UHQ-water and ethanol between the experiments and at the beginning the flume was rotated without samplers to stabilize the OTC concentration. Water temperature during the experiments was 15 °C and the test room was kept dark. Eight Chemcatcher samplers were deployed in one test and four of them were fixed into the flume perpendicular to the water flow and the other four were placed in parallel position. Two parallel and two

perpendicular samplers were retrieved after 5 and 7 days of exposure. Since the perpendicular samplers cause more turbulence to the water, they were fixed in place together with parallel sampler at four places inside the flume. In perpendicular position the area of the exposed receiving phase of the sampler towards to the water flow was the largest which caused the maximum turbulence on the water flow. In the parallel fixing the sampler was exposed sideways, and hence it disturbed the water flow much less than in perpendicular position. The concentration of OTCs was determined in tank water at days 0, 5 and 7. One sample was also taken at day 0 before spiking the tank water with standard solution. Also blank samples were analysed in each sample batch.

4 Results and discussion

4.1 The effect of flow velocity and sampler orientation on the passive sampling process

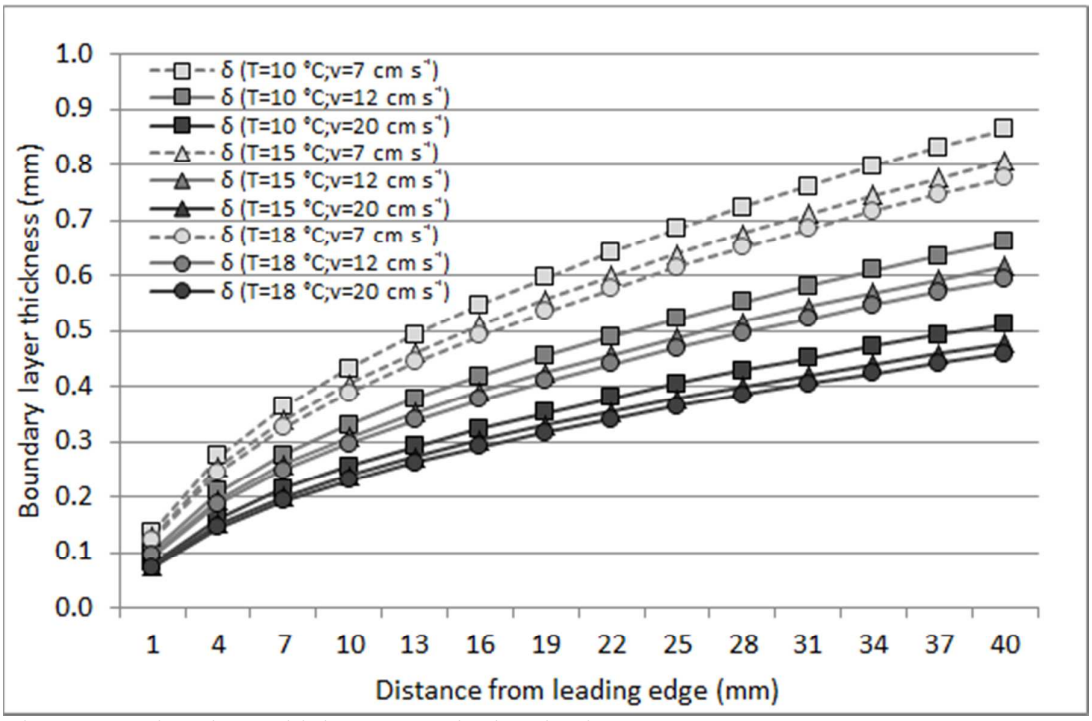

Fig. 4 Boundary layer thickness as calculated using Eq. 3

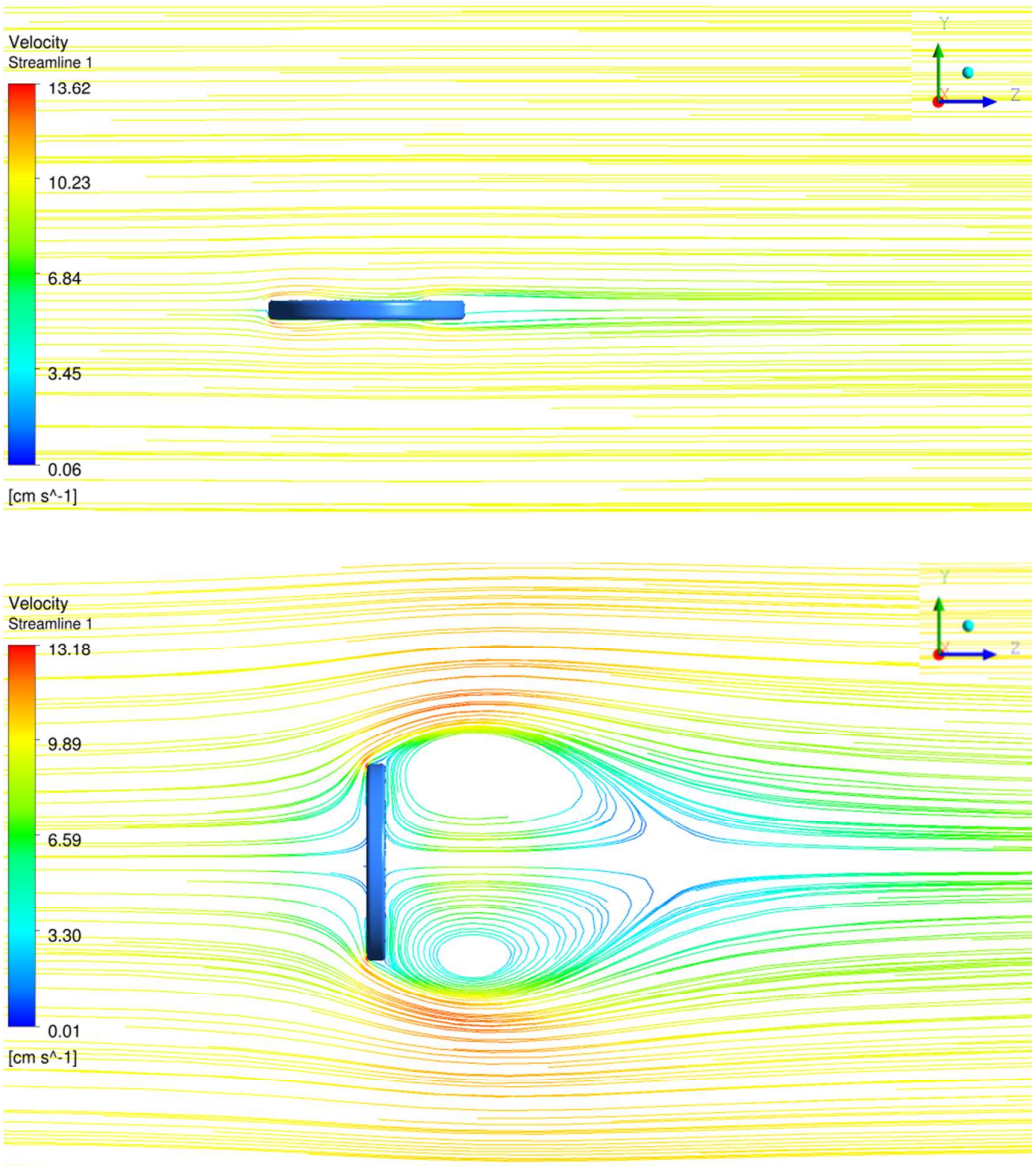

Fig. 5 Streamlines in the case, when the Chemcatcher is oriented 0 (upper) or 90 (lower) degrees against the flow at velocity of 10 cm s^{-1}

Fig. 4 shows the calculated (Eq. 3) thickness of the velocity boundary layer in various temperatures and flow velocities. The layer thickness varied, for example in the middle of the receiving phase (distance from the leading edge was 22 mm) it ranged from 0.34 mm (highest flow velocity and temperature) to 0.64 mm (lowest flow velocity and temperature). Within this layer the viscous forces prevail over the turbulent forces. The thickness of the boundary layer in environmental conditions has been observed to vary from 0.010 mm to 1 mm being thinner in extremely turbulent or high water flow.[30,31]

In Figs. 5-6 a snapshot of numerical simulations concerning the effect of sampler orientation on flow velocity field is presented. When the sampler is in parallel position with the flow, it causes first a stagnant region as the flow passes over the sampler body (Fig. 5, upper). Then vortex formation slightly increases local velocity and decreases it again. After leaving the sampler the flow structure is restored in a fairly

short distance. When the sampler is positioned perpendicularly against the flow two vortexes are formed on the back side of the sampler (Fig. 5, lower) and the wake after the sampler is as its longest. If the sampler is oriented 45 degrees towards to the flow, the velocity is quite evenly distributed over the sampler surface (Fig. 6, upper). One large vortex is formed behind the sampler and the length of the wake after the sampler has increased significantly when compared to the parallel case (Fig. 5, upper). The relative pressure distribution on sampler surface shows higher pressure on upstream side than the downtream side (Fig. 6, lower).

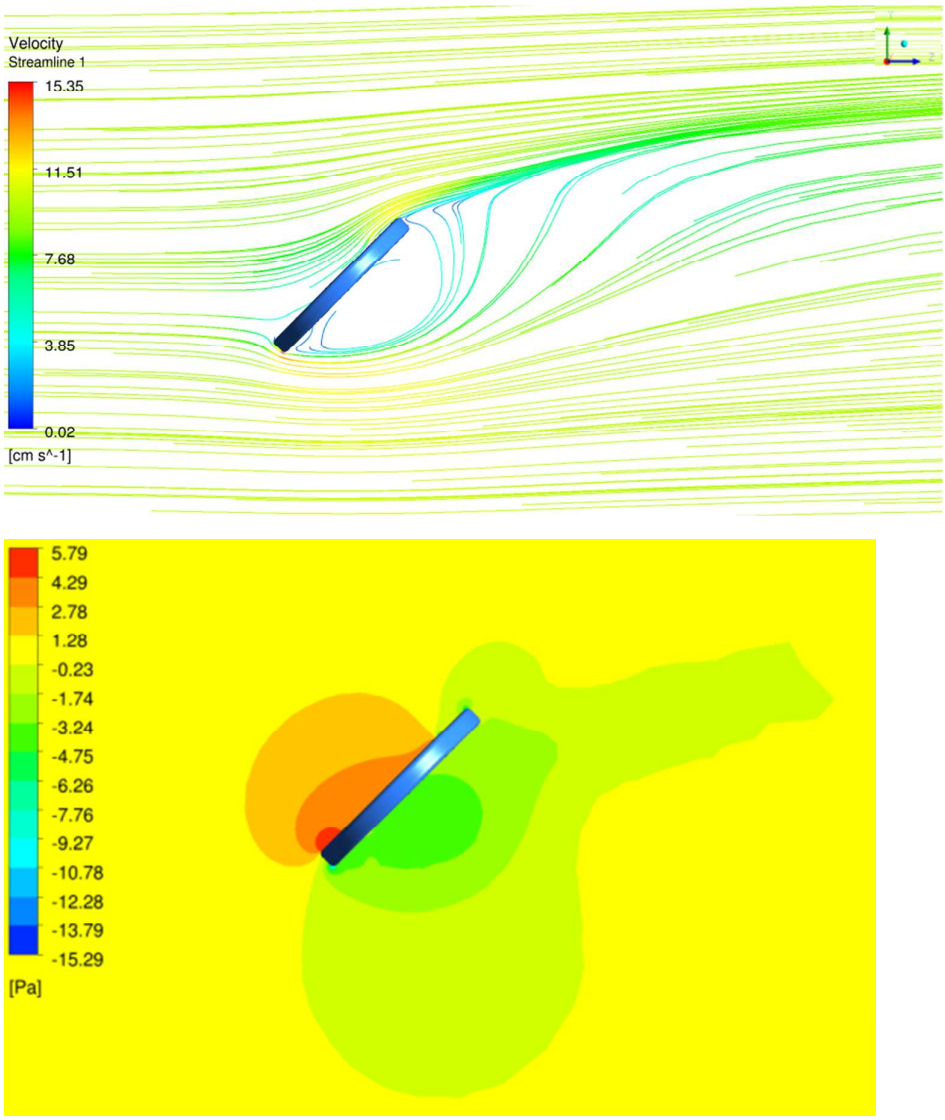

Fig. 6 Streamlines (upper) and relative pressure distribution on the Chemcatcher surface (lower) in the case, when the sampler is oriented 45 degrees against the flow. Note that the flow comes from the left side at velocity of 10 cm s^{-1}

The length of the wake behind the sampler was determined as the length of the region, where the deviation of the local flow velocity was 10 % or less from the main flow velocity (Table 2.). The results confirm the ocular observations, where the length of the wake was determined to 79 cm at maximum (see

chapter "Flume experiments"). Simulated results also support that the flow field structure was restored after each sampler pair, which were placed at the distance of 1.58 m from each other.

Table 2 Wake length (cm) during different flow and sampler position simulations

Flow velocity ($cm\ s^{-1}$)	Sampler orientation		
	Parallel	45° angle	Perpendicular
7	13	31	44
15	20	43	62

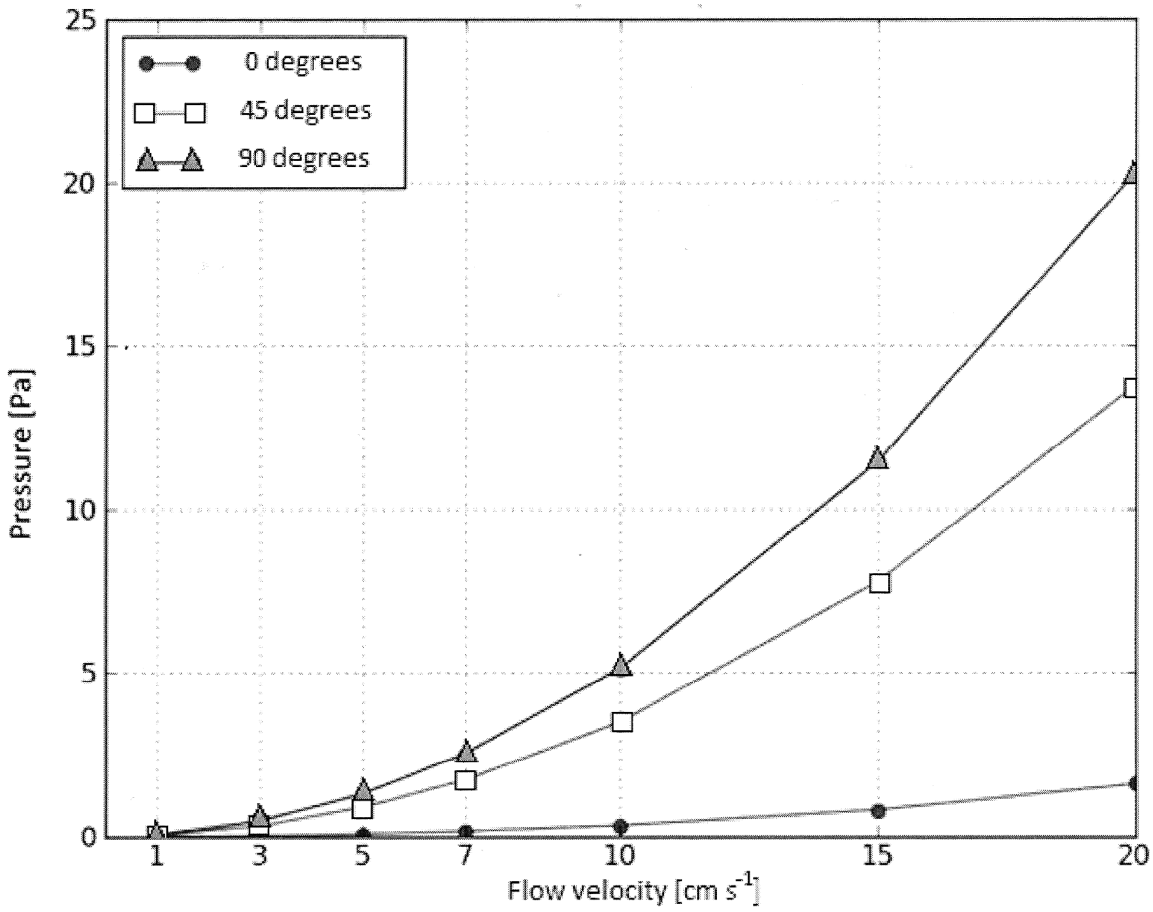

Fig. 7 The relative pressure exerted by the flowing water on the surface of the Chemcatcher sampler when the sampler is tilted to 0, 45 or 90 angle.

The accumulation of molecules in the boundary layer near the receiving phase from the surrounding media is dependent on the pressure exerted by the flowing fluid. Simulation results demonstrate that the pressure grows nonlinearly with flow velocity and tilting of the surface increases pressure significantly (Fig. 7). It seems that effect of flow velocity dominates pressure (sampling) over the orientation in particular with high flow velocities. Our analytical calculations indicate that the boundary layer thickness decreases with increasing flow velocity as well as increasing water temperature (Eq. 3 and Fig. 4)

4.2 Calibration trial

The sampling rate R_S was determined by studying the uptake of each OTC in passive sampler during the laboratory test and the results are presented in Table 3. The uptake of OTCs was linear during the whole calibration time of nine days, as expected. Therefore the uptake can be considered to remain in linear region also in flume experiments which also lasted for nine days and had much less turbulent conditions. The correlation coefficients were significant on the 0.1 % risk level except the one for DOT, which was significant on 1 % risk level. TBT and MPhT had the highest R_S followed by DBT. The pre-concentration capacity of the receiving phase during the 9 days deployment can be expressed as an equivalent sampled volumes were R_S is multiplied with deployment time (Table 4).[16] Aguilar-Martinez et al.[16] obtained equivalent sampled volumes of 0.15-0.31 L for MBT, 1.9-2.9 L for DBT, 1.5-2.8 L for TBT and 0.8-2.7 L for TPhT, which they only studied. Our volumes were several times higher, despite both volumes were calculated based on 14 day deployment. This is due to that our Chemcatcher configuration did not include the diffusion membrane on top of the receiving phase, which decreases the uptake of chemicals. However, both studies indicated that TBT and DBT had the highest sampling rates R_S. In our trial only TeBT, DOT and TOT appeared to have low sampling rates (Table 4) despite their average concentrations in water during the trial were as high as 480 ± 210 ng L^{-1}, 1200 ± 400 ng L^{-1} and 870 ± 60 ng L^{-1}, respectively (Table 5). Still the content of all studied OTCs measured in the samplers increased with deployment time.

Table 3 Linear regressions of the accumulation of OTCs in samplers during the calibration trial (n=8, for each OTC)

Compound		Slope (ng d^{-1})	Correlation coefficient (r)
MBT	Monobutyltin	210.6	0.934***
DBT	Dibutyltin	528.4	0.930***
TBT	Tributyltin	629.4	0.977***
TeBT	Tetrabutyltin	2.8	0.931***
MPhT	Monophenyltin	639.6	0.932***
DPhT	Diphenyltin	5.3	0.902***
TPhT	Triphenyltin	8.0	0.978***
MOT	Mono-octyltin	34.4	0.912***
DOT	Dioctyltin	12.4	0.876**
TOT	Trioctyltin	4.5	0.897***

***Significant on 0.1 % risk level

**Significant on 1 % risk level

Table 4 Chemcatcher sampling rates (R_S) and equivalent sampling volumes during 14 days for OTCs (n=8, for each OTC)

Organotin compound		Sampling rate, R_S [mL day^{-1}]	Sampled volume
MBT	Monobutyltin	0.454 ± 0.051	6.35 ± 0.72
DBT	Dibutyltin	0.702 ± 0.093	9.83 ± 1.31
TBT	Tributyltin	0.877 ± 0.052	12.28± 0.73
TeBT	Tetrabutyltin	0.010 ± 0.001	0.14 ± 0.02
MPhT	Monophenyltin	0.129 ± 0.015	1.80 ± 0.21
DPhT	Diphenyltin	0.472 ± 0.112	6.61 ± 1.56
TPhT	Triphenyltin	0.398 ± 0.019	5.57 ± 0.27
MOT	Mono-octyltin	0.140 ± 0.024	1.95 ± 0.33
DOT	Dioctyltin	0.018 ± 0.003	0.26 ± 0.04
TOT	Trioctyltin	0.010 ± 0.002	0.15 ± 0.03

Table 5 Nominal and measured OTC concentrations during the laboratory experiments

OTC	Calibration trial (ng L^{-1})		Flume experiment 1 (ng L^{-1})	Flume experiment 2 (ng L^{-1})	Nominal concentrations (ng L^{-1})	
	After spiking	After 2-3 days			Calibration trial	Flume experiment
MBT	790 ± 80	81 ± 8	36 ± 22	27 ± 22	301	456
DBT	1100 ± 300	200 ± 110	67 ± 25	210 ± 80	303	283
TBT	1200 ± 500	180 ± 110	45 ± 2	150 ± 120	284	172
TeBT	480 ± 210	3 ± 2			280	
MPhT	7900 ± 870	1200 ± 100			766	
DPhT	10 ± 5	6 ± 4			6	
TPhT	30 ± 5	4 ± 3			1	
MOT	400 ± 80	27 ± 8			267	
DOT	1200 ± 400	48 ± 26			360	
TOT	870 ± 60	72 ± 36			381	

During the calibration trial the spot samples were taken at days 0, 2, 5, 7 and 9 before and after replacing the tank water with freshly spiked one. The measured concentrations of OTCs in water differed from the nominal ones (Table 5). The measured concentrations were used for calculating the sampling rates R_S because that concentration indicates the part of OTCs which is in dissolved form and available for the passive samplers to collect. The TPhT and DPhT concentrations in water were low assumably due to their hydrophobic character since they tend to find particles where to attach.[36] The variation of spot sample concentrations can also occur from the attachment of OTCs in the walls of the water tank. Huang[37] studied several container materials (e.g. glass, polycarbonate, Teflon etc.) and observed that all of them adsorbed OTCs which may lead to underestimation of OTC concentrations in water samples. The aquatic concentrations measured during flume tests at days 0, 5 and 7 are also presented in Table 5. The concentrations of TBT, DBT and MBT in blank samples were 0.5 ng L^{-1}, 3.9 ng L^{-1} and 2.7 ng L^{-1} in Experiment 1 and 3.1 ng L^{-1}, 7.7 ng L^{-1} and below limit of detection in Experiment 2, respectively.

The sampling rate depends on the properties of the studied substances, material of the receiving phase and in addition, several environmental conditions prevailing during the sampling. Vermeirssen et al.[38] studied the accumulation of different types of pollutants (log K_{OW} between -2.6 and 3.8) on Chemcatcher with SDB receiving phase. They observed that the sampling rate increases with the log K_{OW} of the studied substance as well as elevated temperature and flow rate. The ideal situation would be to determine the sampling rate under realistic flow rates and conditions in natural waters.

Flume experiments

The nominal concentrations and measured concentrations of OTCs in aquatic phase varied between the experiments (Table 5). After five days of the first experiment the accumulation factors (AFs) of MBT, DBT and TBT were somewhat higher in samplers deployed in parallel position (Fig. 8). The differences between the sampler orientations were stabilized after seven days of exposure. In Experiment 2 the water flow was higher and the differences between the orientations of the Chemcatchers were smaller than in Experiment 1. The AFs determined for DBT in calibration trial were equal to the ones obtained in Experiment 1. The AFs for MBT were also a bit more similar to Experiment 1 than Experiment 2. For TBT major differences between the AFs determined based on different trials was not observed. With the prevailing precision our experiments were conducted it seems that the orientation of the sampler receiving phase towards the water flow does not have an effect on the accumulation of OTCs.

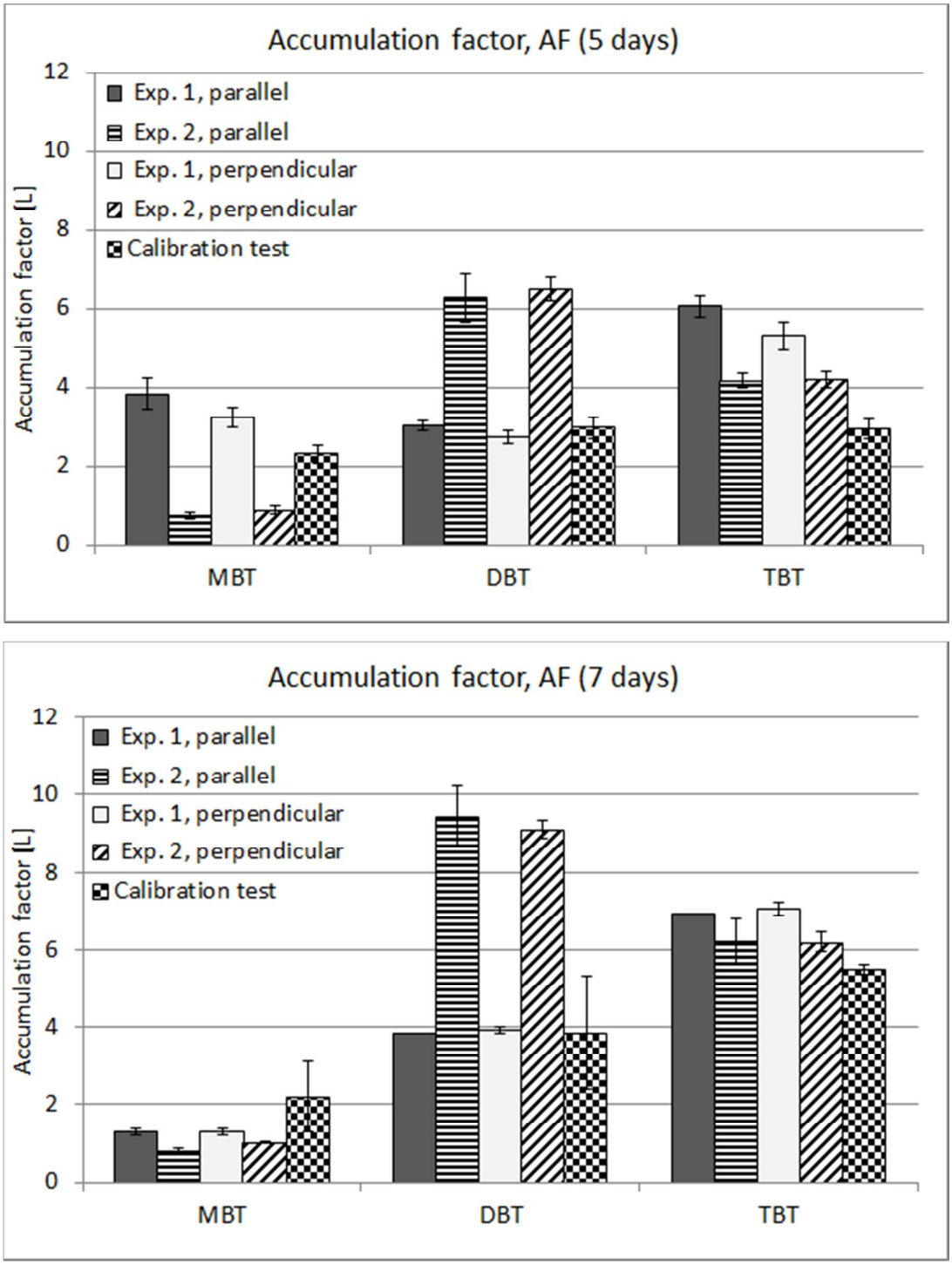

Fig 8 AFs of MBT, DBT and TBT determined in flume experiments

The concentrations of MBT, DBT and TBT in flume water ($C_{sampler}$) were calculated using the sampling rate R_S determined in laboratory calibration test and the concentration of substances accumulated to the passive sampler M_S during the flume experiments. Those were compared with average concentrations measured with conventional spot sampling at days 0, 5 and/or 7 depending on the deployment time of passive samplers. The results for OTCs are plotted in Fig. 9. According to literature the concentrations estimated from passive sampler data tend to be lower than the ones determined from spot samples[39] since in natural waters the contents determined with spot sampling contain also particle bound fraction of

studied compounds. In this study the results suggest rather good response with both sampling methods which may be due to lack of attractive particles in laboratory tests. This implies that only the dissolved part of OTCs is collected with both sampling techniques. The orientation of the sampler had no influence in these results.

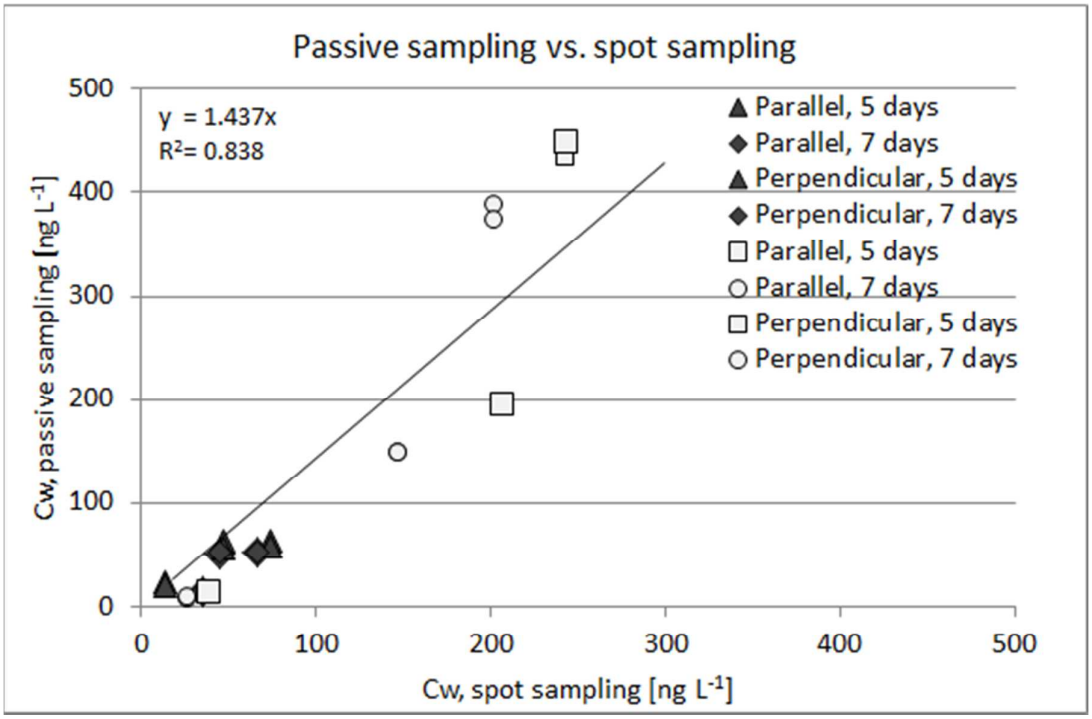

Fig. 9 OTC concentrations determined with spot sampling vs. passive sampling. Black labels denote Experiment 1 and white labels Experiment 2.

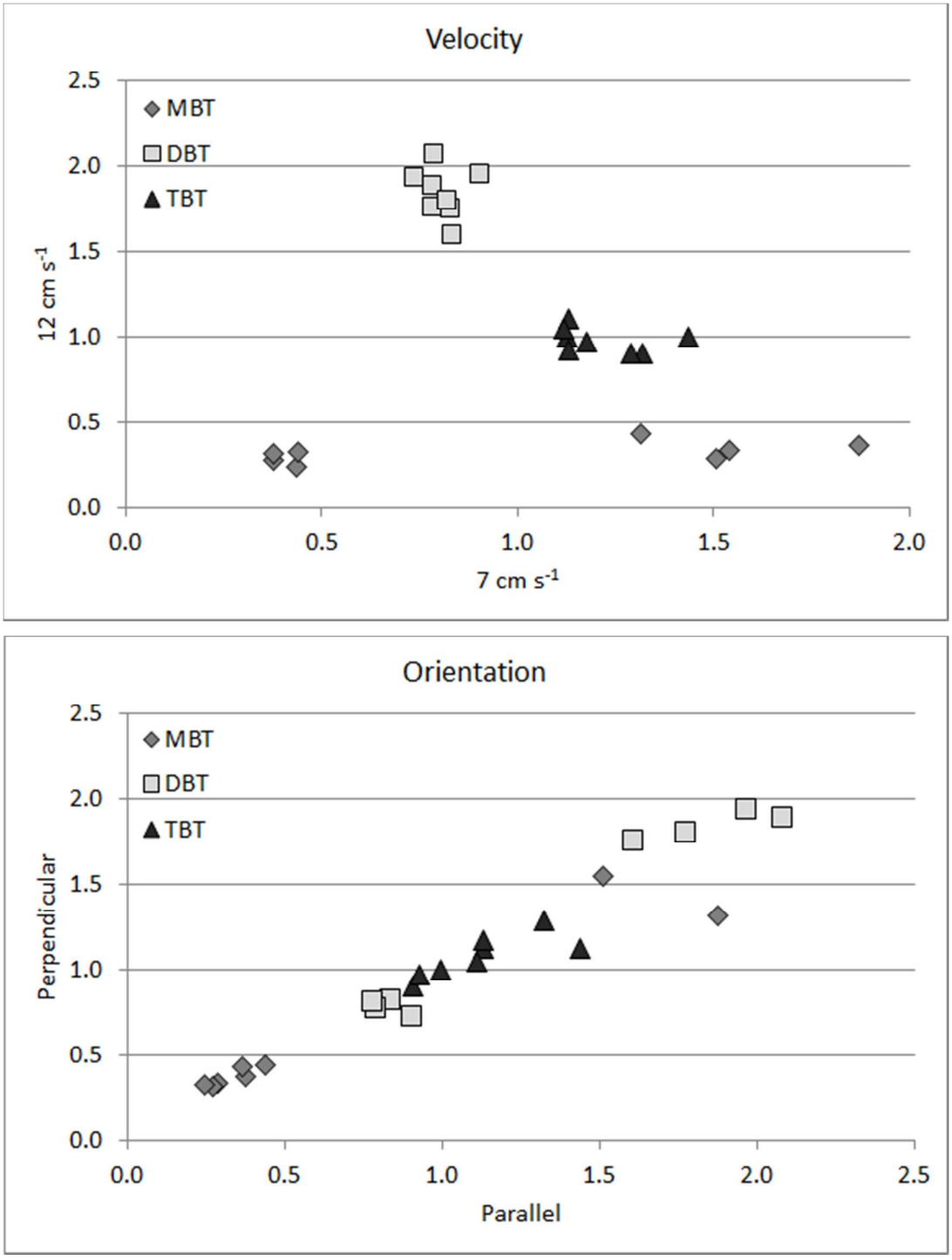

Fig. 10 The effect of flow velocity and orientation on the $C_{sampler}/C_{water}$ of OTC

The transformation of OTCs in water during the trials was not concerned since it was minimized by conducting the tests in dark and below room temperature (at 15 °C or 18 °C) as well as using UHQ-water. However, the concentration of each OTC was monitored within the trials.

The accumulation of MBT and TBT seemed to remain quite constant with flow velocity of 12 cm s^{-1} (Fig. 10, upper). When the flow velocity was 7 cm s^{-1} the accumulation of MBT and TBT was observed

to be higher or equal than with the velocity of 12 cm s^{-1}. One possible implication is that the sampling rate, which was determined in calibration test and used to calculate the $C_{sampler}$, did not represent the conditions prevailing in the flume test for MBT and TBT. For DBT the accumulation seemed to increase with higher flow velocity. In our laboratory studies the orientation of the sampler did not seem to have an effect on accumulation of the compounds (Fig. 10, lower). In different context it has been recognized that the orientation has measurable but small effects to the mass fluxes across the boundary layer.[40]

Previously it has been argued that increasing velocity of water flow automatically would increase the sampling rates and thus the amount of accumulated material. As one can observe from Fig. 10 this is not necessary true. Increased velocity has increased the accumulated material for DBT but for MBT and TBT it is almost the opposite.

According to other previous studies it is recognized that during the linear phase the passive sampler behaves like an infinite sink that is it keeps the molecules it has captured.[41,42]

The simulations suggest that the pressure on the surface of the sampler varies with sampler orientation e.g. tilting the sampler. Even though, based on our experiments, the orientation has no effect or the effect is very small on the accumulation of substances it could have an effect on promoting bio-fouling growth. Simulation shows that the sampler orientation has an effect on the location of stagnation point and to the average velocity near the sampler surface. Therefore one could argue that when velocity near the surface is small the biological processes have more time to occur and probability of biofouling increases. In natural waters this very area is most likely to face biofouling. This implies that it is beneficial to deploy the sampler in such a way that its orientation varies with respect to the main flow. This actually has been the way the samplers have been deployed in Finland and elsewhere. The deployment has been conducted in the epilimnium of the lake in such a way that the samplers were able to swing or flap due to wind induced waves and currents (Fig. 1). The deployment with fixed bars like one attached on the pier would not be favourable, since the local apparent flow due to the movement of the sampler is prevented and according to our simulations the stagnant region would also be unevenly distributed on the sampler surface. In the case of locally moving sampler the stagnant region is evenly distributed over the sampler and biofouling can be minimized by local rinsing.

The sampling rates are usually determined in a laboratory trial where the samplers are attached to a carousel and rotated during the calibration trial. The sampler therefore faces highly turbulent fluid flows which can instantaneously come from different directions to different parts of receiving phase. Although in field deployment the water flow is not necessary coming from one direction at constant velocity it rarely fluctuates as rapidly as in rotating carousel.

In our laboratory experiments the effect of sampler orientation on the accumulation of studied compounds was not observed. The increase of sampling intervals would have provided more information. However, in the flume tests the addition of extra samplers would have caused disturbance due to the reduced distance between the sampler sets. In that case the wake caused by sampler would not vanish but reaches the next set of samplers. In this study the determined sampling rates R_S were used to calculate the concentrations of OTCs during the flume experiments with controlled water flow. The observed correspondence between the analyte concentrations determined with passive sampling and the ones measured by spot sampling was adequate due to similar aquatic conditions and absence of the solid particles (Fig 9).

One hypothesis which could be derived from the results suggests that strong turbulence may cause underpressure on the surface of the receiving phase. The strong local underpressure due to high wave activity in water during strong wind forcing might increase the escaping probability of the captured molecules at least from the boundary layer. Furthermore the concentration of analytes can fluctuate due to turbulence, which might cause the decrease of the analyte content near the receiving phase. This again can derive the analytes to come off from the receiving phase because of the diffusion. One approach to avoid this is to deploy the samplers in deeper water layer with minor wave activity.

Conclusions

The performed laboratory experiments suggest that the orientation of the Chemcatcher passive sampler towards the water flow did not have an effect on the accumulation of OTCs considering the prevailing precision this study was conducted. The OTC concentrations calculated on the basis of Chemcatcher passive sampling data gave good correspondence when compared with conventional spot sampling results. This was because the tests were all carried out using UHQ-water with no particles disturbing the sampling of OTCs. In general the determination of sampling rate is conducted with UHQ-water but the deployment of samplers is e.g. in surface water with different prevailing conditions. Then the results obtained with spot and passive sampling techniques usually are dissimilar. The theoretical calculations and numerical simulation results show that Chemcatcher's ability to collect dissolved molecules increases, when the hydrodynamic conditions are non-stagnant. There obviously are limits, when they start to prevent the optimum collection ability but that remains as a subject for further studies. However, when taking account these issues the Chemcatcher passive sampler provides a practical tool for implementation of WFD.

Acknowledgements

We would like to thank Dr. Juha Järvelä from Aalto University for arranging the loan of the flume. M.Sc. Kimmo Niskanen is greatly appreciated for his invaluable contribution on performing the flume experiments and B.Sc. Tiina Virtanen for her contribution on the calibration trial. M.Sc. Petri Nieminen is also greatly acknowledged for his contribution. This study was supported by Maj and Tor Nessling foundation and Maa- ja vesitekniikan tuki ry.

References

1 EC, Directive 2000/60/EC, 2000, L327:1–72.

2 EC, Directive 2008/105/EC, 2008, L348:84–97.

3 J. P. Meador and C. A. Rice, Mar. Environ. Res., 2001, 51, 113-129.

4 T. Gorecki and J. Namiesnik, Trends Anal. Chem., 2002, 21, 276-291.

5 J. Namiesnik, B. Zabiegala, A. Kot-Wasik, M. Partyka and A. Wasik, Anal. Bioanal. Chem., 2005, 381, 279-301.

6 B. Vrana, G. A. Mills, I. J. Allan, E. Dominiak, K. Svensson, J. Knutsson, G. Morrison and R. Greenwood, Trends Anal. Chem., 2005, 24, 845-868.

7 B. Vrana, E.L.M Vermeirssen, I.J. Allan, J. Kohoutek, K. Kennedy, G.A. Mills and R. Greenwood, Position Paper, Norman Association, No W604002510, 2009.

8 J. K. Kingston, R. Greenwood, G. A. Mills, G. M. Morrison and L. B. Persson, J. Environ. Monit., 2000, 2, 487-495.

9 R. Aguilar-Martinez, M. M. Gomez-Gomez, R. Greenwood, G. A. Mills, B. Vrana and M. A. Palacios-Corvillo, Talanta, 2009, 77, 1483-1489.

10 I. J. Allan, B. Vrana, R. Greenwood, G. A. Mills, B. Roig and C. Gonzalez, Talanta, 2006, 69, 302-322.

11 I. J. Allan, J. Knutsson, N. Guigues, G. A. Mills, A. M. Fouillac and R. Greenwood, J. Environ. Monit., 2008, 10, 821-829.

12 L.B. Persson, G.M. Morrison, J.-U. Friemann, J. Kingston, G.A. Mills and R. Greenwood, J. Environ. Monit., 2001, 3, 639-645.

13 L. B. Blom, G. M. Morrison, J. Kingston, G. A. Mills, R. Greenwood, T. J. R. Pettersson and S. Rauch, J. Environ. Monit., 2002, 4, 258-262.

14 I. J. Allan, J. Knutsson, N. Guigues, G. A. Mills, A. M. Fouillac and R. Greenwood, J. Environ. Monit., 2007, 9, 672-681.

15 R. Aguilar-Martinez, R. Greenwood, G. A. Mills, B. Vrana, M. A. Palacios-Corvillo and M. M. Gomez-Gomez, Int. J. Environ. Anal. Chem., 2008a, 88, 75-90.

16 R. Aguilar-Martinez, M. A. Palacios-Corvillo, R. Greenwood, G. A. Mills, B. Vrana and M. M. Gomez-Gomez, Anal. Chim. Acta, 2008b, 618, 157-167.

17 B. Vrana, G. A. Mills, E. Dominiak and R. Greenwood, Environ. Pollut., 2006, 142, 333-343.
18 H. Ahkola, S. Herve and J. Knuutinen, Environ. Sci. Pollut. Res. Int., 2014, 21, 9182-9192.
19 H. Ahkola, J. Juntunen, S. Herve, K. Krogerus, T. Huttula, P. Tuominen and A. Witick Monitoring of organotin compounds with passive samplers in sewage water treatment plant, manuscript.
20 A.K. Karjalainen, K. Siimes, M.T. Leppänen and J. Mannio, Contaminant monitoring in Finnish surface waters loaded by agriculture and forestry, Monitoring results 2007-2012, Finnish Environment, manuscript.
21 J. Juntunen, H. Ahkola, J. Ropponen, K. Krogerus, S. Herve and T. Huttula, 3-D modelling of harmful substances in Lake Päijänne, manuscript.
22 T. Lobpreis, B. Vrana, E. Dominiak, K. Dercova, G. A. Mills and R. Greenwood, Environ. Pollut., 2008, 153, 706-710.
23 R. Gunold, R. B. Schafer, A. Paschke, G. Schuurmann and M. Liess, Environ. Pollut., 2008, 155, 52-60.
24 E. L. M. Vermeirssen, J. Asmin, B. I. Escher, J. H. Kwon, I. Steimen and J. Hollender, J. Environ. Monit., 2008, 10, 119-128.
25 M. Hoch, Appl. Geochem., 2001, 16, 719-743.
26 P. Mayer, J. Tolls, L. Hermens and D. Mackay, Environ. Sci. Technol., 2003, 37, 184a-191a.
27 A. Kot-Wasik, B. Zabiegala, M. Urbanowicz, E. Dominiak, A. Wasik and J. Namiesnik, Anal. Chim. Acta, 2007, 602, 141-163.
28 J. N. Huckins, G. K. Manuweera, J. D. Petty, D. Mackay and J. A. Lebo, Environ. Sci. Technol., 1993, 27, 2489-2496.
29 M. Shaw, G. Eaglesham and J. F. Mueller, Chemosphere, 2009, 75, 1-7.
30 B. Vrana, G. A. Mills, M. Kotterman, P. Leonards, K. Booij and R. Greenwood, Environ. Pollut., 2007, 145, 895-904.
31 R. W. Gale, Environ. Sci. Technol., 1998, 32, 2292-2300.
32 L. Prandtl Essentials of Fluid Dynamics, Blackie and Son, London, 1969, 117p.
33 F.P. Incropera, D.P. Dewitt, Fundamentals of Heat and Mass Transfer, 5th Editon, Wiley, New York, 2002.
34 K. Mann and J. Lazier, Dynamics of Marine Ecosystems, Blackwell, Oxford, 1991, p. 466.
35 H. Ahkola, doctoral thesis, 0357-346X ; no. 154. University of Jyväskylä, Finland, 2012.
36 X. H. Wang, H. S. Hong, D. M. Zhao and L. Y. Hong, Mar. Pollut. Bull., 2008, 57, 419-424.
37 J. H. Huang, Int. J. Environ. Anal. Chem., 2004, 84, 255-265.
38 E. L. M. Vermeirssen, C. Dietschweiler, B. I. Escher, J. van der Voet and J. Hollender, Anal. Bioanal. Chem., 2013, 405, 5225-5236.
39 N. Mazzella, S. Lissalde, S. Moreira, F. Delmas, P. Mazellier and J. N. Huckins, Environ. Sci. Technol., 2010, 44, 1713-1719.

40 C. J. Kobus and G. L. Wedekind, Int. J. Heat Mass Transfer, 2002, 45, 1159-1163.

41 B. Vrana, G. Mills, R. Greenwood, J. Knutsson, K. Svensson and G. Morrison, J. Environ. Monit., 2005, 7, 612-620.

42 R. Greenwood, G. A. Mills and B. Vrana, Comprehensive Analytical Chemistry Series, vol. 48 Elsevier, Amsterdam Barcelo D. (Ed.), 2007, 453 p.