

# Monitoring and Modelling of Butyltin Compounds in Finnish Inland Lake

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## Research Article

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# 1 **Monitoring and modelling of butyltin compounds in Finnish** 2 **inland lake**

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## 15 **Abstract**

16 Butyltin compounds (BTCs) in surface waters is seldom studied due to their low concentrations and  
17 limitations of analytical techniques. In this study we measured total concentration of BTCs with grab water  
18 sampling, dissolved concentration with passive samplers and particle bound fraction with sedimentation  
19 traps in Finnish inland lake. The sampling was conducted from May to September during two study years.  
20 The differences between sampling techniques and the concentrations were obvious. E.g. tributyltin (TBT)  
21 was detected only in 4-24 % of the grab samples when the detection with passive samplers was 93% and  
22 with sedimentation traps 50%. The dissolved BTC concentrations measured with grab and passive sampling  
23 suggested hydrological differences between the study years. This was confirmed with flow velocity  
24 measurements. However, the annual difference was not observed in BTC concentrations of settled particle.  
25 The extreme value analysis suggested that grab sampling and sedimentation trap sampling results contain  
26 more extreme peak values than passive sampling. This indicates that BTCs are present in surface water in  
27 trace concentrations despite they are not detected with all the sampling techniques.

28 The assumption that WWTP, located in the study area, was the source of BTCs was not valid as elevated  
29 BTC concentrations were detected also at the reference site, located upstream of WWTP. Computational  
30 modelling and back tracking simulations also supported the concept that WWTP cannot be the only source  
31 but BTCs can come even from upstream of the sampling area where there is e.g. wood processing industry.

32 **Keywords:** *butyltin compounds, monitoring, surface water, modelling, back tracking simulation, passive sampling*

## 33 **1 Introduction**

34 Organotin compounds (OTCs) have been widely used in different industrial applications for over 50 years.  
35 (Champ and Seligman, 1996, Fent 1996, Hoch 2001, Dubalska et al. 2013) Due to their versatile properties  
36 OTCs have been utilized as biocides, pesticides, wood preservatives, catalysts and stabilizing agents in  
37 polymers due to their versatile properties. OTCs, especially tri-substituted ones, are toxic to variety of  
38 aquatic organisms (Bryan and Gibbs 1991, Hoch 2001, Aguilar-Martinez et al. 2008a) and the  
39 hazardousness of tributyltin (TBT) for aquatic organisms appears below  $\text{ng L}^{-1}$  concentration levels (Bryan  
40 and Gibbs 1991, Díez et al. 2002). The Annual Average Environmental Quality Standard (AA-EQS)  
41 concentration for TBT is  $0.2 \text{ ng L}^{-1}$  and the maximum allowable concentration (MAC-EQS)  $1.5 \text{ ng L}^{-1}$  (EC  
42 2008a). Considering low aquatic concentrations, the detection of OTCs requires sensitive analytical  
43 techniques.

44 The main source where tri-substituted OTCs entered to aquatic environment was their use in antifouling  
45 paints of ship industry (Champ and Seligman, 1996). In 1st July 2003 EU restricted the use of OTC  
46 containing ship paints in vessels flying the flag of EU country. (EC 2003). In 1st January 2008 the ships  
47 entering to EU country must either have paint with no OTCs or cover OTC-paint with OTC-free paint layer  
48 (EC 2008b). In 2010 the use of tri-substituted OTCs in items which include more than 0.1 % by weight of  
49 tin was banned and in 2012 the restriction was extended to cover dibutyltin (DBT) and dioctyltin (DOT)  
50 EC 2009). Monobutyltin (MBT) and DBT have been used as PVC stabilizers in packaging materials from  
51 which they can leach to foodstuff and beverages (Takahashi et al. 1999, Hoch 2001). Despite the restrictions  
52 these substances are still found in Finnish inland waters where they are released for example via wastewater  
53 treatment plants (WWTP) (Mannio 2011, Vieno 2014, Ahkola et al. 2015).

54 Estimation of the sources and transport of BTC's and especially TBT is difficult due to their low aquatic  
55 concentrations. BTCs are highly attracted by solid particles or bioaccumulated and commonly determined  
56 in sediment samples or aquatic organisms (Page et al. 1996, Harino et al. 1998, Berto et al. 2007, Cole et  
57 al 2018). They also have long transformation chain from tertbutyltin (TeBT) to MBT  
58 (TeBT→TBT→DBT→MBT). The degradation occurs via loss of butyl group caused mainly by photolysis

59 (ultraviolet UV irradiation), bacteria (biological cleavage) or nucleophile or electrophile reagents (chemical  
60 cleavage) (Hoch 2001). The transformation rates are slow when BTCs are attached to particles but notably  
61 faster as they are in their dissolved form (Juntunen et al. 2020). In water column TBT loss occurs mainly  
62 via microbial transformation or adsorption to particles (Stewart and de Mora 1990). When TBT  
63 concentration is low, e.g. in surface water, the bacteria transform it readily, whereas high concentrations of  
64 TBT enriched to sediments inhibits the bacterial activity. The degradation of BTCs in natural waters is  
65 poorly reported which can be due to low aquatic concentrations and limits of analysing techniques. The  
66 studies consider mainly the degradation of TBT in marine environment with tests conducted in a laboratory  
67 conditions (Lee et al. 1989; Seligman et al. 1988) or using microbes isolated from sea water (Harino et al.  
68 1997; Kawai et al 1998, Sampath et al. 2012). However, these results cannot be directly applied to Finnish  
69 inland waters due to differences of microbes and high content of humic substances. The half-life of  
70 biological transformation of TBT varies from three days to several weeks depending on the water matrix  
71 and prevailing test conditions (pH, temperature, turbidity, light) (Stewart and de Mora 1990; Dowson et al.  
72 1996). Due to their low solubility the BTCs tend to attach to particles and sediment where their degradation  
73 is slow being from several weeks to years. The process is considerably slower in anaerobic than in aerobic  
74 sediments (Seligman et al. 1986). Sediments are still not a permanent sink for OTCs since due to mechanical  
75 resuspension they can dissolve back to water column (Page et al. 1996; Filipkowska et al. 2014). Particles  
76 can drift to unpolluted sites where e.g. tidal fluxes and dredging can cause resuspension of BTCs, favouring  
77 the DBT release over TBT (Dowson et al. 1993; Berto et al. 2007). In shallow lakes even waves created by  
78 storms and big boats can cause resuspension. Therefore, the dispersion of BTCs can be considered as  
79 potentially complex process.

80 Due to rather complex physical and chemical characteristics the behaviour of BTCs in aquatic environment  
81 requires complementary monitoring approaches. As the aquatic concentrations of BTCs are expected to be  
82 low, they can remain undetectable with conventional grab water sampling. Passive sampling techniques  
83 collect studied substances during the deployment time from days to weeks which enables the enrichment  
84 of trace concentrations to the measurable level. It has been recognised as a useful screening technique for  
85 several harmful substances (Kingston et al. 2000; Persson et al. 2001, Blom et al. 2002, Górecki and

86 Namieśnik 2002; Vrana et al. 2005a, 2005b; 2009; Allan et al. 2007, de la Cal et al. 2008, Gunold et al.  
87 2008, Sánchez-Bayo et al. 2013, Vermeirssen et al. 2013, Ahkola et al. 2013, 2014, 2015) and has been  
88 applied also in OTC monitoring (Aguilar-Martinez et al. 2008a, 2008b, 2011, Garnier et al. 2020). As a  
89 difference to grab sampling, that determines the total concentration of chemical, passive sampling collects  
90 only the dissolved part of the chemical which is considered to be the most bioavailable and most harmful  
91 part of the substance when considering the environmental effects (Kot et al. 2000, Aguilar-Martinez et al.  
92 2008b). Passive samplers give time weighted average (TWA) concentration of chemical during the  
93 sampling period. TWA concentration is calculated based on the accumulated amount of chemical,  
94 deployment time and the sampling rate which has been determined in a calibration trial (Kingston et al.  
95 2000; Vrana et al. 2006). Chemcatcher samplers has been developed and calibrated for detecting OTCs  
96 marine, sewage and inland waters (Aguilar-Martinez et al. 2008a, 2008b, 2011, Garnier et. al. 2020). As  
97 the passive samplers collect also undetermined, potentially bioavailable chemicals the sampler extracts  
98 have also been used in estimating toxicity of the freely dissolved chemical fraction (Jahnke et al. 2016).

99 Sedimentation traps were used to study the particle bound BTC fraction. The traps are deployed near the  
100 lake bottom for certain time priod (Bloesch and Burns, 1980, Schubert, et al. 2012, Kaitaranta et al. 2013,  
101 Wren at al 2019). Due to gravity the particles drifted with water flow will fall to the trap and the  
102 concentration of studied chemicals can be analysed from the particles.

103 The occurrence of BTCs (MBT, DBT and TBT) was studied in lake conditions with grab water-, passive -  
104 , and sedimentation trap sampling to estimate the concentration of total, dissolved and particle bound BTC  
105 fraction. The results were used in modelling calculations to assess the source and transportation of BTCs  
106 in the study area. The results of different sampling techniques are evaluated with extreme value analysis to  
107 recognize high instant peak concentrations from the prevailing concentration levels.

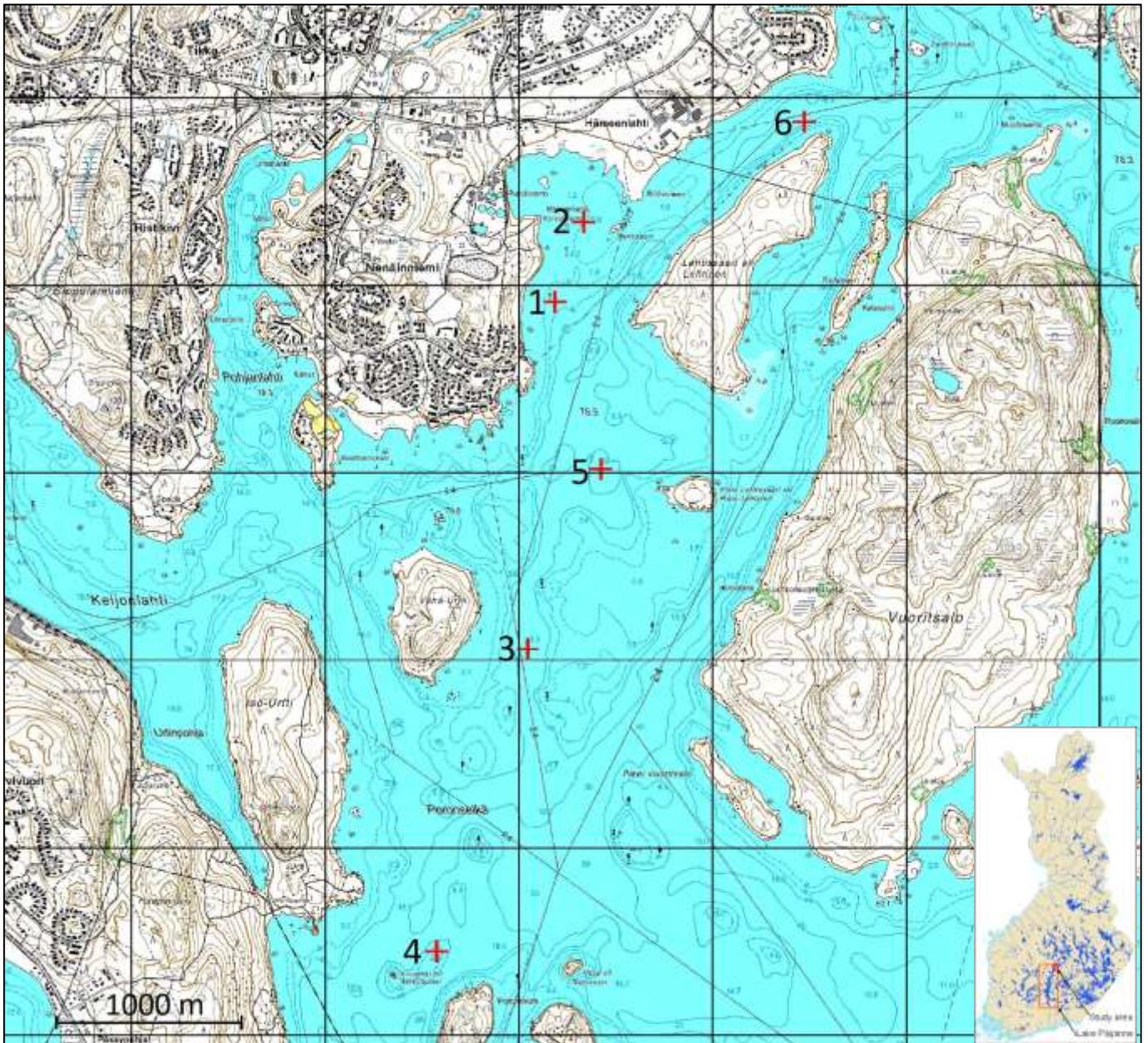
## 108 **2 Experimental**

109 The BTCs were monitored with passive samplers, sedimentation traps, and grab water samples in boreal  
110 lake. Sampling campaigns were conducted at six sampling sites from May to September for two years (Fig.

111 1). Passive samplers and sedimentation traps were deployed for two weeks' time period and grab samples  
112 were taken as the samplers and traps were replaced with new ones. In the first study year (1<sup>st</sup> year, 2012)  
113 ten consecutive passive sampler and sedimentation trap deployments were conducted and in the second  
114 year (2<sup>nd</sup> year, 2013) the number of sampling occasions was eight. The number of grab sampling occasions  
115 in 1st and 2nd study year was 11 and 9, respectively. In addition to comprehensive monitoring campaign  
116 we estimated computationally the probability that particles are released from the discharge pipe of the  
117 wastewater treatment plant (WWTP), located at site 1.

## 118 **2.1 Study area**

119 The study area was located in northern Lake Päijänne (62° 8.9467', 25° 37.6913') in Central Finland (Fig.  
120 1). The sampling site 1 is at the outflow of the WWTP which receives sewage waters from 150 000  
121 inhabitants as well as industrial waste waters (Lindholm-Lehto et al. 2018, Ahkola et al. 2016). During the  
122 study period the annual wastewater discharge was 40 000 m<sup>3</sup> d<sup>-1</sup> and in the beginning of the field trials  
123 WWTP was assumed to be the main source of BTCs. Sites 3-5 are situated downstream from the WWTP.  
124 Sites 4 and 5 are situated at the deepest locations of the study area. Due to water currents wastewaters are  
125 able to drift to site 2 but site 6 was considered as reference site which receives no effluent waters from  
126 WWTP. Validity of this assumption was assessed by modelling the probability of transportation of particles  
127 originating from the WWTP (Chapter 3.7). Detailed information about the WWTP is described in  
128 Lindholm-Lehto et al. 2018. Upstream of the study area is continuous waterway having summer houses,  
129 boats and piers on the shore. Also, wood processing industry is located about 60 km north from the Lake  
130 Päijänne. In the beginning of this study the assumption was that the possible pollution sources upstream  
131 were negligible or so far that the transportation of BTCs via small waterway was unlikely.



132  
 133 Fig. 1. Study area. The depth of the sites was 5 m (sites 1 and 2), 12 m (site 3), 20 m (site 4), 24 m (site 5)  
 134 and 14 m (site 6). Rapid Vaajakoski, the main source for through flow, is located north-east outside the  
 135 figure.

## 136 2.2 Sediment sampling

137 BTCs were determined in sediment samples cored with Limnos sediment sampler which contained series  
 138 of rings and enabled the slicing of sediment layers at exact thickness of 1 cm (Kansanen et al. 1991). The  
 139 samples were collected from five sampling sites (Fig. 1 sites 1, 2, 3, 5, 6) and three depths (0-1 cm, 1-3 cm  
 140 and 3-5 cm) to assess the presence of BTCs in old sediment layers. In the study area the sediment at depth  
 141 of 5 cm is about 10 years old (Paasivirta et al. 1990). If the settling velocity and the water quality have  
 142 remained quite the same the samples taken at depth 2-3 cm can be estimated to be about 5 years old.

### 143 **2.3 Passive sampling**

144 Three replicate Chemcatcher passive samplers with C-18 Empore disk and polycarbonate housing (Ahkola  
145 et al. 2015, 2016) were deployed at each sampling site (1-6, Fig. 1) for two weeks after which they were  
146 retrieved and replaced with new ones. Samplers were deployed 1 m below water surface. The samplers  
147 accumulate dissolved fraction of the chemical which, after the deployment time period, is extracted from  
148 the sampler. TWA concentrations of dissolved BTCs during the two weeks sampling period were calculated  
149 with using sampling rates determined in Ahkola et al. (2015, 2016). Method detection limit (MDL) was  
150 calculated from the analytical limit of detection ( $\text{ng sampler}^{-1}$ ) after 14 days deployment (Table 1).

### 151 **2.4 Sedimentation traps**

152 Sedimentation traps were deployed at each sampling site (1-6, Fig. 1) to study the amount of settling  
153 particles and measure the particle bound fraction of BTCs. Duplicate traps were placed 1 m above the lake  
154 bottom where they collected settled particles for two weeks. After that the samples were collected to glass  
155 jars, and the traps redeployed. The excess water was decanted and discarded, and the samples were stored  
156 at +4°C until analysis. BTCs were analysed from settled particles. The trap consisted of two acrylic tubes  
157 whose diameter (D) was 9.3 cm and the height (H) 50 cm H/D ratio being 5.4. The top part of the tube was  
158 open, but the bottom was sealed to trap the particles. The ratio of height and diameter (H/D) of the tube is  
159 essential to avoid the escaping of particles, Bloesch and Burns (1980) recommended H/D ratio of 5.  
160 According to Lau et al. (1979) the critical stream velocity at 15 °C for H/D ratio of 6.7 was  $26.2 \text{ cm s}^{-1}$  and  
161 for H/D 10 it was  $27 \text{ cm s}^{-1}$ . In this study the ratio was 5.4 so the escaping velocity was  $26.2 \text{ cm s}^{-1}$ . Such  
162 current velocities are extremely rare in Finnish lakes. In this study the currents were also measured at study  
163 sited (Chapter 2.7). The results are presented as dry weight (dw).

### 164 **2.5 Grab water sampling**

165 The concentrations of BTCs were monitored also with grab water samples which were taken every two  
166 weeks at the same time as the passive samplers and sedimentation traps were retrieved or emptied. The grab  
167 samples were taken in darkened glass bottles (1 L) from the depths of 1 meter below surface and one meter  
168 above the lake bottom. At sites 3-6 one grab sample was taken in the middle of the water column. Grab

169 sampling was not conducted at site 3 in the 2<sup>nd</sup> year. The samples were stored at +4°C and they were not  
 170 filtered before analysis. The results are presented as an average of concentrations which exceeded the limit  
 171 of detection (LOD) (Table 1).

## 172 2.6 Sample treatment and analysis

173 The Chemcatcher passive sampler contained C-18 Empore disk receiving phase (47 mm diameter, 3M  
 174 Agilent Technologies Finland Oy) attached to polycarbonate sampler housing (AlControl AB, Linköping,  
 175 Sweden) (Ahkola et al. 2015). After deployment the internal standard (tri-*n*-propyltin) was added to the  
 176 disk which was further extracted with acetic acid–methanol (3:1) in an ultrasonic bath for 10 minutes. The  
 177 sample was let stand for 10 minutes and the ultra-sonication was repeated. 4 mL acetate buffer (1 M, pH  
 178 5.4) was added, BTCs were derivatized with sodium tetraethylborate (NaB(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>) and extracted from  
 179 acetic acid-methanol-acetic acid mixture to hexane which was transferred to a sample vial and analysed  
 180 with GC-ICP- MS (Agilent 6890N gas chromatograph coupled to Agilent 7500ce ICP-MS) (ISO 17353,  
 181 2004, Alonso et al. 2002). After the gas chromatographic separation of BTCs they were quantified  
 182 according to Sn isotopes concentrations using internal standard technique and the results were expressed as  
 183 concentration of each BTC species. The sediment samples and settled particles from sedimentation traps  
 184 were treated according to passive sampler procedure and the BTC concentrations are expressed as dw. The  
 185 internal standard (tri-*n*-propyltin), acetate buffer (1 M, pH 5.4) and sodium tetraethylborate (NaB(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>)  
 186 was added to the grab water samples, the BTCs were extracted to hexane and analysed with GC-ICP-MS  
 187 Before analysis all the samples were stored at +4°C. The passive samplers, sediments and settled particles  
 188 were analysed within 7 days of retrieving. The grab samples were analysed the day after sampling. Blank  
 189 samples were processed and measured alongside every sample treatment. LOD for each sampling technique  
 190 is presented in Table 1.

191 Table 1. LOD of each sampling technique.

Sampling technique	MBT	DBT	TBT
Grab sampling (ng L <sup>-1</sup> )	0.50	0.50	0.20
Passive sampling (ng sampler <sup>-1</sup> )	0.10	0.10	0.10
Passive sampling (ng L <sup>-1</sup> )	0.016*	0.010*	0.0082*
Sedimented particles sampling (µg kg <sup>-1</sup> dw)	0.50	0.50	0.20

192 \* Method detection limit (MDL) calculated for 14 days deployment

## 193 **2.7 Monitoring of water flow**

194 The water flow was monitored with moored recording current meters (Aanderaa RCM-9) placed on sites  
195 1, 2 and 3 to observe the water currents and to estimate the transportation of BTCs in the study area. The  
196 flow was measured at depths 1.1 m (site 1), 1.0 m (site 2) and 2.0 m (site 3) and currents were recorded as  
197 a ten-minute average. Current were measured for 3.5 months in both study years covering the time of  
198 monitoring campaigns.

## 199 **2.8 Computational estimation of BTC sources**

200 Computational simulation was conducted at the study area to estimate the transportation and distribution of  
201 BTCs in lake conditions. In computational transport modelling there are two fundamentally different  
202 approaches to consider dispersion of substances: Eulerian and Lagrangian. While in Eulerian approach  
203 concentration field is evaluated continuously for whole modelled area, in Lagrangian method trajectory for  
204 each particle is modelled individually. This kind of modelling approach enables back tracking calculation  
205 in time and enables estimation of the source of particles observed at the study area (Karjalainen et al. 2019).

206 To computationally estimate sources of BTCs and to create flow model for study area we used Coherens  
207 model V2.11.2 (Luyten 2013). Coherens is an ocean circulation model that solves Navier-Stokes equations  
208 using the Boussinesq approximation and the assumption of vertical hydrostatic equilibrium. The prime  
209 equations are solved in a horizontally uniform rectangular grid with the resolution of 100 m for both  
210 horizontal directions (84 and 115 grid cells in west-east and south-north directions, respectively) and with  
211 10  $\sigma$ -layers. The model runs were started from the rest, i.e. initial values of 0 were used for currents and the  
212 temperature was adjusted to 5°C. Simulation periods were 1.5.2012-20.9.2012 and 1.5.2013-5.9.2013  
213 covering the whole sampling period.

214 Lagrangian particle module implemented to Coherens use currents to model the transportation of the  
215 individual particles. To consider the degradation path from TeBT to MBT we modified the particle module  
216 of Coherens to take account this transformation chain and used degradation rates presented in Juntunen et  
217 al. (2020). Different BTCs are represented as particles with differing properties. Same particle module

218 without degradation chain has been used when estimating the reproducing strategies of larvae in surface  
219 waters (Karjalainen et al. 2019).

220 The modelled area was the north part of the Lake Päijänne. Southern border was located in the middle of  
221 the lake and considered to be far enough so the lack of actual flow data can be neglected. In the model we  
222 considered rapid Vaajakoski at north-east as an incoming boundary and that the discharge in the study area  
223 remained the same.

224 Two different situations were simulated with the model and the possible sources of BTCs was estimated.  
225 Constant presence of BTCs in the vicinity of the sampling sites was assumed. In the first simulation, one  
226 BTC particle for each species was released every minute during the two weeks passive  
227 sampler/sedimentation trap deployment time (20160 particles/2 weeks). In the second simulation, 20160  
228 particles were released at once from the same locations as in the first case which now mimics the timing of  
229 instant grab water sampling. For both release types, either 20160 particles in two weeks or 20160 particles  
230 at once, the location of particles was back tracked to the beginning of simulation period. With back tracking  
231 calculation the probability that particles were released from the WWTP (site 1) was assessed.

### 232 **3 Results and discussion**

233 To explain the transportation phenomena, it is important to understand the water currents prevailing in the  
234 study area. Knowledge concerning the currents also promotes to estimate the probability of resuspension  
235 from sediments and hence the release of BTCs back to dissolved form. High flow velocity correlates rather  
236 well with the flow environment where instantaneous forces affect the suspended particulate matter and  
237 hence might release attached BTC from the particles. Furthermore, measured velocities can be used to  
238 estimate the accuracy of the computational model applied in this paper.

#### 239 **3.1 Hydrological conditions and measured water currents**

240 The study years were hydrologically very different. The average inflow to Lake Päijänne during the study  
241 period May-September was higher in the first year ( $264 \text{ m}^3 \text{ s}^{-1}$ ) than the second one ( $164 \text{ m}^3 \text{ s}^{-1}$ ) (Database  
242 for hydrological observations, SYKE). Also, the water levels during May-September differed being 230 cm

243 in first study year and 212 cm in the second one. The runoff waters originated from watershed could have  
 244 brought more pollutants to study area.

245 When considering the flow velocity and current direction in lake (Table 1) the transportation of released  
 246 effluent from site 1 downstream to site 3 lasts about 0.5 days. Site 4 is located twice as far away so the  
 247 effluent reaches it in one day. Though the current is not moving straightforward to south but circulates, the  
 248 results suggest that effluent can spread to the whole study area approximately in two days. The average  
 249 water velocities during the two weeks sampling period varied especially at site 3 where the highest  
 250 velocities occurred during the time period of the deployments 5 and 6 (1<sup>st</sup> year) and deployments 1 and 2  
 251 (2<sup>nd</sup> year), being 5.8 cm s<sup>-1</sup> and 5.0 cm s<sup>-1</sup>, respectively (Table 2). However, the velocities were clearly  
 252 below the limit value 26.2 cm s<sup>-1</sup> so the solid particles unlikely escaped from the trap. According to the  
 253 measurements in Table 2 the water currents may circulate the effluent waters upstream from site 1 to the  
 254 upstream site 2 occasionally. This observation is supported also by the modelling results. The flow roses  
 255 (Fig. 2) show that currents from site 1 towards site 2 are higher during the 2<sup>nd</sup> study year than in 1<sup>st</sup> year.  
 256 The hydrological differences between the study years can be observed at site 3 where varying flow direction  
 257 mix the water column during the 2<sup>nd</sup> study year.

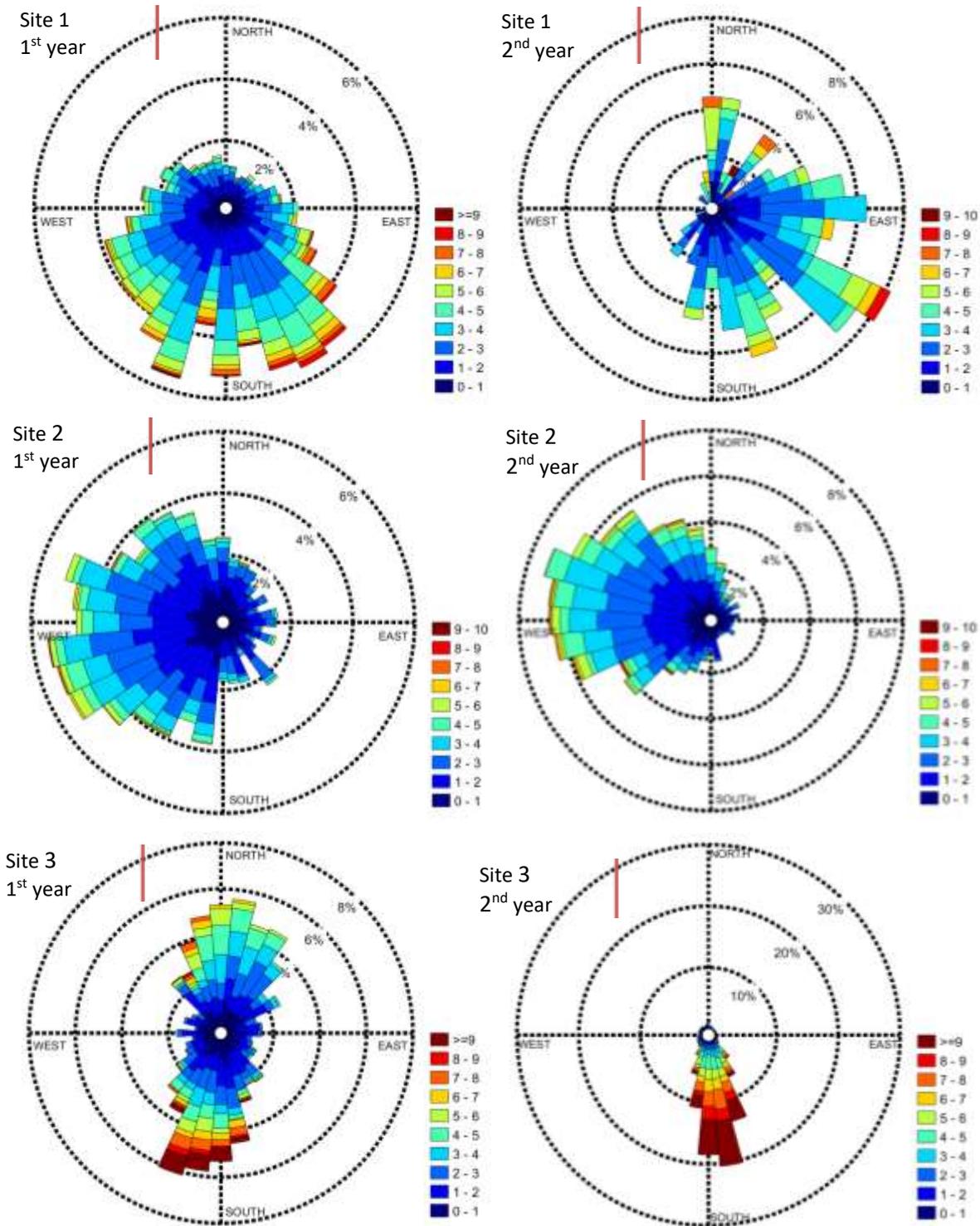
258 Table 2. Mean water velocity and average direction at sampling sites 1, 2 and 3 during the study years.

Sampling occasion	Site 1 (cm s <sup>-1</sup> )	Site 2 (cm s <sup>-1</sup> )	Site 3 (cm s <sup>-1</sup> )	
1 <sup>st</sup> year	Deployment 1	2.9 	2.2 	2.7 
	Deployment 2	3.2 	2.3 	3.3 
	Deployment 3	3.2 	2.6 	2.0 
	Deployment 4	2.9 	3.3 	3.4 
	Deployment 5	3.2 	2.7 	4.9 
	Deployment 6	3.5 	3.1 	5.6 
	Deployment 7	3.8 	2.2 	2.5 
	Deployment 8	3.9 	2.3 	2.6 
2 <sup>nd</sup> year	Deployment 1		2.5 	5.8 
	Deployment 2		2.1 	5.0 
	Deployment 3	2.0 	2.7 	3.2 
	Deployment 4	5.0 	2.9 	3.1 
	Deployment 5	3.9 	2.7 	2.7 

259

260

261 Fig. 2. Flow rose figures for sites 1, 2 and 3 (from top to bottom) for both study years, 1<sup>st</sup> year on the left  
 262 and second year on the right.



263

### 264 3.2 Sediment samples

265 The highest content of MBT, DBT and TBT were found at site 1 which receives effluent waters including  
 266 particles from the WWTP (Fig. 3). At site 1 the TBT content increased with the core depth ( $1.4 \mu\text{g kg}^{-1}$ ,  
 267  $54 \mu\text{g kg}^{-1}$  and  $64 \mu\text{g kg}^{-1}$  from core depths 0-1 cm, 1-3 cm and 3-5 cm, respectively) which suggests that

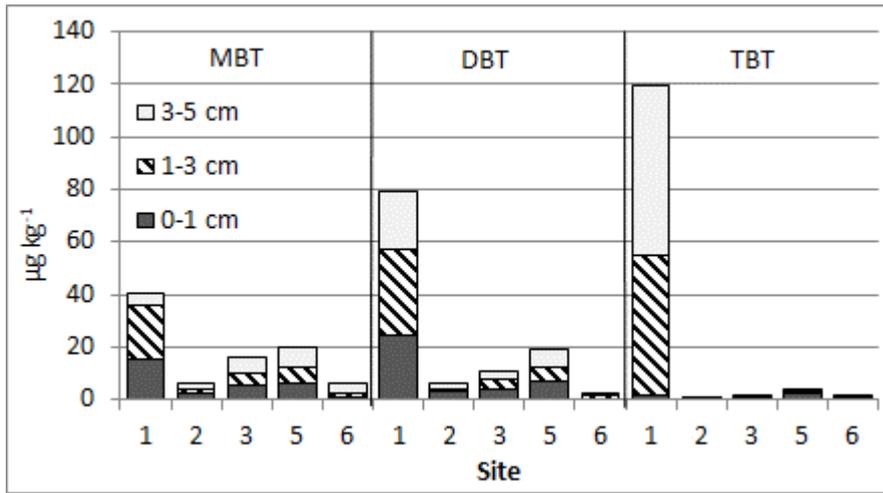
268 the release of TBT has diminished in recent years. According to simultaneous study OTCs are released  
269 from the WWTP since the effluent waters contained 0.2-2.0 ng L<sup>-1</sup> TBT, 1-18 ng L<sup>-1</sup> DBT and 2.4-51 ng L<sup>-1</sup>  
270 MBT (Ahkola et al. 2016).

271 Sediment samples at sites 5 and 3, located at deep parts of the lake and downstream from the WWTP, had  
272 higher concentrations of BTCs than the reference site 6 (Fig. 3). This indicates that at least WWTP  
273 originated particles drift mainly downstream and those sites can act as sedimentation sinks. The site 6 is  
274 the main waterway and boat traffic may disturb the lake bottom, cause resuspension and hinder the  
275 sedimentation process. Site 2 is in the shallow part of the lake away from the main waterway and due to  
276 currents receives some effluent from the WWTP.

277 In Lake Päijänne BTCs have been previously measured in surface sediment from the study area near sites  
278 1 and between sites 3 and 4. The samples at depth of 2-3 cm and the contents for MBT, DBT and TBT were  
279 8.6 µg kg<sup>-1</sup>, 1.8 µg kg<sup>-1</sup> and 0.9 µg kg<sup>-1</sup>, respectively (Mannio et al. 2011). These results were somewhat  
280 lower than the ones observed in this study.

281 As there is no classification system for contaminated sediments in Finland, the concentrations can be  
282 compared with Norwegian and Swedish EQS values which are for TBT 0.002 µg kg<sup>-1</sup> and 1.6 µg kg<sup>-1</sup>,  
283 respectively (Olsen et al. 2019). The Norwegian EQS values were exceeded at all sampling sites but the  
284 Swedish EQS only at site 1 on core depths 1-3 and 3-5. This suggests that the sediment in the study area is  
285 contaminated by TBT.

286



287

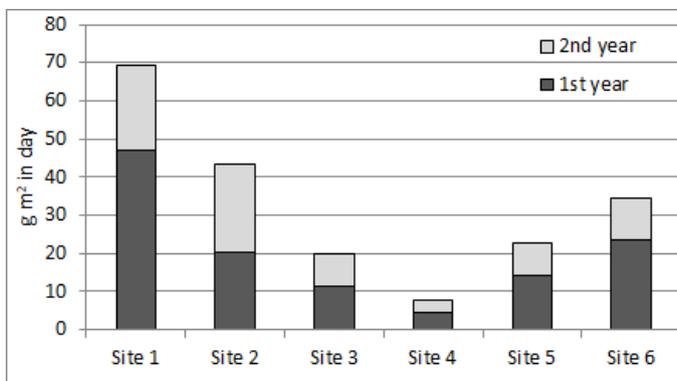
288 Fig. 3. Concentration of BTCs in sediment samples.

289

290 **3.3 Sedimentation traps**

291 **3.3.1 Settling particles in sedimentation traps**

292 The highest amount of particles settled into sedimentation traps (as dw) was measured at site 1 which  
 293 receives the effluent waters directly from the WWTP (Fig. 4). At reference site 6 the amounts of settling  
 294 particles in 1<sup>st</sup> study year were higher than at sites 3-5 being twice as high than in the 2<sup>nd</sup> year. This implies  
 295 that particles drift upstream from the study area to the site 6. In 2<sup>nd</sup> year the highest amount of settling  
 296 particles was measured at site 2 which is located at shallow part of the lake and has lots of aquatic  
 297 vegetation. Due to currents site 2 also receives effluents from WWTP which can bring particles to the area.  
 298 The amount of particles was the lowest at site 4 which is located furthest from the WWTP.



299 Fig. 4. Amount of settling particles in sedimentation traps.

### 3.3.2 BTC concentrations in settling particles of sedimentation traps

The highest BTC concentrations (as dw) were measured at the outlet of WWTP (site 1, Fig. 5). The high amount of settling particles found at sites 2 and 6 did not increase the BTC concentration (Fig. 4 and 5). Apparent connection between the particle amount and the BTC concentration in settling particles was not observed. The BTC concentrations were slightly higher in 1<sup>st</sup> year at all sites except for site 6. However, the differences are negligible. The relative abundance of MBT, DBT and TBT at site 1 differed from the ones detected at the other sampling sites as at site 1 the DBT dominated whereas MBT was the prevailing BTC at the rest of the sites (Fig. 5). The high particle bound BTC release from the WWTP in the 1<sup>st</sup> year can derive from the pipe broke which released activated sludge to effluent and further to the watercourse. This accident is further discussed in Chapter 3.6.

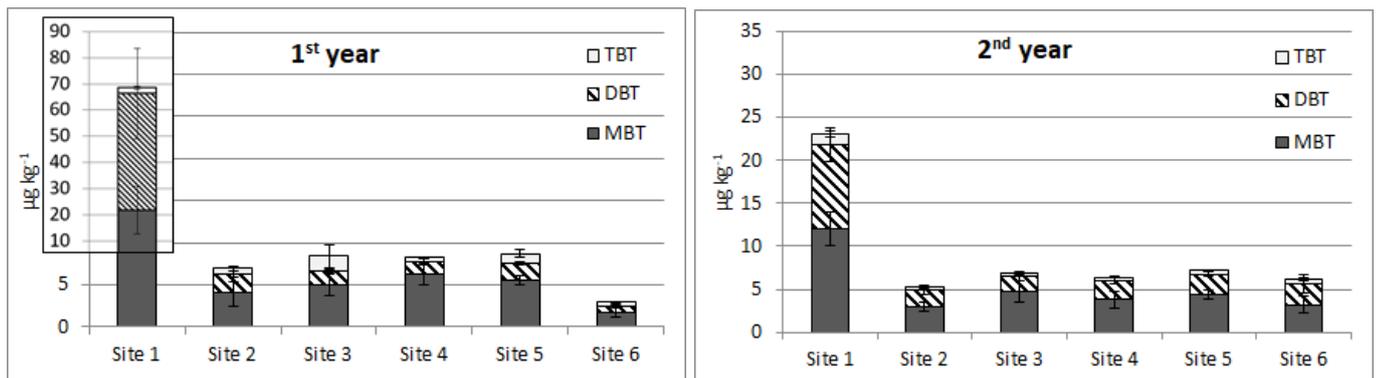
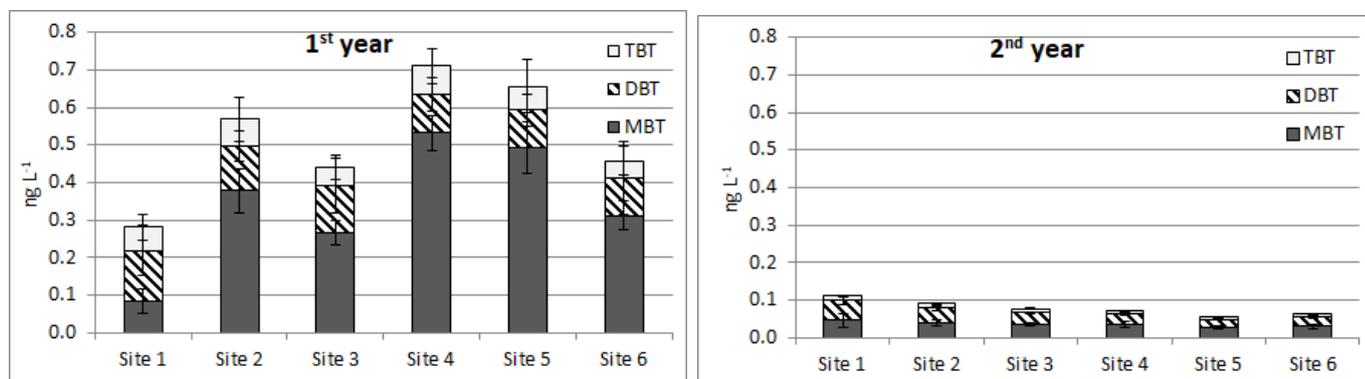


Fig. 5. Average of MBT, DBT and TBT concentration in settling particles. Notice the scaling of the 1<sup>st</sup> years chart.

### 3.4 Passive sampling

The concentrations of BTCs observed with passive sampling were not clearly higher at WWTP outflow (site 1) than at other sites (Fig. 6). One reason is that the BTCs are bound to particles present in effluent waters and are not available for passive samplers. Higher BTC concentrations were detected in all

316 Chemcatcher passive samplers deployed in 1<sup>st</sup> year than in 2<sup>nd</sup> year. According to the results the dissolved  
 317 fraction of BTCs remained quite stable during each study year.

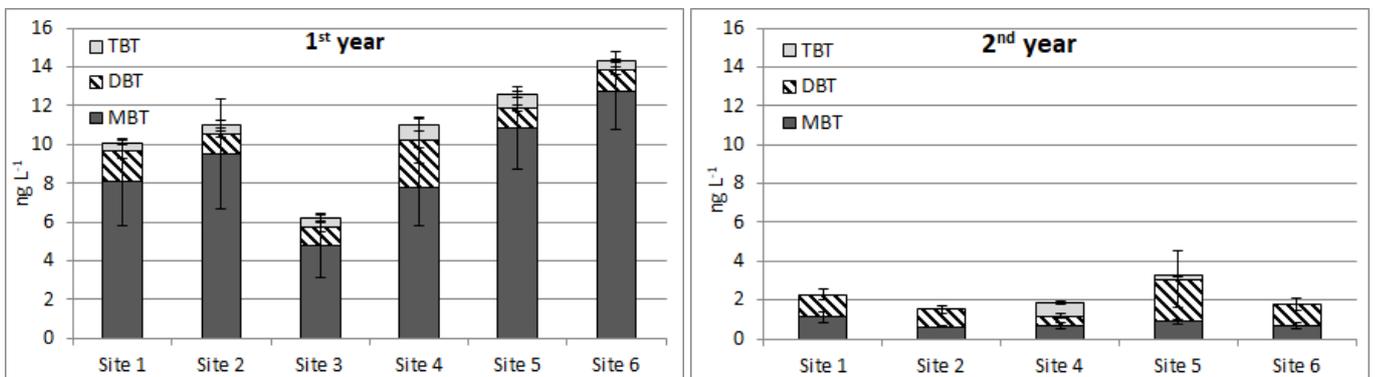


318 Fig. 6. Average of MBT, DBT and TBT concentrations in Chemcatcher passive samplers.

### 319 3.5 Grab sampling

320 The concentration of BTCs in grab water samples was expected to be low and only concentration which  
 321 exceeded LOD were included in the calculations. The MAC-EQS of TBT was exceeded only once in one  
 322 grab sample taken during the first study year (Table S2). As the LOD of TBT was the same as AA-EQS it  
 323 was exceeded when observed. According to literature there are not many studies concerning determination  
 324 of BTCs in inland waters, possibly due to analytical restrictions deriving from the low concentrations.  
 325 According to study of Aguilar-Martinez et al. (2011) the concentration of TBT in inland waters (Lake San  
 326 Juan, Spain) remained below LOD both in grab and passive sampling, TBT LODs for grab samples was 9  
 327  $\text{ng L}^{-1}$  and for passive samplers 1.2  $\text{ng L}^{-1}$ . MBT was detected in grab samples (4.0  $\text{ng L}^{-1}$ ) and passive  
 328 samplers (9.1  $\text{ng L}^{-1}$ ) as well as DBT (9.0  $\text{ng L}^{-1}$ ) and (2.6  $\text{ng L}^{-1}$ ), respectively. In Finland, BTCs have been  
 329 studied in wastewater where MBT and DBT were detected in concentrations of 4-20  $\text{ng/L}$  and 1.6-5.6  $\text{ng/L}$ ,  
 330 respectively (Mannio et al. 2011). However, the TBT concentrations remained below the detection limit  
 331 (0.5  $\text{ng/L}$ ). Also Vieno (2014) measured TBT from 60 WWTP effluents and detected it at four samples  
 332 with average concentration of 0.22  $\text{ng/L}$ . As with passive sampling data the MBT and DBT concentrations  
 333 were considerably higher in 1<sup>st</sup> year than in the 2<sup>nd</sup> year (Fig. 6 and 7). In TBT concentrations this was  
 334 observed as well but it was not that evident. However, the concentrations between these two sampling  
 335 techniques are significant as grab samples include both dissolved and particle bound fraction. All in all, the

336 concentrations were mainly below the LOD throughout the sampling campaign in both years being even  
 337 lower in the 2<sup>nd</sup> year.



338 Fig. 7. Average BTC concentrations in grab water samples.

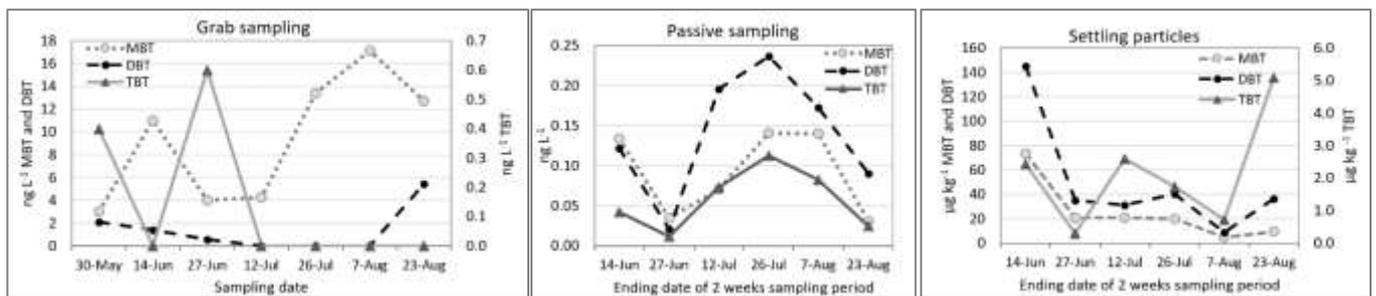
### 339 3.6 Summary of the sampling techniques

340 The passive sampling technique had the lowest LOD expressed as MDL for 2 weeks deployment than grab  
 341 sampling (Table 1). MBT was detected in 29-87% and DBT in 29-55% of grab samples (Table 3). With  
 342 passive sampling the detection percentage for MBT and DBT was 96-100% and with sedimentation traps  
 343 67-79%. However, TBT was detected only in 4-24 % of the grab samples when the detection with passive  
 344 samplers was 90-94% and with sedimentation traps 50-52%. When the concentration of TBT in grab  
 345 samples remained below LOD (0.2 ng L<sup>-1</sup>) it does not necessarily mean that the TBT is not present in  
 346 aquatic environment. Passive samplers collect BTCs for longer time period and if BTCs are present at even  
 347 trace concentrations they will be enriched to the sampler. As TBT is detected more often in passive samplers  
 348 than in grab samples the samplers were able to detect the concentrations which in grab samples would  
 349 remain undetected. This suggests that with passive sampling the presence of TBT in surface waters can be  
 350 detected more reliably than with grab sampling.

351 Table 3. Detection of BTCs with different sampling techniques.

Sampling technique	% of samples in which MBT was detected		% of samples in which DBT was detected		% of samples in which TBT was detected	
	1 <sup>st</sup> year	2 <sup>nd</sup> year	1 <sup>st</sup> year	2 <sup>nd</sup> year	1 <sup>st</sup> year	2 <sup>nd</sup> year
Sedimentation traps	79	79	67	67	52	50
Passive sampling	96	100	98	100	94	90
Grab sampling	87	29	55	29	24	4

353 The pipe broke at WWTP released activated sludge with effluent waters to Lake Päjänne and site 1. The  
 354 leak was noticed in in the beginning of the 1<sup>st</sup> years sampling campaign on 31<sup>st</sup> May and was fixed at 7<sup>th</sup>  
 355 June so it took place during the first passive sampler and sedimentation trap deployment. The grab sampling  
 356 was conducted 8 days after the leak (14<sup>th</sup> June) and this leak was not noticed, only slightly elevated MBT  
 357 concentrations were detected. Two weeks deployment of passive samplers during the leak (30<sup>th</sup> May-14<sup>th</sup>  
 358 June) implied elevated concentrations of dissolved BTC and the concentrations decreased in the next  
 359 sampling occasion. However, the concentrations increased again as the deployment trials continued. In  
 360 settling particles data, the sludge release was discovered as high concentrations, which in case of MBT and  
 361 DBT diminished as the trials continued. As the BTCs are released with activated sludge their detection in  
 362 settling particles is more probable than with grab or passive samples.



363 Fig. 8. Concentration of BTCs at site 1 during the pipe broke at WWTP. Notice that the x-axis of passive  
 364 samplers and sedimented particles describe the retrieval date after two weeks deployment but in grab  
 365 sampling the exact sampling date.

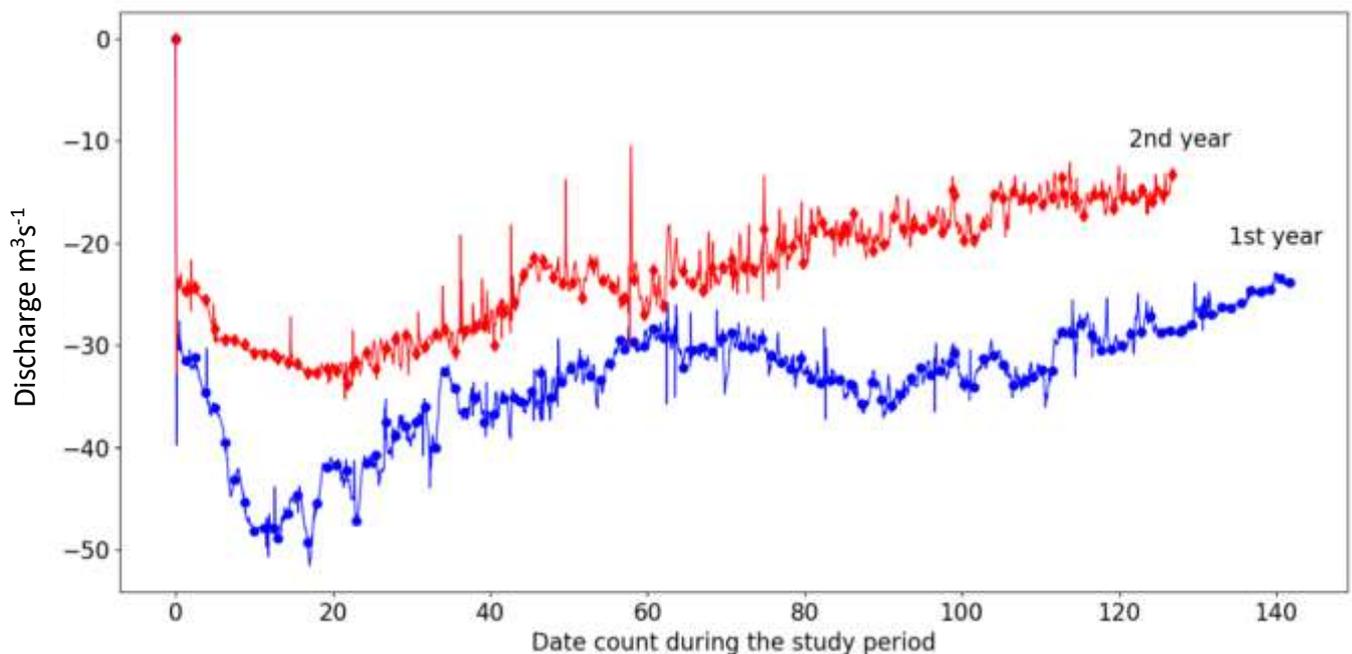
366

367

368

### 379 3.7 Computational estimation of sources of BTC

370 The computational modelling results imply that the effluent waters do not reach site 6 in conditions  
 371 prevailing in the study area (Fig. 9). Positive values would indicate that the BTCs spread from site 1  
 372 upstream to site 6, but as the modelling results presented negative values (Fig. 9), the discharge spreads  
 373 downstream. The grab water sampling and Chemcatcher passive sampling results suggest that site 6 has  
 374 rather high content of dissolved BTCs as they are detected with those techniques. In settled particles  
 375 collected with sedimentation traps the BTC contents were low which also implies that BTCs were in their  
 376 dissolved form. However, the modelling reveals that these particles do not originate from the WWTP.



377 Fig. 9. Modelling the spreading of BTC particles from the site 1 (WWTP). Negative values indicate  
 378 discharge downstream towards site 3 and positive values mean discharge upstream towards site 6.

379 According to calculations the BTCs detected at site 1 are most apparently originated from WWTP (Table  
 380 4). This is obvious as site 1 receives the WWTP effluents. The next sites assumable receiving BTCs from  
 381 WWTP are 5, 2 and 3 but their order varies between the study years e.g. the prevailing currents (Fig. 2).  
 382 The most unlikely sites to have particles originating from WWTP are sites 4 and 6 which also supports the  
 383 assumption that BTCs found at site 6 are from another source than the WWTP.

384

385

386 Table 4. The estimated probability class that the detected BTCs originate from WWTP

Probability	1 <sup>st</sup> year	2 <sup>nd</sup> year
High	Site 1	Site 1
Medium	Site 3	Site 5
	Site 5	Site 2
Low	Site 2	Site 3
	Site 4	Site 4
	Site 6	Site 6

387 The difference between the study years was also observed in the transportation simulations. Probability that  
388 BTC is discharged from WWTP and travels to location  $i$  ( $P_i$ ) was systematically higher in the 1<sup>st</sup> study year  
389 than the 2<sup>nd</sup> one. This appeared regardless of the simulation method used, mimicking passive sampling  
390 (continuous release of BTCs during the two weeks period) or grab sampling (same amount of BTCs released  
391 at once in every two weeks). The simulation results show that it is nearly impossible that the observed BTCs  
392 would have come from the upstream site 6. When comparing the ratios of the most likely and most unlikely  
393 locations  $R_i = \max(P_i) / \min(P_i)$  we notice deviation between the study years and apparent difference between  
394 the simulation methods (Table 5). It is expected that if number of BTCs released during the two weeks'  
395 time period (passive sampling) increase, the ratio of most likely and most unlikely locations would increase  
396 as well. However, the ratios  $R_i$  were systematically lower for simulation mimicking passive sampling than  
397 the one mimicking grab sampling. This means that the most likely and most unlikely locations differ more  
398 when mimicking grab sampling release and suggests that timing of instant grab sampling plays more  
399 significant role in detecting pollutants as expected.

400 Table 5. Ratios ( $R_i$ ) of maximum and minimum probabilities for TBT.

Release type	Year	Site 2	Site 3	Site 4	Site 5
Passive sampling	1 <sup>st</sup> year	70	41	5.0	17
	2 <sup>nd</sup> year	1.7	11	31	4.3
Grab sampling	1 <sup>st</sup> year	2100	200	500	71
	2 <sup>nd</sup> year	1200	30	61	23

401 **3.8 Extreme value analysis**

402 Determining BTCs from grab water samples require analytical techniques with low quantification levels.  
403 By grab sampling BTCs are seldom detected in surface waters despite they are present at trace  
404 concentrations. Only the high peak concentrations of the underlying continuous time series are observed.  
405 This however does not mean that all observed values would be extreme values. In such cases traditional

406 statistical analysis does not apply i.e., statistical test (such as Student t-test) assuming normality, fails.  
 407 However, there is an own line of statistics called “extreme value theory” which can be applied to study the  
 408 behaviour and statistics of extreme values.

409 We perform extreme value analysis using peak-over threshold approach (POT-analysis). It is well known  
 410 fact that excess  $x_j$  i.e., value  $(y_i)$ -threshold  $(u)$  is distributed as generalized pareto distribution (GPD) (Bezak  
 411 et al. 2014):

$$412 \quad G_\varepsilon(x) = \begin{cases} 1 - \left(1 - \varepsilon \frac{x}{\beta}\right)^{\frac{1}{\varepsilon}}, & \varepsilon \neq 0 \\ 1 - e^{-x/\beta} & , \varepsilon = 0 \end{cases} \quad [1]$$

413 where  $\varepsilon$  is shape parameter and  $\beta$  is scale parameter. The range of  $x$  is  $0 \leq x < \infty$  for  $\varepsilon \leq 0$  and  $0 \leq x \leq$   
 414  $\beta/\varepsilon$  for  $\varepsilon > 0$ . When  $\varepsilon > -1$  expected value for excess  $x$  is

$$415 \quad \mathbb{E}(x) = \frac{\beta}{1+\varepsilon} \quad [2]$$

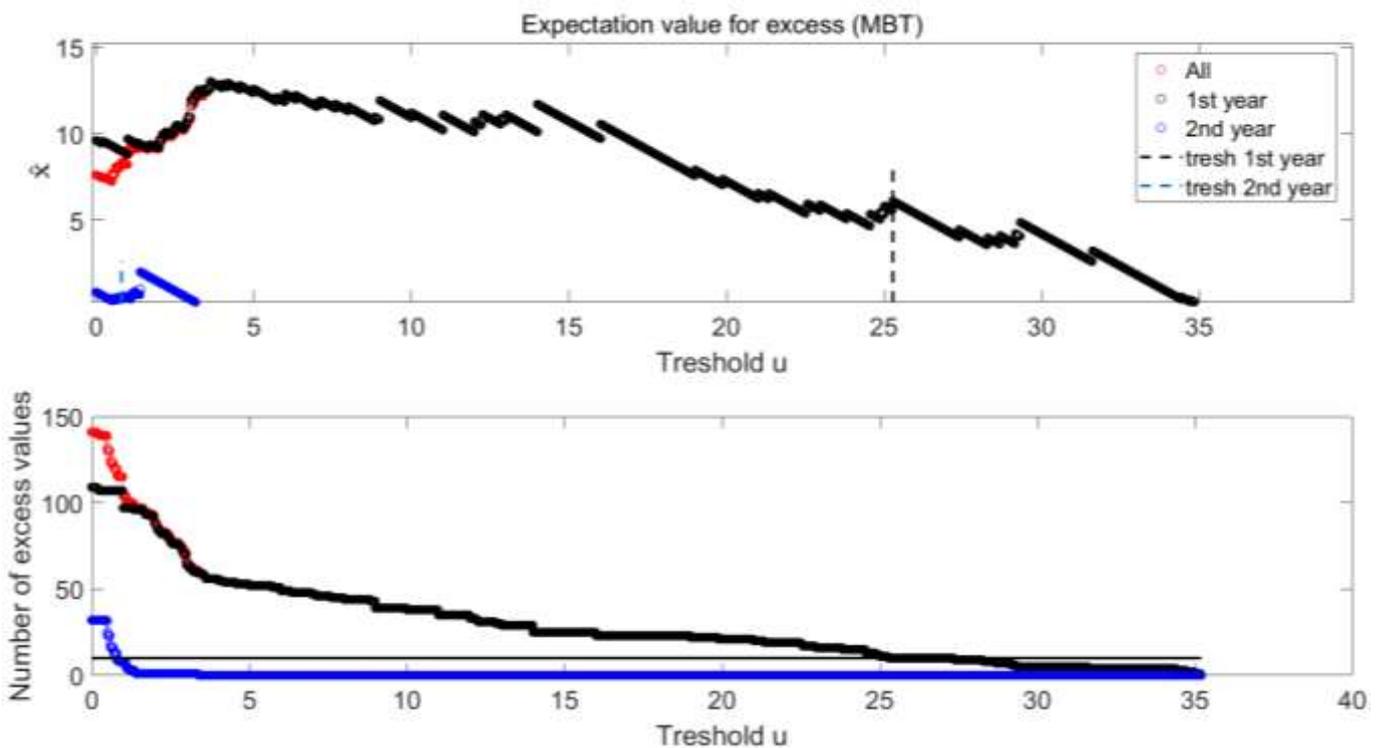
416 and variance

$$417 \quad \sigma^2 = \frac{\beta^2}{(1+\varepsilon)^2(1+2\varepsilon)} \quad [3]$$

418 that is finite only when  $\varepsilon > -(1/2)$ . If GPD is valid for excess values over threshold  $u_0$  it is valid also for  
 419 other excess values if  $u > u_0$ . Expectation value function for the excess is thus

$$420 \quad e(u) = \frac{\beta_0}{1-\varepsilon} + \frac{\varepsilon}{1-\varepsilon} u \quad [4]$$

421 Expectation value function for the excess as a function of threshold is thus linear when  $u > u_0$ . This  
 422 provides one visual approach to select the threshold value  $u$ . In brief, after choosing a good threshold value  
 423  $u$  the dependency between  $u$  and empirical estimation of expected value seems linear. Determination of  
 424 correct or even satisfactory value for  $u_0$  is not trivial or easy to do (Roth et al. 2016). From Fig. 10 we  
 425 observe that even after suitable  $u_0$  linear behaviour does not necessarily apply. In tail only few values  
 426 exceeding thresholds cause large variation for graphs. Thus, we cannot be sure that the selected threshold



427 values are suitable ones.

428 Fig. 10. Expectation value function for MBT for 1<sup>st</sup> and 2<sup>nd</sup> (upper) study year and corresponding number  
 429 of those exceeded values  $e$  and function of threshold  $u$  (lower).

430 POT analysis can be made regardless of the measuring strategy. The results are presented in Tables 6-8. At  
 431 first, we will examine the processes that BTCs undergo when considering different sampling techniques.  
 432 The biggest difference is that grab sampling is instantaneous sampling technique, while passive sampling  
 433 and sedimentation traps are integrative sampling methods. Processes effecting the accumulation of BTCs  
 434 to the samplers and to the settled particles may help in the interpretation of differing results. For passive  
 435 samplers there are physical limits how much material can be accumulated into sampler which sets limit to

436 the sampling capacity. Furthermore, since samplers are not selective the sampler's capacity can be taken  
437 by some unknown chemical which is not studied.

438 We use method suggested by Choulakian and Stephens (2001) i.e., goodness of fit -approach where GPD  
439 and empirical cumulative distribution function (CDF) are compared statistically. Estimations for shape  $\epsilon$   
440 and scale  $\beta$  parameters were found by maximum likelihood method and here we use Cramér-von Mises  
441 statistic  $W^2$  and the Anderson-Darling statistic  $A^2$ . Acceptable p-value for good fit is 0.1 but as appears in  
442 Tables 6-8 all presented parameters produced higher p-values than 0.1 which makes them plausible.

443 Threshold values  $u$  for concentrations, after which measurement are considered as extreme, are close to the  
444 LOD especially for TBT (Tables 6-8). For 2<sup>nd</sup> study year's threshold values for grab and passive samplers'  
445 results are smaller than for the 1<sup>st</sup> study year. Generally short-tailed distributions ( $\epsilon > 0$ ) are especially  
446 interesting since they indicate maximum possible value for observation. Based on shape parameters  $\epsilon$ ,  
447 presented in Tables 6-7, this is quite common. For grab samples the distributions for MBT and TBT in 1<sup>st</sup>  
448 year were short-tailed ones. From Table 7 we see that for MBT and DBT value  $\epsilon > 0$  in the 1<sup>st</sup> year while  
449 for TBT  $\epsilon > 0$  in the 2<sup>nd</sup> year. Only for BTC measured from settled particles in sedimentation traps were  
450 systematically  $\epsilon < 0$ . Furthermore, different BTCs can be short or long tailed in same year. When  
451 considering MBT from grab samples the parameter describing the distributions of exceedances  $\beta$  deviates  
452 greatly between the 1<sup>st</sup> and the 2<sup>nd</sup> year (Table 6). None of the values observed in 2<sup>nd</sup> year even exceeded  
453 the threshold of the 1<sup>st</sup> year. For DBT the obtained values were much closer to each other. For TBT the  
454 number of observed values in the 2<sup>nd</sup> year were so small that analysis was not reasonable.

455 For grab sampling even long-tailed distribution ( $\epsilon < 0$ ) values were  $\epsilon > -0.5$  which means that distributions  
456 have limited variance (Table 6). For BTC determined from passive samplers or settled particles in  
457 sedimentation traps this does not apply anymore (Tables 7 and 8). One distribution for BTC gathered with  
458 sedimentation traps is so long-tailed that even expected value  $u$  cannot be determined (Table 8).

459 If considering number of grab sampling observations that were higher than threshold value  $u$ , the MBT had  
460 the lowest percentage (51 % 1<sup>st</sup> year, 56% 2<sup>nd</sup> year) while DBT and TBT had percentages over 70% (Table

461 6). This indicates that values of DBT and TBT indeed are extreme values. For passive sampling the  
 462 percentage of extreme values were significantly lower. This is expected since passive sampling concentrates  
 463 the low concentrations to detectable level and the peak concentrations integrates to TWA concentration.  
 464 For MBT about 60%, TBT about 37% while for DBT the percentages differed lot between years being 44%  
 465 and 81 %. For BTC determined with sedimentation trap sampling smallest percentage value was 69%.

466 The results suggest that grab sampling and sedimentation trap sampling results contain more extreme peak  
 467 values than passive sampling. Deviation between threshold values  $u$  and LOD values indicates applicability  
 468 and usability of the sampling method. If the deviation is small majority of observed values are extreme  
 469 values and the mean or median of underlying concentration timeseries is very low, and vice versa. Extreme  
 470 value analysis can therefore be used to estimate actual level of average concentration of BTC.

471 Table 6. Shape and scale parameters for grab sampling from POT analysis.

Compound	Year	$\epsilon$	$\beta$	$u$	$N_{tot}$	$N_{ab}$	$W^2$	$A^2$
MBT	1 <sup>st</sup> year	0.7465	24.1836	3.621	109	56 (51%)	0.1554 ( $p>0.1$ )	0.8331 ( $p>0.1$ )
MBT	2 <sup>nd</sup> year	-0.2386	0.3481	0.6	32	18 (56%)	0.0584 ( $p>0.25$ )	0.4450 ( $p>0.25$ )
DBT	1 <sup>st</sup> year	-0.3654	0.66873	0.60	71	51 (72%)	0.0735 ( $p>0.25$ )	0.6124 ( $p>0.1$ )
DBT	2 <sup>nd</sup> year	-0.4247	0.4313	0.4966	30	26 (87%)	0.03 ( $p>0.5$ )	0.3658 ( $p>0.25$ )
TBT	1 <sup>st</sup> year	0.2755	0.5823	0.2	30	23 (77%)	0.0793 ( $p>0.25$ )	0.5994 ( $p>0.25$ )
TBT	2 <sup>nd</sup> year				4	1		

472 Table 7. Shape and scale parameters for passive sampling from POT analysis.

Compound	Year	$\epsilon$	$\beta$	$u$	$N_{tot}$	$N_{ab}$	$W^2$	$A^2$
MBT	1 <sup>st</sup> year	0.0689	0.0862	0.05	37	22 (59%)	0.0144 ( $p>0.5$ )	0.1389 ( $p>0.5$ )
MBT	2 <sup>nd</sup> year	-0.5290	0.0096	0.02681	42	26 (62%)	0.0379 ( $p>0.5$ )	0.3026 ( $p>0.5$ )
DBT	1 <sup>st</sup> year	0.2728	0.0978	0.1224	39	17 (44%)	0.1238 ( $p>0.1$ )	0.7183 ( $p>0.1$ )
DBT	2 <sup>nd</sup> year	-0.3172	0.0098	0.02302	42	34 (81%)	0.0448 ( $p>0.5$ )	0.2969 ( $p>0.5$ )
TBT	1 <sup>st</sup> year	-0.5557	0.0161	0.08	39	15 (38%)	0.0275 ( $p>0.5$ )	0.1961 ( $p>0.5$ )
TBT	2 <sup>nd</sup> year	0.3023	0.0058	0.009542	38	14 (37%)	0.0538 ( $p>0.5$ )	0.5374 ( $p>0.25$ )

473 Table 8. Shape and scale parameters for sedimentation trap sampling from POT analysis.

Compound	Year	$\epsilon$	$\beta$	$u$	$N_{tot}$	$N_{ab}$	$W^2$	$A^2$
MBT	1 <sup>st</sup> year	-0.0831	3.4035	0	38	38 (100%)	0.0590 ( $p>0.5$ )	0.5060 ( $p>0.25$ )
MBT	2 <sup>nd</sup> year	-0.2017	2.9002	1.976	33	32 (97%)	0.0295 ( $p>0.5$ )	0.1958 ( $p>0.5$ )
DBT	1 <sup>st</sup> year	-1.5084	0.8597	1.214	32	22 (69%)	0.0393 ( $p>0.5$ )	0.3130 ( $p>0.5$ )
DBT	2 <sup>nd</sup> year	-0.3906	1.9096	1.04	28	26 (93%)	0.0383 ( $p>0.5$ )	0.3756 ( $p>0.25$ )
TBT	1 <sup>st</sup> year	-0.6912	0.2796	0.23	25	20 (80%)	0.0268 ( $p>0.5$ )	0.2551 ( $p>0.5$ )
TBT	2 <sup>nd</sup> year	-0.4894	0.2692	0.2703	21	19 (90%)	0.0326 ( $p>0.5$ )	0.2276 ( $p>0.5$ )

## 475 **4 Conclusions**

476 In this study the occurrence of BTCs as total-, dissolved or particle bound fraction was monitored with grab  
477 water-, passive -, and sedimentation trap sampling for two years from May to September. The study years  
478 were hydrologically different which was observed as higher dissolved BTC concentrations during the first  
479 year. Still their concentration in particle bound fraction remained the same. The hydrological differences  
480 can be observed at site 3 where varying water current direction mix the water column more efficiently  
481 during the 2<sup>nd</sup> study year than in the 1<sup>st</sup> year. Also, the currents from site 1, which releases effluent from  
482 the WWTP, towards site 2 are higher in the 2<sup>nd</sup> study year.

483 In this study even the trace concentrations of BTCs were detected due to enhanced sensitivity of the  
484 analysing and sampling techniques. This enables more accurate estimation of concentrations and to assess  
485 the condition of watercourse more precisely. As AA-EQS of TBT was exceeded several times during the  
486 1<sup>st</sup> study year the lake does not seem to be in good chemical conditions, when considering TBT. However,  
487 this assumption is not supported when considering the 2<sup>nd</sup> study year when only few exceedings were  
488 observed.

489 To assess if the measured BTC concentrations prevail at the study area instead of being just high instant  
490 peak concentrations, we performed innovative statistical extreme value analysis. The results suggest that  
491 grab sampling and sedimentation trap sampling results contain more extreme peak values than passive  
492 sampling. This proposes that the reliability of grab sampling is the lowest from the assessed techniques  
493 when the presence of BTCs are studied.

494 The assumption that BTCs are released only from WWTP was not valid as high concentrations were  
495 detected from sampling site 6 located upstream of WWTP which was at the beginning of this study  
496 considered as reference site for determining background concentration. By computational modelling and  
497 back tracking simulations we were able to detect the possible sources of BTCs and found that they can  
498 come upstream of the sampling area where is summer houses, boats, piers and wood processing industry.  
499 Hence WWTP cannot be considered as the only source of BTCs.

500 As the techniques enable to detect BTC concentrations near their EQS it increases the reliability of the risk  
501 assessment. However, this leads also to the detection of pollutants at levels which may not have  
502 environmental effects. On the other side, as hydrophobic pollutants tend to accumulate to organism's and  
503 due to mixture effect the knowledge of these low concentrations may become essential. The trace  
504 concentrations can pose a risk if water is used e.g. for food production. Lake Päijänne provides raw water  
505 for drinking water production to the capital area and trace concentrations of harmful chemicals can pose a  
506 contamination.

507 There is no superb monitoring method for assessing the fate of organic chemicals in aquatic environment  
508 with complicated properties. With grab sampling BTC concentrations can remain below the detection limit  
509 while integrative sampling methods i.e., passive sampling and sedimentation traps measure chemicals from  
510 different matrix and hence they should be considered as a complementary method when studying e.g. BTCs.

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516 vesitekniikan tuki ry.

## 517 **Supplementary tables:**

518 Table S1. Concentrations of BTCs in sediment samples.

519 Table S2. Concentrations of BTCs in grab samples during the 1st study year.

520 Table S3. Concentrations of BTCs in grab samples during the 2nd study year.

521 Table S4. TWA concentrations of BTCs in passive samplers during the 1st study year.

522 Table S5. TWA concentrations of BTCs in passive samplers during the 2nd study year.

523 Table S6. Concentrations of BTCs in settled particles during the 1st study year.

524 Table S7. Concentrations of BTCs in settled particles during the 2nd study year.

525

526

**527 Declarations****528 Ethics approval and consent to participate**

529 Not applicable

**530 Consent for publication**

531 Not applicable.

**532 Availability of data and materials**

533 All data generated or analysed during this study are included in this published article [and its supplementary  
534 information files].

**535 Competing interests**

536 The authors declare that they have no competing interests.

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**540 Authors' contributions**

541 Heidi Ahkola was the main contributor in writing the manuscript. HA participated in planning of field trials  
542 and taking the passive, sediment and water samples.

543 Janne Juntunen performed hydrological data handling, computational estimation of BTC sources and  
544 extreme value analysis. JJ participated in planning of field trials and taking the passive, sediment and water  
545 samples.

546 Kirsti Krogerus performed the planning of field trials and taking the passive, sediment and water samples.

547 Timo Huttula performed the planning of field trials and taking the passive, sediment and water samples.

548 All authors read and approved the final manuscript.

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551 greatly appreciated. The effort of B.Sc. Saara Haapala, M.Sc. Tiina Virtanen, Ms. Rauni Kauppinen, Mr.  
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553 **References**

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