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Occurrence and trophic transport of organic compounds in sedimentation ponds for road runoff

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HIGHLIGHTS
• Ecosystem in sedimentation ponds for road runoff receives several organic pollutants.
• Water, sediment, plants, larvae and fish were analysed for 4 contaminant groups.
• Higher levels of pollutants in sedimentation ponds vs. reference were observed.
• Bioaccumulation observed for PACs and PBDEs, but all 4 groups detected in fish.
• Biomagnification was documented for PBDEs, alkylated PACs important in road runoff.

GRAPHICAL ABSTRACT

ABSTRACT

Sedimentation ponds have been shown to accumulate several groups of contaminants, most importantly polycyclic aromatic compounds (PACs) and metals. But also, other urban organic pollutants have shown to be present, including polybrominated diphenyl ethers (PBDEs), organophosphate compounds (OPCs) and benzothiazoles (BTs). This investigation aimed at determining the occurrence of these four groups of contaminants in sedimentation ponds and determine their transport from water/sediment to organisms. PACs, including alkylated PACs, PBDEs; OPCs and BTs were determined in water, sediment, plants, dragonfly larvae and fish from two sedimentation ponds and one reference site. Fish were analysed for PAC metabolites. Overall, higher concentrations of all four pollutant groups were detected in water and sediment from sedimentation ponds compared to two natural lakes in rural environments (reference sites). The concentration difference was highest in sediments, and >20 higher concentration was measured in sedimentation ponds (3.6–4.4 ng/g ww) compared to reference (0.2 ng/g ww) for sum BDE6. For PACs and PBDEs a clear transport from water/sediment to organisms were observed. Fish were the highest trophic level organism (3.5–5) in our study, and all four pollutant groups were detected in fish. For PBDEs a trophic biomagnification (TMF) was found both in sedimentation ponds and reference, but higher concentrations in all matrices were measured in sedimentation ponds. TMF was not calculated for PACs since they are metabolised by vertebrates, but a transfer from water/sediment to organisms was seen. For BTs and OPCs, no consistent transfer to plants and dragonfly larvae could be seen. One
1. Introduction

The economy of many countries relies heavily on road transport, with e.g., goods and car passengers accounting for 46% and 73% of intra-EU transport (European Commission, 2012). In addition, road freight traffic and car passenger transport are forecasted, in the period 2010–2050, to grow by about 57% and 30%, respectively (European Environment Agency, 2016). Subsequently, roads and road transportation have a large impact on the environment in terms of land use change causing habitat fragmentation, habitat loss and spreading of invasive organisms, noise, CO₂ emissions causing climate change, emissions of particles and a range of chemicals polluting local air, soil and water bodies (European Environment Agency, 2017). Typical examples of pollutants from roads and traffic are particles, nutrients (nitrogen and phosphorus), metals (e.g., Cu, Pb, Ni, Zn, As, Sb), road salt (NaCl) and polycyclic aromatic compounds (PACs) (Brown and Peake, 2006; Hwang et al., 2016). These road and traffic related pollutants are readily washed out from the road surface to the surrounding environment during storm events and may finally end up in the aquatic environment being potentially detrimental for aquatic organisms (Meland et al., 2010). Hence, polluted road runoff is now acknowledged by most national road administrations (NRAs) and environmental authorities as a significant source of diffuse pollution, and mitigation measures are therefore normally part of road building schemes (Meland, 2016). Several mitigation measures exist to protect the aquatic environment from polluted road runoff. One of the most popular is wet sedimentation ponds. These ponds, having permanent water (opposed to dry detention ponds), mimic natural processes and treat road runoff by retaining particle bound pollutants through sedimentation processes. In addition, dilution, chemical and biological degradation of pollutants are also important. Well-functioning sedimentation ponds have proved to protect nearby water bodies since they significantly reduce the concentrations of many pollutants. Sedimentation ponds are therefore recognised as a robust and cheap way of protecting nearby water bodies. Hence, thousands of sedimentation ponds have been built covering an area of ca. 880 m², while SVassum has both an open forebay and main pool covering an area of ca. 880 m², while SVassum has both an open forebay and main pool covering an area of 400 m². Both sedimentation ponds have developed a dense vegetation within and along the edges of the ponds. The reference sites are two lakes that are in rural environments with little influence from traffic.

2. Materials and methods

2.1. Study sites

Two highway sedimentation ponds (Skullerud and Vassum, hereafter denoted SSkullerud and SVassum) and two natural references (Svartoren and Lyseren, hereafter denoted RSvartoren and RLyseren) were included in the study (Fig. 1 and Table 1). The two sedimentation ponds have previously been investigated by us (Grung et al., 2016a). The ponds are situated in the greater Oslo area. SSkullerud and SVassum receive runoff from the four-lane highway E6. In addition, SVassum receives regularly tunnel wash water from three tunnels (Nordbytunnelen, Smiehagentunnelen and Vassumtunnelen). SSkullerud has a closed forebay and a main pool covering an area of ca. 880 m², while SVassum has both an open forebay and main pool covering an area of 400 m². Both sedimentation ponds have developed a dense vegetation within and along the edges of the ponds. The reference sites are two lakes that are in rural environments with little influence from traffic.

2.2. Sampling of water, sediment and biological material

The sampling took place in June–August 2016. All matrices were sampled in incinerated glassware and kept at −20 °C until analysis if not otherwise indicated. All biological samples except fish were pooled and analysed for each station. The sampling methods are presented in Table 2. The significance for interpretation of the sampling is shortly addressed here. The water samples were not filtered, whereby a small amount of particles would be present. However, upon visual inspection the samples looked clear. At the sedimentation ponds, moss (Fontinalis antipyretica) was sampled upstream at the receiving stream and transferred to the sedimentation pond in June. The moss was sampled in August. At the reference site (RLyseren), moss (Fontinalis sp.) was sampled at the same time, but not transplanted like in the sedimentation ponds. Fish from SSkullerud and perch from RLyseren were caught by net and length and weight were measured (see Table S1, supporting material). The sex of the fish was noted when possible. The bile was sampled by means of a capillary tube.
For several years, a small population of minnow (Phoxinus phoxinus) was established in SSkullerud, and was investigated by us in 2014 (Grung et al., 2016a). We also wanted to investigate the minnows for this study, but instead of minnows we found pikes (Esox Lucius) in SSkullerud. In 2016, the upstream river was flooded. This caused an overflow of SSkullerud, whereby pikes were trapped in SSkullerud as the overflow subsided. After the pikes appeared, minnows have not been detected in SSkullerud, despite several attempts of both el-fishing and translocation of minnows from the nearby river. When designing this project, minnows were our target organism. However, since there were no minnows present in SSkullerud, the pikes were caught and analysed. Half of the pikes with content in their stomach contained minnows. We tried to get pikes from a nearby clean site, but no pikes of comparable size were found. We therefore analysed perch (Perca fluviatilis) from a nearby clean lake (RLyseren) to serve as a clean reference site for the pikes from SSkullerud. The perch were of roughly the same size as the pikes (Table S1, Fig. S3), and of the same trophic level (Figs. S1 and S2). The two reference locations (RSvartoren and RLyseren) are not very far from each other in distance (12 km), with low levels of urbanisation and traffic.

### 2.3. Chemical extraction and analyses

The chemical analyses are described below. The quality assurances for the different methods are given as text in the supplementary material and Tables S4–S7 (supplementary material).

#### 2.3.1. Analyses of total dry matter, organic carbon and lipid

Total dry matter in the sediments and biota was analysed gravimetrically. Sediment subsamples were freeze-dried, crushed, and acidified (1 N HCl) and analysed for total organic carbon (TOC) by catalytic combustion at 1800 °C in a Carlo Erba 1106 elemental analyser (Carlo Erba SpA, Rodano, Italy). Aliquots of the homogenised biota material from each of the groups were used to determine the lipid content gravimetrically, after lipid extraction (cyclohexane and acetone).

#### 2.3.2. PAC including alkylated PACs

Water samples (1 L) were added internal standards and extracted with dichloromethane (150 mL) twice under vigorous shaking (1 h). The aliquots were dried (Na2SO4), and the aliquots combined. Sediments and biological material were homogenised with equal amounts hydromatrix in an IKA 11® sample mill and extracted through pressurised liquid extraction in an ASE200 system. The extraction cell for the sediment samples consisted of 4 g of activated silica, bottom layer, 4 g of acidified copper powder (to bind elemental sulphur), 5 g of sample mix, and topped off with Ottawa sand. The extraction cell for the plant samples consisted of 4 g of activated silica (chlorophyll retainer), bottom layer, 2–5 g of sample mix, and topped off with Ottawa sand. The extraction cell for the animal samples consisted of 4 g 2% deactivated silica (as a fat retainer), bottom layer, 2–5 g of sample mix, and topped off with Ottawa sand. 200 μL (8 μg/mL) internal standard mix (Gallotta and Christensen, 2012) was added to the samples before extraction. The following extraction parameters were used: Pressure: 1500 psi, preheat time: 2 min, static time: 5 min, flush.
ferred to HPLC vials. The HPLC used was a Waters 2695 Separations module with a 2475 fluorescence detector attached. The column was a Waters PAH C18 (4.6 × 250 mm) with 5 μm particles. The mobile phase consisted of a gradient from 40:60 acetonitrile:ammonium acetate (0.05 M, pH 4.1) to 100% acetonitrile at a flow of 1 mL/min. The column temperature was kept at 35 °C. Fluorescence was measured at (excitation/emissions wavelengths: 1-OH-phenanthrene 256/380; 1-OH-pyrene 346/384; triphenylamine 300/360; 3-OH-benzo[a]pyrene 380/430). 25 μL of extract was injected for each analysis. The results were calculated by use of the internal standard method. The calibration standards utilised were obtained from Chiron AS, Trondheim, Norway; and were in the range 0.2–200 ng/g.

2.3.4. PBDEs

The analytical method for PBDEs was based on a method described by Covaci et al. (2002). Water samples (1 L) were added internal standards and extracted with dichloromethane (150 mL) twice under vigorous shaking (1 h). The aliquots were dried (Na2SO4), and the aliquots combined. Freeze dried sediment samples (2–5 g) were extracted with dichloromethane (20 mL) in an ultrasonic bath for 120 min. Internal standards for were added during the first extraction step. This step was repeated with fresh dichloromethane (20 mL) for 60 min and the extracts combined. Biota samples were homogenised and added sodium sulphate and extracted with cyclohexane: ethyl acetate (1:1). The extracts for analyses were cleaned by partitioning with concentrated sulphuric acid, and thereafter acetonitrile, reduced in volume, and analysed by means of GC/MS. Analysis for PBDE congeners was performed with a Hewlett Packard 6890Plus GC linked to a Hewlett Packard 5973 MS detector operated in negative chemical ionization (with methane) and SIM mode. A pulsed splitless injection (4 mL, injector temperature of 280 °C and pulse pressure of 50 psi held for 2 min) was used to transfer analytes onto a DB-5MS column (Agilent Technologies; 15 m, 0.25 mm i.d., 0.1 μm film thickness). The oven temperature was set to 120 °C and held for 2 min before being increased to 345 °C at the rate of 25 °C/min and then held for 5 min. The helium flow was set to 1 mL/min for the first 13 min and increased to 1.4 mL/min at the rate of 0.1 mL/min and held for a further 8 min. Temperatures of the ion source, quadrupole, and transfer line were 250 °C, 150 °C, and 325 °C, respectively. Ion fragments m/z 79 and 81 were used for qualifying and quantifying PBDEs. Internal standards used for PBDEs were BDE-119 and BDE-181.

2.3.5. Organophosphate compounds (OPCs)

The method for OPCs has previously been described previously (Allan et al., 2018), and therefore only an overview is described here. Deuterated OPCs were used as internal standards for all sample matrices and were added during the extraction step. Water (200 mL) was extracted by solid phase extraction (Oasis HLB (500 mg) cartrigdes). OPCs were eluted with methanol:hexane (50:50). Freeze-dried sediment samples (0.5 g) were extracted ultrasonically with dichloromethane (4 mL, 60 min) twice. Biota samples (for fish the filet was used) were homogenised before extraction with acetonitrile:ethyl acetate (70:30, 10 mL). Extracts were concentrated and added sodium sulphate to remove water. Supercritical fluid chromatography (SFC) with MS/MS analysis was used for quantification. The following OPCs were analysed (CAS registry number in parentheses): TCEP (115-96-8), TCP (13674-84-5), TBP (126-71-6), TCPD (13674-87-8), TBOE (78-51-3), TNBP (126-73-8), TPP (115-86-6), DCP (26444-49-5), TCP (1330-78-5), EHDP (1241-94-7) and TEHP (78-42-2).

2.3.6. BT

The analytical method was based on a method described by Asheim et al. (2019). Water (200 mL) was added internal standard (sulfamethoxypyridazine-3-d3 which was used for all matrices) and added onto Oasis HLB (500 mg) solid phase extraction cartridges. BTs were eluted with 6 mL methanol:hexane (50:50). Freeze-dried sediment samples (0.5 g) were added internal standard and extracted

Table 2

| Sample         | Reference sites | Sedimentation ponds |
|----------------|-----------------|---------------------|
| Water          | No samples collected | Spot samples collected by means of large steel container. Water was thereafter transferred to large glass flasks (3 L). Water samples were not filtered. |
| Sediment       | No samples collected | 3–5 sub-samples of the upper 5 cm layer were collected by means of a van Veen grab and combined. |
| Pondweed       | No samples collected | Leaves (no stems or roots) were collected from the surface. |
| Moss           | No samples collected | Moss was collected twice at the same timepoints as first and second sampling in sedimentation ponds. Moss upstream the sedimentation ponds were collected and transplanted for 2 months in the sediment ponds. |
| Dragonfly larvae | No samples collected | Dragonfly larvae were sampled using a pond net. |
| Fish           | Perch collected by means of a net and killed by a blow to the head. | No fish samples collected. In RStomach only minnows were present, and in Rmuscle, no fish species were living. Pikes collected by means of a net and killed by a blow to the head. |
ultrasonically with methanol (5 mL, 60 min) twice. Biota samples were extracted as described for OPCs. BTs were analysed by LC-MS/MS with the following conditions: They were separated on an Acquity UPLC (Waters, Manchester) using a BEH C8 column (100 × 2.1 mm, 1.7 μm) (Waters, Sweden) with an acetonitrile and water (5:2 mM ammonium acetate) mobile phase. Gradient elution was from 50% to 100% acetonitrile over a 10 min program. The UPLC system was connected to a mass spectrometer (Xevo G2S QTof, Waters, Manchester) operated in electrospray ionization mode. Detection limits (DL) was calculated for each sample individually using the standard method of calculation of 3 x s/n ratio. It was not possible to use labelled internal standards because these were not commercially available. This will result in an uncertainty of 35–50% depending on the analytes and sample matrix. Very few of the BTs were available as certified standards, where available they were purchased from Sigma-Aldrich (Germany). The following BTs were analysed: 2-hydroxybenzothiazole (2-OH-BT), 2-Phenyl-1,3-benzothiazol (phenyl-BT), 2-buty1-1,2-benzisothiazol-3 (2H)-one and N-cyclohexyl-2-benzothiazosulfenamide (the two last BTs were not detected in any matrices).

2.3.7. Stable isotope

Stable isotope of nitrogen (δ15N air) was analysed and used for assessment of trophic level of biota samples. δ13C VPDB (Vienna Pee Dee Belenmite) was also included to identify the carbon sources. The isotope analyses were performed by the Institute for Energy Technology (IFE-Kjeller, Norway) according to standard protocols (Ruus et al., 2015). The stable isotopes were calculated according to Eq. (1) as follows:

$$\delta X = \left( \frac{R_{\text{Sample}}}{R_{\text{Standard}}} - 1 \right) \times 1,000$$

(1)

2.4. Calculation of BAF, BSAF and trophic biomagnification

The bioaccumulation factors (BAF) were calculated according to the Eq. (2) (Borgå and Ruus, 2019):

$$\text{BAF} = \frac{C_{\text{biota}}}{C_{\text{water}}}$$

(2)

The biota to sediment accumulation factors (BSAF) were calculated according to Eq. (3):

$$\text{BSAF} = \frac{C_{\text{biota (lw)}}}{C_{\text{sediment (oc)}}}$$

(3)

$$C_{\text{biota (lw)}}$$ is the lipid normalised concentration of a compound in biota

$$C_{\text{sediment (oc)}}$$ is the organic carbon normalised concentration of a compound in sediment

The relative trophic level (TL) of each sample (consumer) was calculated from δ15N (Eq. (4)) using an enrichment factor ΔN of 3.4% between integer trophic levels (Borgå et al., 2012). The lowest plant δ15N (Potamogeton) was defined as the baseline primary consumer of trophic level 1:

$$\text{TL}_{\text{consumer}} = \frac{\delta^{15}\text{N}_{\text{consumer}} - \delta^{15}\text{N}_{\text{plant}}}{\Delta N} + 1$$

(4)

Trophic magnification factors (TMFs) were calculated as the antilogarithm of the slope (b) of the linear regression between the natural logarithm of the lipid normalised contaminant concentration and the trophic level of the sample/species in question (Fisk et al., 2001) (Eqs. (5) and (6)):

$$\ln \left[ \text{contaminant} \right]_{\text{lw}} = a + b \times \text{TL}$$

(5)

$$\text{TMF} = e \times b$$

(6)

TMFs were only calculated for the brominated flame retardants BDE47, BDE99 and BDE153 as too many samples had concentrations below the DL for other compounds analysed.

2.5. Statistics

Data treatment, statistical analyses and graphical outputs were performed with JMP version 15.0.0 (SAS Institute Inc.). Regression analyses were performed by the least square’s method.

3. Results and discussion

3.1. Occurrence in water

The water samples were not filtered prior to analyses, therefore the concentrations reported may be a result of analytes bound to particles. The concentrations for all investigated contaminants are listed in Supplementary Tables S8 and S9. Only two PBDEs (BDE47 and 99) were detected in water samples collected from all three sampling sites, while BDE153 was only detected in the sedimentation ponds (SSkullerud and SVassum). The concentrations were consistently lower in RSkvartoren (reference site), and the ∑BDEs was 0.006 ng/L in RSkvartoren, and 0.023–0.033 ng/L in SVassum and SSkullerud respectively. These levels are considerably lower than the maximum allowable concentration (MAC) in the water framework directive (EU European Union, 2013) 140 ng/L based on acute toxicity studies. The WFD has not listed an annual average (AA) based on chronic toxicity data for PBDEs.

The low ring PACs (up to 4 rings) were detected in water sampled from all three sites investigated, but the higher ring sizes were only detected in the sedimentation ponds. The levels were highest in SSkullerud where PAH16 was 170 ng/L, while the concentration in RSkvartoren and SVassum was 6.6 and 22 ng/L respectively. Several of the PACs (anthracene, fluoranthene, naphthalene and benzo[a]pyrene) have been assigned AA and MAC in freshwater systems. Only the AA of benzo[a]pyrene (0.017 ng/L) was exceeded in SSkullerud, while the other results were below AA and MAC. Since the DL for benzo[a]pyrene was higher (0.7 ng/L) than the AA it is not known if the AA was exceeded in SVassum and RSkvartoren.

All OPCs investigated were detected in water samples from SSkullerud and SVassum, while only half of the investigated OPCs were detected in RSkvartoren (Table S5, supporting material). The levels were higher in SSkullerud than SVassum (0.7 ng/L) than the AA it is not known if the AA was exceeded in SVassum and RSkvartoren.

Previous investigation of the levels of OPC in urban areas have been done. In a study of tunnel wash water, many of the same OPCs were detected in high concentrations (Meland and Roseth, 2011). Their findings suggested that sedimentation ponds are a suitable mitigation strategy for removing OPCs, but removal percentage increased by adding peat or active carbon filter sorbents. SVassum receives tunnel wash water, while SSkullerud receives only road runoff. The levels of OPCs in snow nearby airport, road and reference were measured by Marklund et al. (2005). They observed a general decrease in OPC concentrations with distance from the road (2, 100 and 250 m). In line with our findings,
TCP was found in high concentrations (110–170 ng/kg), also at the reference site (68 ng/kg; Marklund et al., 2005). Yet, the levels of TCP in our study were substantially higher in sedimentation ponds (1400–2000 ng/L). Also, the levels of TCEP in sedimentation ponds (140–410 ng/L) in our study were substantially higher than what was measured in snow nearby a road in Umeå, Sweden (12 ng/kg; Marklund et al., 2005). A study of water from rivers in South Korea was investigated by Yoon et al. (2010). Both clean sites and sites influenced by effluents from sewage treatment plants (STPs) were investigated. Again, the levels of TCP in sedimentation ponds were higher than in creeks strongly influenced by STP effluent. In a study of rivers in Spain (Cristale et al., 2013) levels were in general low, but near urban influence (Barcelona) and STPs, levels up to 1800 ng/L (TCP) and 330 ng/L (TCEP) were observed.

In a non-target study of tunnel particles, three BTs were identified in tunnel particles, BT, 2-OH-BT and phenyl-BT (Grung et al., 2017). BTs in traffic environment are strongly linked to emissions of tire wear (Asheim et al., 2019). Regardless of that, BTs have gained little attention in previous pollution studies of road runoff compared to other organic pollutants (e.g. PACs). Only two of the BTs investigated were detected in any of the matrices investigated, 2,OH-BT and phenyl-BT (Table S8 and S9, supporting material). For the water phase, only phenyl-BT was detected in low concentrations in water from SSkullerud and SVassum (6.6–19 ng/L), but not in the water from RSvartoren. BTs are not listed in the WFD.

Water is not the preferred analytical matrix for many of the compounds reported here, especially PACs and PBDEs with a high logKow (range 3.34–6.22 and 5.6–8.27 respectively) are mainly particle bound. In addition, the concentrations in water will be highly variable since a dilution will take place after each rainfall. The analysis of the water was done mainly to account for compounds with a low logKow (OPCs (1.44–9.49) and BTs (1.8–4.26)), and to calculate BAFs of compounds that were detected both in water and in biota. However, because of the highly variable concentrations and since we have only done one measurement of water, the results reported here must be interpreted with caution. Yet, we believe that the general pattern that all the compound classes investigated have higher concentrations in water from sedimentation ponds than at the reference site are valid.

3.2. Occurrence in sediment

Elevated levels of PACs were detected in sediment from sedimentation ponds SSkullerud and SVassum compared to the reference site (RSvartoren) (Table S8, supporting material). PACs are the most abundant pollutant in the sedimentation ponds of the target analytes included in this study as can be clearly seen from the sediment results. Some PACs are regulated in the WFD. In addition to the environmental quality standards (EQS) for the EU prioritised compounds (EU European Union, 2013), Norway has EQS for the sum of PAH16 since PACs are considered an environmental risk in Norway (Direktoratsgruppen vanndirektivet, 2018). The PAH16 concentrations in sediments are listed in Table 3 and are classified according to the national guidelines. In short, a yellow, orange or red colour indicate exceedance of the EQS, and a higher level of toxicity from yellow to red, while blue (background), and green (no toxic effects) are concentrations not exceeding EQS. In addition, Norway’s National EQS for sum of PAH16 has been used for its usefulness for an overall risk (Direktoratsgruppen vanndirektivet, 2018). The concentrations of PAH16 in sedimentation ponds were similar to the levels that was previously reported for SSkullerud and SVassum in 2016 (Grung et al., 2016a). The concentration in SSkullerud then was higher (4200 vs. 3000 ng/g dw now) while concentration in SVassum was similar (1900 vs. 2200 ng/g dw now).

Contrary to our previous analyses of PACs in sediment, this time the alkylated homologues of selected PACs (naphthalene, fluorene, phenanthrene/anthracene, pyrene/fluoranthene and chrysene) were also analysed in sediment (Table). As can be clearly seen, the alkylated PACs were very high in sediment from SSkullerud and SVassum, while substantially lower/non-existing at RSvartoren (Fig. S4, supporting material). High occurrence of three-four ring alkylated PACs is an indication of petrogenic origin of the PACs and may stem from the bitumen of the asphalt, spilled lubricating oils or soot. Commercial extraction of bitumen has led to increased environmental levels of alkylated PACs in a lake in Alberta, Canada (Korosi et al., 2013). In Norway, asphalt wear is particularly high in the winter season when studded winter tires are commonly used. The alkylated PAC pattern was typically bell-shaped (Stogiannidis and Laane, 2015), with the C3 alkylated homologues as the highest, indicating a petrogenic origin (Fig. S4, supporting material). The alkylated chrysenes were of the highest concentrations among the alkylated PACs, and the histogram of PACs of the sedimentation ponds resembled the road asphalt shown in Stout et al. (2004).

By assuming that the alkylated homologues exert the same toxicity as the non-alkylated PACs (Richter-Brockmann and Achten, 2018; Wayland et al., 2008), an estimation of the associated risk can be made. It is evident that inclusion of alkylated homologues of PAH16 changes the risk of hazardous effects to sediment living organisms (Table 3). Notably, the change in the environmental risk of chrysenes has changed dramatically for the two sedimentation ponds. Also, the change in the classification for PAH16 has changed from exceeding the AA (yellow) to exceeding the MAC (orange) for the two sedimentation ponds, while RSvartoren has changed classification from background (blue) to good (green). Since the toxicity of all alkylated PACs have not been investigated, this is for the present only an approximation. However, we believe that until the toxicity has been estimated, this approximation is a valid precautionary principle.

There are several reports linking exposure of alkylated PACs to toxicity (Andersson and Achten, 2015), Raine et al. (2017) found that lower embryo survival corresponded to higher total and alkylated PAC content in a 31 day exposure of fish to oil sands tailings pond sediments in the laboratory. In addition, delay in development and increased percentages of larvae with heart and yolk sac oedema, cranial and spinal malformations were observed. Lee et al. (2017) showed that PACs (naphthalene, fluorene, dibenzothiophene, phenanthrene and chrysene) and their alkylated analogues disrupt endocrine functions. Especially 1-methylchrysenes, followed by phenanthrene and its alkylated analogues possessed endocrine mediating potencies. In a binding study with aryl hydrocarbon receptor (AhR), 1-methylchrysenes and 1,2,6,9-tetramethylphenanthrene were shown to possess high binding-potencies (145% and 83% of TCDDmax respectively) (Lee et al., 2015). Vignet et al. (2014) ascribed a large part of the toxicity to alkylated PACs for the toxicity observed after exposure to PAC fractions representative of either pyrolytic or petrogenic composition.

The petrogenic composition is characterised with high occurrence of alkylated PACs, especially phenanthrenes, naphthalenes and anthracenes. In addition to the toxic concerns of alkylated PACs, several investigations have shown that alkylated PACs are more persistent in the environment than the parent PACs (Barron and Holder, 2003). We therefore believe that environmental management need to take into consideration the increased risk associated with alkylated PACs in the sedimentation ponds. We have previously shown that alkylated PACs are found in tunnel particles (Grung et al., 2017), and the same is true for sedimentation ponds receiving road runoff.

The levels of PBDEs in sediments were quite low both in sedimentation ponds and reference site. The ΣBDEs were 4 ng/g dw in both sedimentation ponds and 0.20 ng/g dw in RSvartoren. These concentrations are substantially lower than the EQS for sediment (310 ng/g dw). There are few investigations of PBDEs in sedimentation ponds, probably since PBDEs are not assumed to be one of the major organic pollutants in such ponds. The results reported for PBDEs are somewhat lower than previously reported concentration in SVassum of 21 ng/g dw of penta-BDEs (Meland, 2012). In a study of stormwater ponds in South Carolina (Crawford et al., 2010), no PBDEs were detected above the detection limit of 6–10 ng/g dw.
Table 3
PAH16 and alkylated PACs in sediment (µg/kg dw). Sum alkylated PACs are the sum of C1–C4 naphthalenes, C1–C3 fluoranthenes, C1–C4 phenanthrenes/anthracenes, C1–2 pyrenes/fluoranthenes and C1–C3 chrysenes. Percent alkylated are the percentage of alkylated divided by the sum of PAC and alkylated PACs. Letters in red are above the detection limit (DL), but below the LOQ (limit of quantification). The colour of each cell indicate classification according to Direktoratsgruppen vanndirektivet (2018). PACs marked with an asterisk are prioritised pollutants according to Ei, while the others are prioritised by Norway, including the sum of PAH16. Two significant digits are used.

| Sample name       | PAC | Sum alk. | % alk | PAC | Sum alk. | % alk | PAC | Sum alk. | % alk |
|-------------------|-----|----------|-------|-----|----------|-------|-----|----------|-------|
| Naphthalene*      | 45  |          | 76    | 63  | 79       | 470   | 86  | 56       | 310   | 85   |
| Acenaphthylene    | 9   |          |       | 32  |          |       | 18  |          |       |      |
| Acenaphthene      | 4   |          |       | 9   |          |       | 5   |          |       |      |
| Fluorene          | 22  |          |       | 28  | 1,200    | 98    | 61  | 1,400    | 96    |      |
| Phenanthrene      | 4   | 20       | 43    | 30  | 3,400    | 94    | 25  | 3,200    | 93    |      |
| Anthracene*       | 32  |          |       | 360 |          |       | 310 |          |       |      |
| Fluoranthene*     | 29  |          |       | 730 |          |       | 570 |          |       |      |
| Pyrene            | 11  |          |       | 80  |          |       | 50  |          |       |      |
| Benzo(a)-anthracene| 18  |          | 18    | 50  | 400      | 8,000 | 95  | 270      | 6,100 | 96  |
| Chrysene          | 23  |          |       | 240 |          |       | 130 |          |       |      |
| Benzo(b)fluoranthene* | 18  |          |       | 100 | 82       |       |     |          |       |      |
| Benzo(k)fluoranthene* | 11  |          |       | 99  |          |       |     |          |       |      |
| Benzo(a)pyrene*   | 15  |          |       | 150 |          |       | 82  |          |       |      |
| Indeno(1,2,3-c,d)pyrene* | 15  |          |       | 150 |          |       | 82  |          |       |      |
| Dibenzo(ah)anthracene | nd |          |       | 58  |          |       | 37  |          |       |      |
| Benzo(g,h,i)pyrene* | 14  |          |       | 330 |          |       | 220 |          |       |      |

| ∑PAH16 | 260 | 110 | 30 | 3,000 | 15,000 | 83 | 2,200 | 13,000 | 86 |

In sediment samples, fewer OPCs were detected than in water, and TCEP, TIBP, and TnBP were not detected in any sediment samples. Overall, levels were higher in sediment from Sskullerud and SVassum than from RSVartoren. The highest levels were observed for TEHP (530 ng/g dw) and TCP (70 ng/g dw) which are among the OPCs investigated with highest logKow. Only for the OPCs with logKow > 5 there was a clear tendency that the concentrations in sediments from sedimentation ponds were higher than from the reference site.

BTs were detected in sediment samples from both sedimentation ponds, and phenyl-BT (90–140 ng/g dw) and 2-OH-BT (520–1000 ng/g dw) were detected. No BTs were detected in the sediment from RSVartoren. In a study of BTs in road dust samples from Trondheim in Norway (Asheim et al., 2019), 2-OH-BT was found in concentrations of 100–1100 ng/g dw depending on the season. 2-OH-BT constituted roughly 70–90% of total BTs investigated, and 2-OH-BT is a probable degradation product of several other BTs. In a study of BTs in road dust and roadside soil, 2-OH-BT was also the major BT in both matrices alongside benzothiazole (Zhang et al., 2018).

3.3. Occurrence in biota
The data for concentrations in plants and dragonfly larvae are shown in Table S8 (supporting material), while the concentrations in individual fish are shown in Table S9 (supporting material). The transplantation of moss showed little accumulation of contaminants. This was probably due to contamination from traffic reaching the locations upstream the sedimentation ponds where the mosses were sampled. In Table S8 (supporting material), the mosses have therefore been treated as two individual samples of moss (Table S8).

The PAC concentrations were in general twice as high in biota from SSkullerud and SVassum than from the two reference sites. However, with this drawback of confounding, some important conclusions can be drawn from the comparison of perch from RLyseren and pike from Sskullerud in biota. The detection frequency of OPCs was much less than for water and sediments. Only for EHD and TEHP a consistent detection was observed in plants. Only TPP was detected above the DL, but below the LOQ (limit of quantification). The colour of each cell indicate classification according to Direktoratsgruppen vanndirektivet (2018). PACs marked with an asterisk are prioritised pollutants according to Ei, while the others are prioritised by Norway, including the sum of PAH16. Two significant digits are used.

PACs are not accumulated in fish, but metabolised and excreted via bile. However, the PAC-metabolites in bile are exposure markers for approximately the last week prior to sampling (Jonsson et al., 2004). Therefore, bile samples were analysed for PAC-metabolites, and results for 1-OH-pyrene and 1-OH-phenanthrene are shown in Fig. 2. The ICES guidance limits for background assessment criteria (BAC) and environmental assessment criteria (EAC) for marine fish species (Hylland et al., 2012) are indicated. 1-OH-pyrene and 1-OH-phenanthrene were not detected in bile of fish from RLyseren. In Sskullerud, 1-OH-pyrene and 1-OH-phenanthrene were detected in all fish. The minnows from Sskullerud in our previous study had significantly higher levels of 1-OH-phenanthrene (median 3600 (min-max, 480–12,000 ng/g bile)) than the pikes. One explanation may be the difference in diet. Minnows were probably a substantial part of the pikes’ diet. Minnows have already metabolised the PACs, thereby facilitating a rapid excretion in the pikes, and lowering their exposure to PACs.

There are some limitations to interpretation of data from fish. The species are not the same but are similar in size trophic level and eating habits. More importantly the location of reference for fish (RLyseren) are different from reference site for water and sediment (RSvartoren). The plan was to investigate minnow which had been living in Sskullerud for years and was investigated in our previous study (Grung et al., 2016a). However with this drawback of fish species and location in mind some important conclusions can be drawn from the comparison of perch from RLyseren and pike from Sskullerud in biota. The detection frequency of OPC were much less than for water and sediments. Only for EHD and TEHP a consistent detection was observed. Only TPP was detected above the DL, and only in fish from Sskullerud. The detection frequency was 45%, and the mean level was 1.5 ng/g ww. For BTs there were very few detections in plants. Both 2-OH-BT and phenyl-BT were detected in fish from Sskullerud, but not in fish from RLyseren. 2-OH-BT was detected in many of the fish, 82% had concentrations above the DL. The mean level was 11 ng/g ww (range <1–16). 2-OH-BT is the probable transformation product of several BTs, and an increase in concentration after a period of storage of 2-OH-BT has been observed in other studies at NIVA. Phenyl-BT had a lower detection frequency (36%), and the concentrations were also lower (mean 0.40 ng/g ww, range <0.30–0.42).
The levels of $\sum$BDE6 in plants and dragonfly larvae were low in matrices from both reference site (Rsvartoren) and sedimentation ponds. However, the levels in matrices from sedimentation ponds were higher than matrices from the reference site, and more congeners were detected in matrices from sedimentation ponds. The levels in perch from R Lyseren were comparable to brown trout from two non-polluted lakes in Norway (lake Femunden 0.49 ng/g ww, and lake Eikedalsvannet 0.18 ng/g ww) (Jartun et al., 2018). The brown trout in lake Mjøsa in Norway used to be heavily contaminated with PBDEs due to releases from a nearby factory, but the levels have been significantly reduced from >300 to 8.0 ng/g ww in 2017 (Jartun et al., 2018). The current levels in pike from Lake Mjøsa were comparable to the levels observed in pike from RLyseren (9.3 ng/g ww). The levels in pikes from SSkullerud were significantly higher than in perch from RLyseren. The levels of $\sum$BDE6 from both locations were higher than the EQS (0.0085 ng/g ww). The EQS of $\sum$BDE6 is often exceeded in fish species, also in pristine rivers in Norway (Moe et al., 2019). Analysing the liver with higher fat content than filet was considered a worst-case scenario, and levels in filet were probably lower.

3.4. Transfer of contaminants to plants and biota

The concentrations in water, plants and organisms are shown in Fig. 3. Since few compounds were detected in all matrices, bioaccumulation factors were calculated using the sum of the contaminant groups. This is an approximation of the reality but illustrate the difference in potential of bioaccumulation for the four different contaminant groups. The bioaccumulation potential of $\sum$BDE6 can clearly be seen, while PACs also were shown to accumulate in plants. However, PACs are metabolised by most vertebrates, and therefore further bioaccumulation in higher trophic levels is discontinued. For these two groups, there was an obvious pattern that levels in sedimentation ponds were higher than in reference for all matrices. For the OPCs there was no indication of bioaccumulation, while for BTs there seemed to be higher levels in plants and organisms than in water. However, especially for BTs with exception for sediments and fish, there was no consistent pattern of higher levels in sedimentation ponds than reference site. The analyses of BTs in water and organisms were challenging.

BAFs, BSAFs and TMFs were estimated for the compounds/sites where concentrations were above DLs. The results are shown in Fig. 3.
Table 4

| Compound     | LogKow | Min | Max | Mass | Potamogeton | Dragonfly | Fish | BAF  | TMF  |
|--------------|--------|-----|-----|------|-------------|-----------|------|------|------|
| Phenyl-BT    | 4.76   | 4.59| 4.71| 4.39 | 4.39        | 4.62      | 4.39 | 4.10 | 4.10 |
| TPP          | 4.88   | 4.38| 4.88| 4.38 | 4.38        | 4.88      | 4.38 | 4.10 | 4.10 |
| Fluoranthene | 5.16   | 5.16| 5.16| 5.16 | 5.16        | 5.16      | 5.16 | 4.10 | 4.10 |
| TCPP         | 5.48   | 5.48| 5.48| 5.48 | 5.48        | 5.48      | 5.48 | 4.10 | 4.10 |
| HEDP         | 6.21   | 6.21| 6.21| 6.21 | 6.21        | 6.21      | 6.21 | 4.10 | 4.10 |
| BDE47        | 7.32   | 7.32| 7.32| 7.32 | 7.32        | 7.32      | 7.32 | 4.10 | 4.10 |
| BDE99        | 7.90   | 7.90| 7.90| 7.90 | 7.90        | 7.90      | 7.90 | 4.10 | 4.10 |
| BDE153       | 7.90   | 7.90| 7.90| 7.90 | 7.90        | 7.90      | 7.90 | 4.10 | 4.10 |

Sedimentation ponds are the most common mitigation strategy for road runoff, and therefore contain traffic related organic compounds.
such as PACs, OPCs, BTs and BDEs. PACs are the most prominent organic contaminant in sedimentation ponds, and levels exceed levels that are expected to affect sediment living organisms. Concentrations of alkylated PACs were high in sedimentation ponds, and the percentage was higher in sedimentation ponds compared to reference. Alkylated PACs are expected to be of the same toxicological concern as parent PACs and should be included in future analyses of sediments in traffic-related matrices. BDEs were shown to bioaccumulate and biomagnify both in sedimentation ponds and in reference, and concentrations were higher in sedimentation ponds than reference. The bioaccumulation potential of PACs and BTs were low. However, concentrations of compounds from both these groups were only detected in fish from sedimentation ponds, not in fish from reference sites. PACs have low potential to bioaccumulate in higher organisms due to metabolic conversion and excretion but accumulate in plants and non-metabolising organisms. Furthermore, PACs also bind strongly to particulate phases such as soot and therefore may be less bioavailable for uptake.

**CRediT authorship contribution statement**

Merete Grung: Conceptualization, Methodology, Formal analysis, Writing - original draft, Writing - review & editing, Visualization.
Sondre Meland: Conceptualization, Methodology, Writing - original draft, Writing - review & editing.
Alfhild Kringstad: Conceptualization, Methodology, Writing - review & editing.
Eirik Fjeld: Conceptualization, Writing - original draft.
Anders Ruus: Writing - original draft, Writing - review & editing.
Jan Thomas Rundberget: Formal analysis, Writing - review & editing.
Jan H. Christensen: Resources, Writing - review & editing.

**Declaration of competing interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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### Table 5

| Reference | Sedimentation ponds |
|-----------|---------------------|
| Site      | R<sub>fish av</sub> | R<sub>min - max</sub> |
| Matrix    | Moss | Potamogeton | Dragonfly |
| Pyrene    | 0.23 | 0.084 | 0.016 | 0.47 | 0.081 | 0.021 | 0.46 | 0.053 | 0.017 |
| Fluoranthene | 0.44 | 0.019 | 7.5 | 0.46 | 0.11 | 0.02 | 0.42 | 0.03 | 0.02 |
| BDE47     | 1.2 | 0.12 | 2.8–21 | 0.23 | 0.059 | 0.016 | 0.28 | 0.026 | 0.0069 | 2 |
| BDE99     | 0.32 | 0.07 | 0.059 | 0.031 | 0.023 | 0.24 | 0.014 | 0.0037 | 1.4 |

**Appendix A. Supplementary data**

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2020.141808.

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