Organophosphorus Compounds in Road Runoff

Sedimentation and filtration as a mitigation strategy

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Abstract— **Organophosphorus compounds (OP) are used in a wide range of products as flame retardants, plasticizers, antifoaming agents and additives in lubricants and hydraulic fluids. The present paper has documented that traffic is a significant source of OP compounds and that these compounds are discharged within polluted wash water during cleaning of road tunnels. The concentrations found in the present study are to some extent comparable with concentrations measured in waste water treatment plants (WWTP). Finally, treatment of polluted tunnel wash water by the means of sedimentation followed by filtration through active carbon reduced the OP concentrations and appeared in that respect to be an effective mitigation strategy.**

Keywords-component; organophosphorus compounds; flame retardants; plasticizers; highway runoff; tunnel wash

I. INTRODUCTION

Organophosphorus compounds (OPs) are extensively used in a broad range of products as flame retardants, plasticizers, antifoaming agents and as additives in lubricants and hydraulic fluids. For example, approximately 91 000 tons of OPs were used as flame retardants in 2006 in Western Europe [1]. Hence, many OP compounds are regarded as high-production volume chemicals. Due to their broad range of applications and wide spread use, trace concentrations of these anthropogenic compounds have been measured in surface waters in urban areas as well as in more remote areas during the past decade [2-4]. OPs have therefore recently been considered as emerging pollutants [3, 5]. In addition, several compounds within this group are believed to be carcinogenic, genotoxic and neurotoxic [5], making them even more alarming.

OPs are passively diffused into the environment by volatilization, leaching and abrasion. One of the main distribution routes for OPs into the environment are believed to be waste water and discharges from waste water treatment plants (WWTP). In addition, the presence of OPs in remote areas such as volcanic lakes highlights also air transportation as an important distribution route of OPs into the environment. Despite increased awareness of the ubiquitous presence of OPs in the aquatic environment, scientific studies reporting on the presence of OPs in highway runoff are to our knowledge missing. However, several have addressed traffic as an important source of OPs into the environment [6, 7]. In that respect, measuring highway tunnel wash water runoff is useful as it only reflects traffic derived contaminants and no other anthropogenic sources such as depositions of long-range air contaminants [8]. In addition, frequent discharges of polluted tunnel wash water runoff represent a significant threat to the aquatic environment in Norway as the national road network consists of more than 1000 tunnels having a combined length close to 800 km.

The present study quantifies the concentrations of traffic related OPs discharged during washing of the Nostvedt tunnel outside the city of Oslo, Norway. In addition, the removal rate by the means of sedimentation and two types of filtration sorbents, one consisting of an organic sorbent based on worked peat and one consisting of activated carbon acting as an inorganic sorbent.

II. MATERIALS AND METHODS

A. Study Site

The experiment was conducted in early February 2011 during washing of the 3.7 km long Nostvedt tunnel, which is situated along the motorway E6, approximately 20 km south east of the city of Oslo, Norway. The tunnel opened in 2009 and consists of two separate tubes with two driving lanes in the south ban direction and two + three lanes in the north ban direction. The walls and the roof are covered with light weight concrete elements. The annual average daily traffic (AADT) is 31 500 vehicles. Due to a cold period with decreasing temperatures the contractor was only able to wash the south ban tube. Hence the OP loadings in the present study represent 50 % of a normal washing event. In addition, only the road surface and the walls were washed (so called "half wash") which is known to be less polluted compared to a so called "full wash" where washing of the roof is also included.

During washing, the polluted water is discharged into a 700 m^3 large constructed sedimentation basin inside the tunnel. After sedimentation the wash water is pumped into the Bunnefjorden which is part of the Oslo fjord.

B. Experimental Setup and Water Sampling

The experimental setup is displayed in Fig. 1. In brief, polluted wash water was allowed to settle for 3.5 days before it

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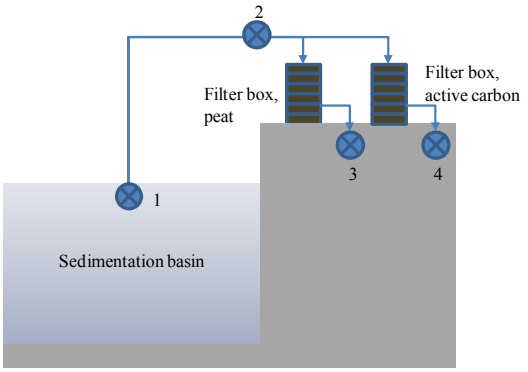

Figure 1. Outline of the experimental setup. Arrows indicate the water flow through the experiment. Crossed circles represent the various water sampling locations: 1 = pre sedimentation during the tunnel wash, 2 = after sedimentation, 3 and 4 = after filter treatment unit (FTU) filled with peat and activated carbon, respectively.

was pumped to two filter treatment units (FTU). Both FTUs consisted of six rectangular boxes stacked on top of each other. Each box had a filter surface area of 0.25 m^2. The bottom of each box was perforated with small holes to provide uniform distribution of the wash water through the FTUs. The top-box was empty while the sorbent media was placed in the four consecutive boxes each filled with approximately 30 L of sorbent material (a total of 120 L sorbent material in each FTU). The treated wash water was drained from the empty bottom-box into a bucket where the final water sampling was performed. Four liters of wash water was pumped during a period of 30 s followed by a 3.5 min pause. Hence, the water flow was 1 L/min and a total of 1440 L wash water was filtrated during a period of 24 h, giving a hydraulic loading rate (HLR) of 5.76 $m^3 \times m^{-2} \times day^{-1}$.

Two different commercially available filter sorbents were used in the present experiment, one consisting of an organic sorbent based on thermally worked peat (Filterabsorbent AFX©, Axon Environment Technique) and one consisting of activated carbon acting as an inorganic sorbent (Organosorb 10, Desotec Activated Carbon).

Water samples were collected by using 4 automatic water samplers. One was applied to collect wash water during the tunnel wash and was installed prior to the sedimentation basin (pre sedimentation). The other three samplers were collecting wash water during the filtration experiment; one collecting samples from an inlet box prior to the FTUs, representing concentrations after sedimentation, and the other two samplers were applied to collect wash water from the outlet of each FTU, respectively. The water sampler collecting water during the tunnel wash was programmed to collect four sub-samples in a polyethylene bottle each hour before moving forward to the next bottle in line. A total of 24 bottles were collected during a period of 24 h. A composite sample, stored in 2 x 1 L glass bottles, was made from the respective 24 bottles representing an average of the OP concentrations from the present tunnel wash. During the filter experiment the three automatic water samplers were programmed to collect 0.3 L every 6 h (i.e. 1.2 L per 24 h) in 5 L polyethylene bottles, representing an average OP concentration of a period of 4 days. The composite samples were stored in 2 x 1 L glass bottles and kept cold and dark prior to the OP analysis. The analysis which was performed by the commercial laboratory ALS Laboratory Group Norway AS (www.alsglobal.no) using gas chromatography – mass spectrometry detector (GC-MSD) included 13 different OP compounds (the abbreviation is given in brackets): tri(2-chloroisopropyl)phosphate (TCPP), tri(2-chloroethyl)phosphate (TCEP), tri-n-butyl phosphate (TBP), tri(1,3-dichloro-2-propyl)phosphate (TDCP/TDCPP), tricresyl phosphate (TCrP), triphenyl phosphate (TPhP), tri-isobutyl phosphate (TiBP), tri-o-cresyl phosphate (ToCrP), tri(2-butoxyethyl)phosphate (TBEP), 2-ethylhexyl diphenyl phosphate (EHDPP), dibutyl phenyl phosphate (DBPhP), diphenyl butyl phosphate (DPhBP), tri(2-ethylhexyl)phosphate (TEHP).

C. *Statistics*

The statistics were conducted by using Minitab 15 software. One-way ANOVA followed by Tukey Simultaneous Tests were applied to test for any significant difference between the various treatment steps regarding the overall removal rate in percent (%) of OP compounds. Due to skewed normality the data were transformed (Johnson transformation) prior to the statistical analysis. In addition, the data were checked for equal homogeneity (Levene's test). $P<0.05$ was set as criteria for significance.

III. Results and Discussion

A. *Concentrations and Sources*

Approximately 130 m^3 water and 0.35 – 0.40 m^3 detergent were used during washing of the south ban tube in the Nostvedt tunnel. Of the 13 different OP compounds only TCPP, TCEP, TBP, TDCP/TDCPP, TPhP, TiBP and TBEP were present at concentrations above the limit of quantification (LOQ) (Fig. 2). It should be stressed that the samples in the present study represent a time weighted average of the tunnel wash and not the maximum concentrations. Hence, the presence of other OPs in the discharged tunnel wash water cannot be totally excluded. Based on the samples from the pre sedimentation sampling the ranking of the 7 OP compounds was in decreasing order: TBP > TBEP > TCPP > TCEP > TiBP > TDCP/TDCPP > TPhP.

The concentrations found in the present study were generally comparable with measurements done in Austrian, German and Swedish WWTPs [4, 9, 10] and storm water runoff [7], but considerable higher than measurements done in various surface waters from both urban and remote areas [2-4]. In a Swedish study performed by Marklund et al. [6] the concentrations of the OPs TCPP, TCEP, TPhP and TBEP measured in snow samples were clearly reduced by increasing distance from a road intersection indicating a strong relationship to traffic. All these compounds were present in elevated concentrations in the present study manifesting traffic as an important source. Interestingly, TBP which was the dominant OP compound in the present study and TDCP/TDCPP did not correlate with traffic in the study by Marklund et al. [6]. This might indicate that TBP and TDCP/TDCPP have an origin more related to the tunnel body and/or technical equipment inside the tunnel rather than from

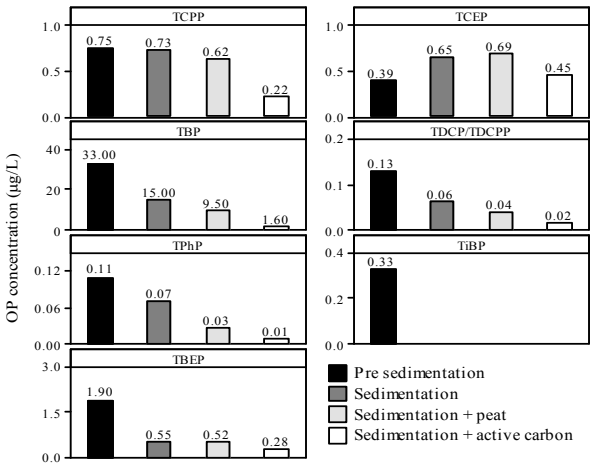

Figure 2. Concentrations of TCPP, TCEP, TBP, TDCP/TDCPP, TPhP, TiBP and TBEP in tunnel wash water during the tunnel wash (black bars), after sedimentation (dark grey bars), after sedimentation and peat FTU (light grey bars) and finally after sedimentation and active carbon FTU (white bars). Measured OP concentrations are given above each corresponding bar.

the vehicle. For example both TBP and TDCP/TDCPP are commonly used as anti-foam agents and could therefore possibly be linked to the detergents used in the tunnel wash. However, neither TBP and TDCP/TDCPP nor other OP compounds are listed on the material safety data sheet (MSDS) for the detergent used by the current contractor [11]. In addition to be used as antifoam agents TBP is used in concrete to regulate the concretes elasticity and pore size [4], and this may be a plausible explanation of the high TBP concentrations in the present study.

Although TCEP since the mid 1990s has been substituted by TCPP in the European industry, TCEP is still found in relatively high concentrations in the environment [7]. The elevated TCEP concentrations found in the present study confirm this picture and both TCEP and TCPP have been linked to traffic related sources. For example, Marklund et al. [6] suggested that these two compounds originated from the car interior and further emitted through the ventilation system as the compounds are used in polyurethane polymers that are used in e.g. car seats. The same authors claimed that traffic was a major source of TEHP as high levels of that compound were measured in snow samples adjacent to roads. This is contradictory to the results in the present study where TEHP was below LOQ.

B. Sedimentation and Filter Treatment Experiment

Apart from TCEP, which for some reason had negative removal rate (i.e. higher concentrations in the treated wash water effluents), all OP compounds had reduced concentrations and removal rates after the sedimentation basin (Fig. 2 and TABLE I). Excluding TCEP, the removal rate for the various OP compound ranged from 3 – 71 %, 17 – 75 % and 39 – 95 % for treatment by the means of sedimentation, sedimentation and peat sorbent and sedimentation and active carbon sorbent, respectively. The chlorinated compound TCPP was apparently the OP compound with the lowest removal rate in the present

TABLE I. ESTIMATED REMOVAL RATES IN PERCENT (%) FOR THE VARIOUS OP COMPOUNDS BASED ON THE CONCENTRATION DATA DISPLAYED IN FIG. 2.

OP compound	% removal		
	Sedimentation	*Sedimentation + peat*	*Sedimentation + active carbon*
TCPP	3	17	71
TCEP	-67	-77	-15
TDCP/TDCPP	52	68	87
TBP	55	71	95
TPhP	35	75	91
TiBP[a]	39 - 100	39 - 100	39 - 100
TBEP	71	73	85

a. Reduction calculated with respect to LOQ (0.02 µg/L).

study. In contrast, the highest removal rates were observed of the non-chlorinated OP compounds TBEP, TPhP and TBP. Hence, the results indicate that chlorinated OPs are apparently less effectively removed compared to non-chlorinated OPs by the means of sedimentation and filtration. This is in accordance with measurements done in influents and effluents from WWTPs [9, 12].

Overall the concentration of the various OP compounds was reduced on average by 43 % in the sedimentation basin, indicating that a major fraction of these contaminants in tunnel wash water is associated to particles (Fig. 3). By including a filtration step with active carbon the treatment was significantly improved, and an overall reduction of 86 % was achieved. In contrast, filtration by using peat as a sorbent did not significantly improve the overall removal rate of OP compounds beyond that achieved by sedimentation alone. To our knowledge no studies regarding treatment of OP compounds in stormwater- or highway runoff presently exists. However, Andresen and Bester [13] documented that active carbon filtration was effective in eliminating both chlorinated OPs and non-chlorinated OPs in drinking water purification. In addition, they documented that chlorinated OPs such as TDCP, TCEP and TCPP were poorly removed by e.g. precipitation with aluminum salts and multilayer filter consisting of gravel and sand. Hence, their findings are to some extent concurrent with the results in the present study although the concentrations levels are quite different.

IV. CONCLUSION

The present study has documented that traffic is both a significant source and a significant distribution route for several OP compounds into the aquatic environment. The measured concentrations in the tunnel wash water were to some extent comparable with concentrations normally present in WWTPs around Europe. Finally, sedimentation followed by filtration through active carbon appeared to be an effective mitigation strategy in order to reduce the concentration levels and thereby protecting the aquatic environment from OP pollution. However, this experiment should be followed up to better understand the removal mechanisms and to determine the performance of the filter sorbents over time to reveal problems related to e.g. saturation and clogging of the sorbents.

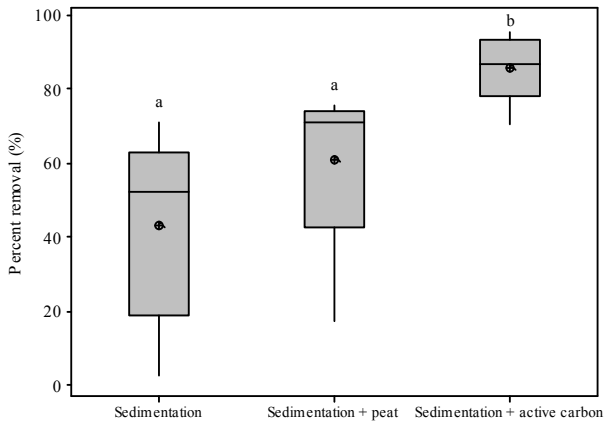

Figure 3. Box plot showing the overall removal rate in percent (%) for the OP compounds TCPP, TBP, TDCP/TDCPP, TPhP and TBEP (n = 5) after sedimentation and the two separate filter treatment boxes filled with peat and active carbon. TCEP and TiBP were excluded from this analysis due to negative removal rate (see TABLE I) and concentrations below LOQ, respectively. The rectangular box for each group represents the interquartile range of the data including the median value displayed as a horizontal line, while the whiskers extending from the boxes represent the upper and lower 25 % of the distribution. The mean values are denoted by a cross-filled circle. Significant differences between the various treatment steps are indicated by different lower-case letters.

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