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# **Relationship between accumulation and influx of pollutants in highway ponds**

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## **Abstract**

The paper discusses the long term mass balance of pollutants in highway ponds. The accumulations of five polycyclic aromatic hydrocarbons (PAHs) and six heavy metals have been measured in eight Danish detention ponds, which receive runoff from highways only. For each pollutant the accumulation has been compared to the long-term influx, estimated from short-term measurements of concentrations in highway runoff. The results show that a large proportion of the incoming heavy metals in short-term runoff events has accumulated in the ponds. This is not the case for the toxic organic compounds. The results also show that the accumulation rates for the heavy metals depend significantly on the relative pond area (pond area divided by catchment area). The conclusion is that the mass balances of heavy metals and PAHs in highway ponds can be estimated with acceptable accuracy from a combination of short-term and long-term measurements.

## **Keywords**

Heavy metals, mass balance, PAH, runoff, sediment, xenobiotics

## 1. Introduction

Most ponds have been designed for peak flow control; however, studies have shown that they also have high capacity for removing suspended solids, including heavy metals and organic compounds (Van Buren, Watt & Marsalek, 1997; Petterson, German & Svensson, 1999; Comings, Booth & Horner, 2000). The removal efficiency for particulate pollutants is highly dependent on both pond geometry and hydraulic retention time.

In most studies the efficiency of pollutant removal is calculated from an event-based mass balance, where flow and inlet and outlet concentrations have been measured.

The mass balance equation is:

$$\textit{Accumulation} = \textit{Influx} - \textit{Degradation} - \textit{Outflux}$$

where Accumulation and Degradation are the masses of accumulated and degraded material, respectively, and Influx and Outflux are the masses (the fluxes integrated over time) of the incoming and outgoing pollutant, respectively.

In short-term (event-based) studies only Influx and Outflux can be measured. Long-term studies allow estimation of Accumulation only and rough estimation of Influx.

This study is based on the measurements of the masses of three hydrocarbon fractions, five PAHs and six heavy metals accumulated in the bed sediment in eight wet highway detention ponds. The loads (Influxes) of the pollutants to each pond have been estimated from generalized values of concentrations based on measurements from a number of locations. The advantage of dealing with accumulated masses in the ponds instead of concentrations in the runoff is that many years are taken into account and time variations of the pollutant loads are averaged out.

The pollutants considered here were selected due to their frequent occurrence in highway runoff and their toxicological effects on the environment and human beings (Makepeace, Smith & Stanley, 1995).

The objective of the present study is to quantify the relationship between the mass of accumulated pollutant and the total load on a long-term basis. This relationship can be used to estimate the long-term mass balance from short-term events. The work is a preliminary study of an ongoing detailed description and modelling of the removal of pollutants in highway ponds.

## **2. Methods**

The eight ponds (Table 1) investigated in this study were selected using the following criteria:

- The pond only receives water from highway runoff.
- The drainage system is a closed pipe system without open ditches.
- The highway has curbs and gullies.
- The eight highway catchments cover a wide range of areas.

### **2.1. Accumulation**

Each pond was divided into ten areas of equal size and one sample was taken from each of the ten areas (Figure 1). The samples were taken with a 56-mm diameter cylinder pushed vertically down to the bottom of the sediment (1 to 20 cm). The ten samples were mixed to form compound samples, one for each pond. The compound samples were analysed and two measures calculated:

- 1) Mass of accumulated pollutant (Accumulation), based on the mass of dry sediment and the concentration of the pollutant
- 2) Annual accumulation rate per hectare catchment area, based on the age of the pond and the catchment area

## 2.2. Influx

Then mass of incoming pollutant (Influx) was determined from generalized values of concentration (literature values) in highway runoff multiplied by the runoff:

The concentrations (Table 2) were averages of concentrations of 24 runoff samples from two highway locations in Denmark, where all runoff water was collected each month over one year and analysed for pollutants (POLMIT, 2002) and 60 event mean concentrations (EMC) from highway runoff in the UK (Crabtree, Moy & Whitehead, 2005).

The runoff was determined as the local annual rainfall (Table 1) subtracted by an initial loss of 0.6 mm per rain event (average annual value) corresponding to 140 mm/year (Bentzen, Larsen, Thorndal & Rasmussen, 2005).

## 2.3. Degradation and Outflux

It is not possible to differentiate between Degradation and Outflux, in principle. However, heavy metals do not degrade due to their state of elements; hence, for heavy metals Outflux can be calculated as the difference between Influx and Accumulation.

The PAHs are biodegradable either as carbon/energy sources or in co-metabolic processes. The half-life period for the PAHs varies between 6 and 12 years (Environmental Protection Agency, 1996). Determination of in situ annual degradation rates are subject to further investigations and values cannot be given here. Thus, for PAHs it is not possible to distinguish between Outflux and Degradation.

## 3. Results

The average annual increase in sediment was 1.0 cm/year for ponds with an age of 6 years and 0.6 cm/year for ponds with an age of 11 years – properly due to consolidation. The mean concentrations

in the sediments (Table 3) are within the range of what can be found in the literature, e.g. German & Svensson (2005), Durand, Ruban, Amblès, Clozel & Achard (2003) and Marsalek & Marsalek (1997). The annual accumulation rate in each pond and a catchment area weighted mean accumulation rate for each of the 15 pollutants are presented in Table 4. Note that the calculated accumulation rates are based on ponds that receive runoff from highways only.

Calculated values of the annual accumulation relative to the annual influx (Figure 2) are similar to (but slightly lower than) values from efficiency studies based on inlet and effluent concentrations for the metals (Comings et al., 2000; Crabtree et al., 2005; Petterson et al., 1999; Statens Vegvesen, 2005). Figure 1 shows values higher than 1 for especially chromium and nickel in some of the ponds. These values are, of course, unrealistic and reflect the high uncertainty related to the estimated loads from runoff. Still, the high values indicate high retention. With a moderate part (5 % – 40 %) of the metal influxes being dissolved - the high relative accumulations for some of the metals indicate that outflux and resuspension of sediments have an insignificant role for the pollutant transport out of the ponds. For the organic compounds the relative accumulations are generally much lower (approx. 50%) than the values from the efficiency studies. This is probably due to degradation within the pond sediments.

The results show that the accumulation rate for heavy metals significantly depends on the relative pond area (pond area divided by catchment area) (Figure 3). Similar relationships are found by Petterson et al. (1999). The curves in this study do not have the same ‘flattening-out’ tendency at a relative pond area of 250 m<sup>2</sup>/ha as in Petterson et al. (1999).

The relationship between annual accumulation rate and relative pond area for the PAHs (Figure 3) is not as clear as for the metals, probably due to various degradation conditions.

#### **4. Conclusions**

The investigation shows that:

- The bulk of the incoming heavy metals accumulate

- Only parts of the organic compounds accumulate
- The outflux and the resuspension are of minor importance
- The accumulation increases with increasing relative pond area (pond area divided by catchment area)
- A mass balance approach for the long-term removal of pollutants can be coupled to the short term mass balances of the individual runoff event

## **Acknowledgement**

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**Table 1.** Site descriptions.

Pond/Station number	306.7	302.9	205.4	195.9
Nearby town	Hjallerup	Vodskov	Randers S	Hadsten N
Pond area [m <sup>2</sup> ]	1500	2299	2300	3480
Catchment area [ha]	1.7	2.7	3.7	6.0
Opening year for traffic	1999	1999	1994	1994
Annual day traffic in 2004	15400	14800	32100	30200
Annual precipitation [mm]	820	820	690	690

**Table 1. continued.** Site description.

Pond/Station number	187.5	95.3	95.1	92.4
Nearby town	Grundfoer	Fredericia	Fredericia	Fredericia
Pond area [m <sup>2</sup> ]	2300	200	380	600
Catchment area [ha]	4.1	0.8	2.2	1.6
Opening year for traffic	1994	1994	1994	1994
Annual day traffic in 2004	33800	24100	24100	24100
Annual precipitation [mm]	690	770	770	770

**Table 2.** Applied average runoff concentrations in [ $\mu\text{g/l}$ ].

Pollutant	Concentration	Pollutant	Concentration
$\Sigma$ C6-C35	1623	Lead (Pb)	20.0
Flouranthene	0.19	Cadmium (Cd)	0.4
Benzo(b+j+k)flouranthene	0.19	Copper (Cu)	50.2
Benzo(a)pyrene	0.10	Chromium (Cr)	5.4
Dibenzo(a,h)anthracene	0.08	Nickel (Ni)	5.3
Indeno(1,2,3-cd)pyrene	0.07	Zinc (Zn)	156.7
$\Sigma$ PAH	0.63		

**Table 3.** Concentrations [mg/kg DM] in the sediments in eight ponds.

Pollutant	Pond no.	306.7	302.9	205.4	195.9	187.5	95.3	95.1	92.4	Mean
C6H6 - C10	13	9	13	11	26	13	19	12	14	
C10-C25	215	140	290	155	460	250	505	390	301	
C25-C35	902	655	1220	625	2175	1195	2375	1655	1350	
THC	1140	805	1530	790	2640	1460	2895	2075	1667	
Flouranthene	0.14	0.07	0.32	0.11	0.36	0.21	0.47	0.89	0.32	
Benzo(b+j+k)flouranthene	0.23	0.12	0.43	0.14	0.53	0.23	0.61	1.06	0.42	
Benzo(a)pyrene	0.06	0.04	0.12	0.04	0.14	0.07	0.19	0.28	0.12	
Dibenzo(a,h)anthracene	0.01	0.01	0.04	0.01	0.05	0.02	0.05	0.10	0.04	
Indeno(1.2.3-cd)pyrene	0.09	0.05	0.17	0.06	0.14	0.09	0.25	0.36	0.15	
ΣPAH	0.53	0.28	1.07	0.35	1.21	0.62	1.56	2.68	1.04	
Lead (Pb)	20	10	37	22	68	22	51	47	35	
Cadmium (Cd)	0.5	0.3	0.5	0.6	0.9	0.4	0.7	0.8	0.6	
Copper (Cu)	54	27	125	66	220	81	165	160	112	
Chromium (Cr)	24	12	37	22	46	20	43	45	31	
Nickel (Ni)	21	10	22	18	33	18	31	35	23	
Zinc (Zn)	240	115	420	325	1045	710	1150	715	590	
Dry matter fraction	27 %	31 %	38 %	31 %	18 %	29 %	19 %	24 %	27 %	
Organic content (Loss of ignition)	11 %	6 %	9 %	19 %	16 %	9 %	14 %	15 %	12 %	

**Table 4.** Annual accumulation rates per hectare of impervious catchment [ $\frac{g}{yr\cdot ha}$ ]. The mean value (Mean) is weighted by catchment area.

Pollutant	Pond no.	306.7	302.9	205.4	195.9	187.5	95.3	95.1	92.4	Mean
C6H6-C10	43	45	22	25	22	11	6	11	24	
C10-C25	723	683	507	346	402	216	172	372	430	
C25-C35	3033	3195	2131	1396	1900	1035	809	1579	1881	
THC	3835	3927	2673	1765	2307	1264	986	1980	2337	
Fluoranthene	0.47	0.35	0.56	0.24	0.31	0.18	0.16	0.84	0.37	
Benzo(b+j+k)fluoranthene	0.77	0.57	0.74	0.32	0.46	0.20	0.21	1.01	0.51	
Benzo(a)pyrene	0.21	0.17	0.21	0.08	0.12	0.06	0.06	0.27	0.14	
Dibenzo(a,h)anthracene	0.03	0.05	0.06	0.02	0.04	0.02	0.02	0.09	0.04	
Indeno(1.2.3-cd)pyrene	0.29	0.25	0.29	0.14	0.12	0.08	0.08	0.34	0.19	
$\Sigma$ PAH	1.77	1.38	1.86	0.79	1.06	0.54	0.53	2.56	1.24	
Lead (Pb)	67	51	65	49	59	19	17	45	51	
Cadmium (Cd)	1.8	1.5	0.8	1.3	0.8	0.3	0.2	0.7	1.0	
Copper (Cu)	182	129	218	146	192	70	56	153	156	
Chromium (Cr)	79	59	64	48	40	17	14	43	48	
Nickel (Ni)	69	50	38	40	29	16	10	33	37	
Zinc (Zn)	807	561	734	726	913	615	392	682	709	

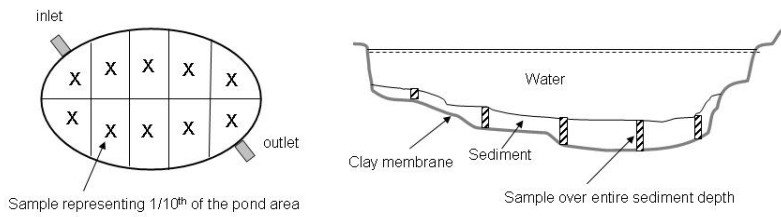


Figure 1. Sampling method.

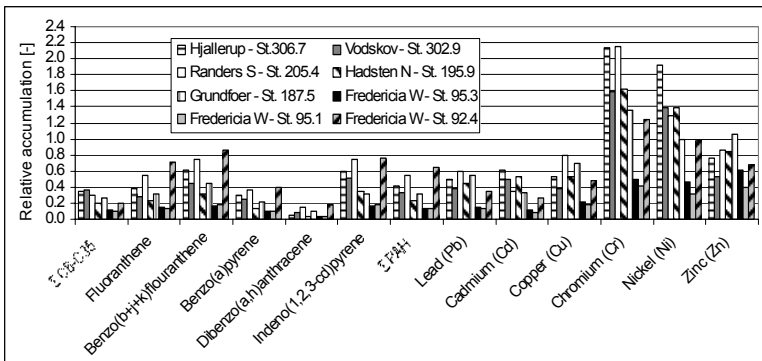


Figure 2. Relative accumulation (annual accumulation / annual influx).

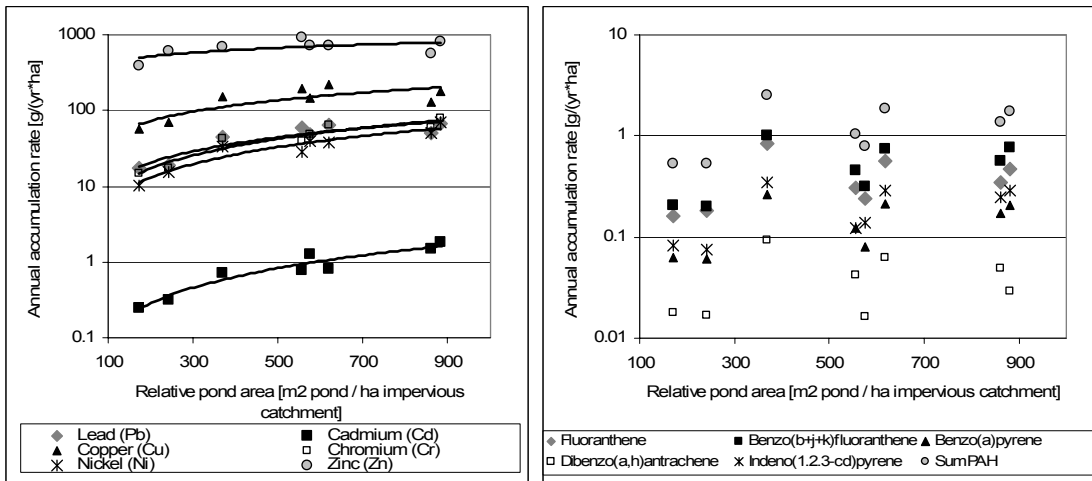


Figure 3. Annual accumulation rate as function of relative pond area.