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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:

Accumulation = Influx - Degradation - 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 halflife 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 m²/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 ²] | 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 ²] | 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 $[\mu g/l]$.

| Pollutant | Concentration | Pollutant | Concentration |
|--------------------------|---------------|---------------|---------------|
| Σ 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 |
| ΣΡΑΗ | 0.63 | | |

| Pollutant | Pond no. | 306.7 | 302.9 | 205.4 | 195.9 | 187.5 | 95.3 | 95.1 | 92.4 | Mean |
|-----------------------------------|--------------|-------|-------|-------|-------|-------|------|------|------|------|
| С6Н6 - С10 | | 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)pyren | ie | 0.06 | 0.04 | 0.12 | 0.04 | 0.14 | 0.07 | 0.19 | 0.28 | 0.12 |
| Dibenzo(a,h)a | ntracene | 0.01 | 0.01 | 0.04 | 0.01 | 0.05 | 0.02 | 0.05 | 0.10 | 0.04 |
| Indeno(1.2.3-c | d)pyrene | 0.09 | 0.05 | 0.17 | 0.06 | 0.14 | 0.09 | 0.25 | 0.36 | 0.15 |
| ΣΡΑΗ | | 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 frac Organic conter | | 27 % | 31 % | 38 % | 31 % | 18 % | 29 % | 19 % | 24 % | 27 % |
| (Loss of ignition | | 11 % | 6 % | 9 % | 19 % | 16 % | 9 % | 14 % | 15 % | 12 % |

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

Table 4. Annual accumulation rates per hectare of impervious catchment $\begin{bmatrix} g'_{yr-ha} \end{bmatrix}$. The mean value (Mean) is weighted by catchment area.

| Pollutant Po | nd 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 | 303 | 3 3195 | 5 2131 | 1396 | 1900 | 1035 | 809 | 1579 | 1881 |
| THC | 383 | 5 3927 | 2673 | 1765 | 2307 | 1264 | 986 | 1980 | 2337 |
| Fluoranthene | 0.4 | 7 0.35 | 0.56 | 0.24 | 0.31 | 0.18 | 0.16 | 0.84 | 0.37 |
| Benzo(b+j+k)fluorar | thene 0.7 | 7 0.57 | 0.74 | 0.32 | 0.46 | 0.20 | 0.21 | 1.01 | 0.51 |
| Benzo(a)pyrene | 0.2 | 1 0.17 | 0.21 | 0.08 | 0.12 | 0.06 | 0.06 | 0.27 | 0.14 |
| Dibenzo(a,h)antrach | ene 0.0 | 3 0.05 | 0.06 | 0.02 | 0.04 | 0.02 | 0.02 | 0.09 | 0.04 |
| Indeno(1.2.3-cd)pyre | ene 0.2 | 9 0.25 | 0.29 | 0.14 | 0.12 | 0.08 | 0.08 | 0.34 | 0.19 |
| ΣΡΑΗ | 1.7 | 7 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 |
| | | | | | | | | | |

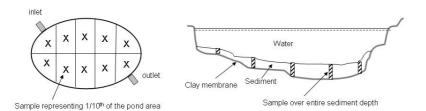


Figure 1. Sampling method.

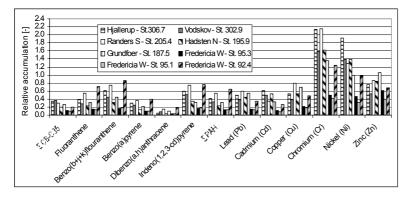


Figure 2. Relative accumulation (annual accumulation / annual influx).

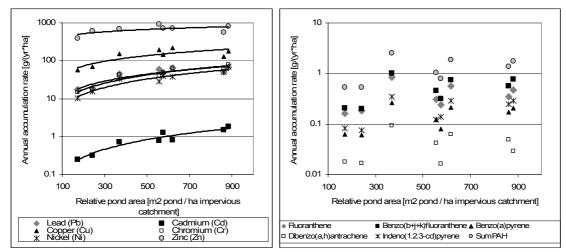


Figure 3. Annual accumulation rate as function of relative pond area.