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Can we close the long term mass balance equation for pollutants in highway ponds?

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Abstract

The paper discusses the prospects of finding the long term mass balance on basis of short term simulations. A step in this process is to see to which degree the mass balance equation can be closed by measurements. Accordingly the total accumulation of heavy metals and PAH’s in 8 Danish detention ponds only receiving runoff from highways have been measured. The result shows that the incoming mass of heavy metals from short term runoff events is accumulated. This is not observable in the same magnitude for the toxic organic compounds. The results also show that the accumulation rates significantly depend on the relative pond area (defined as the pond area divided by the catchment area). The conclusion is that the investigation indicates that a combination of short and long term viewpoints can close the mass balance for highway ponds with an acceptable accuracy.

Keywords

Heavy metals, xenobiotics, PAH, sediment, runoff, mass balance
1. Introduction

Variants of sedimentation ponds are commonly used as treatment facilities for polluted highway runoff. Many ponds have been designed only for flow control and peak reduction but studies have shown particularly high removal efficiencies for suspended solids and thereby also for heavy metals and organic compounds due to their sorption affinity [19], [13] and [2]. The removal efficiency for settleable particulate-bound pollutants is thereby highly dependent on the pond geometry and corresponding hydraulic retention time. Optimizing of pond geometry for higher removal rates has been investigated in various studies e.g. [18], [12], [20], [7] and [8]. It is generally agreed that the removal efficiency varies from one facility to another [18] and from one event to another, even including negative efficiencies due to short circuiting flow, resuspension, release of pollutants due to changes e.g. oxygen condition in the sediment [9].

In many studies the efficiencies of pollutant removal in the detention ponds are calculated from event based mass balances, where flow, inlet and outlet concentrations have been measured. The question is now whether these short term balances hold in respect to balances over many years of function. The mass balance equation runs as:

\[
\text{Accumulation} = \text{Influx} - \text{Degradation} - \text{Outflux}
\]

In short term studies only influx and outflux can be measured and in long term studies only accumulation and rough estimates of influx can be determined. This study is based on the total accumulated masses of the pollutants in the bottom sediment in 8 Danish highway wet detention ponds. The sizes of the ponds and the connected catchments areas are varying. The corresponding load (influx) to the ponds has been estimated on basis of generalised measurements from a number of locations. The advantage of dealing with the total accumulated masses in the ponds instead of concentration is that many years are taken into account and therefore event, season and yearly variations of the pollutant loads are averaged out. The pollutants considered in this paper are chosen due to their prevalent presence in highway runoff [15] and toxicological effects onto the environment and humans [10]. The aim of the present study is to quantify the relation between the total accumulation and the total load on a long term basis, in order to make probable that a long term mass balance realistically seen can be calculated from a sum of short term events. The work should also be
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understood as a preliminary study of an ongoing detailed description and modelling of the removal of pollutants in highway ponds.

2. Method

In order to state the terms in the mass balances for the pollutants in the 8 wet detention ponds, following measurements and approaches have been taken.

The 8 Danish ponds investigated in this study have been selected under four following criteria: The ponds should only receive water from highway runoff. The drainage systems should be closed so no infiltration or sedimentation in ditches occurs. The highway is established with curbs so that all runoff water is collected in gullies. The catchment area to the pond should differ from site to site. Site details can be seen in table 1.

2.2. Accumulation

10 samples (fig. 1) were taken with a 56 mm cylinder in each pond representing 1/10th of the bottom area. Each sample within the ponds was taken out in the entire sediment depth, so that a mix of all 10 samples was representing the entire pond.
The total mass of the ten wet sediment samples from each pond was measured and mixed heavily with a whisk on a drill machine, packed in 2x250 ml glass jars and kept cool until shipment to 2 independent accredited laboratories. Furthermore information on sediment depths and general background information was also taken. Based on the dry matter fractions of the sediment the total masses of dry sediment in the ponds were calculated. Based on the total masses of dry sediment and the measured concentrations the total masses of accumulated pollutants were calculated and based on the total accumulations, the age of the ponds and connected catchment area the annual accumulation rate per hectare impervious catchment area were calculated.

2.4. Influx

In absence of inlet pollutant flux measurements under each rain event during the past 6 or 11 years, two opportunities are available to predict the flux of pollutants to the ponds: Either a pollution buildup/wash off model for the catchments or a mean highway runoff concentration model. It is not possible to state which model is the most suitable for this purpose but since the basis for getting concentration data are fairly good, the influx to the ponds are based on literature values for pollutant concentrations in highway rain runoff, local annual rain fall and annual initial rain loss. The use of literature values may be highly questionable for short term event based balances due to the temporal and spatial variability in runoff concentrations. By dealing with long term balances the temporal variability can be ignored. The spatial variability can of course not be ignored due to the long time frame. But it must be remembered that this paper is not about whether one term in the mass balance equation is completely correct but about the prospects to close the mass balances for highway ponds based on short term flux measurements and long term accumulation measurements. The estimated annual pollutant influxes are based on following data:
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Concentration and flow data

- An average of concentrations of 24 runoff samples from two highway location in Denmark, where all runoff water was collected each month over one year and analysed for pollutants [14] and 60 EMC from highway runoff in the UK [3]. The concentrations applied are seen in table 2

- Annual rainfall measured within a maximum distance of 20 km to the catchments and averaged over the years of pond function (c.f. table 1) [4] and a mean annual initial loss. The initial loss during one rain event was assumed to be 0.6 mm for all highway catchments. The loss has in preceding studies [1] been studied for the catchment to the Vodskov 302.9 detention pond. Based on the average number on rain events over a 20 years period and a initial loss of 0.6 mm for rain events over 0.6 mm (215 events) and a initial loss of 0.3 mm for rain events under 0.6 mm (50 events) the annual initial loss has been estimated to 140 mm per year.

Table 2. Applied average runoff concentrations in [µg/l]

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Concentration</th>
<th>Pollutant</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Σ C6-C35</td>
<td>1623</td>
<td>Lead (Pb)</td>
<td>20.0</td>
</tr>
<tr>
<td>Flouranthene</td>
<td>0.19</td>
<td>Cadmium (Cd)</td>
<td>0.4</td>
</tr>
<tr>
<td>Benzo(b+j+k)flouranthene</td>
<td>0.19</td>
<td>Copper (Cu)</td>
<td>50.2</td>
</tr>
<tr>
<td>Benzo(a)pyrene</td>
<td>0.10</td>
<td>Chromium (Cr)</td>
<td>5.4</td>
</tr>
<tr>
<td>Dibenz(a,h)anthracene</td>
<td>0.08</td>
<td>Nickel (Ni)</td>
<td>5.3</td>
</tr>
<tr>
<td>Indeno(1,2,3-cd)pyrene</td>
<td>0.07</td>
<td>Zinc (Zn)</td>
<td>156.7</td>
</tr>
<tr>
<td>Σ PAH</td>
<td>0.63</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2.5. Degradation and outflux

The degradation term in the mass balances for the heavy metals are not considered due to their state of elements. The annual outflux from the ponds can be calculated as the difference between the influx and accumulation. It has be stated that the organic compounds incl. the PAH’s are biodegradable either as carbon/energy source or in a co-metabolic process. The biological half-life period for the PAH’s varies approximately between 6 to 12 years [17]. The organic outflux from the ponds can due to that not be calculated as for the metals. The local degradation rates are a product of many parameters such as, presence of easily biodegradable substances, oxygen-, pH-, temperature conditions etc. A determination of annual degradation rates is subject to further investigations that can not be done within the frames of this paper. The deficit between the annual influx
and accumulation in the mass balances is owing to that a sum of annual degradation and annual outflux.

### 4. Results

The average annual increase in sediment depth in the ponds with an age of 6 years was calculated to 1.0 cm/year and for ponds with an age of 11 years to an average of 0.6 cm/year. In previous studies [1] the annual load of suspended solids from the catchment area to the detention pond Vodskov st. 302.9 was approximately 200 kg/(year·ha). Based on the measurements in this study the annual SS load is 25 times higher - showing that the contributor to the accumulated solids may not be the road runoff itself but also solids from nearby surroundings. The mean pollutant concentrations in the pond sediments and ranges are presented in figure 2. The concentrations in the ponds are within the range of what can be found in literature e.g. [6], [5] and [11]. The variation between the ponds is to be expected, due to very different locations with a variance in: surroundings, vegetation, pH, redox potentials, microbiology etc. These parameters are not to be considered any further in this paper. The annual accumulation rate in each pond and a catchment area weighted mean accumulation rate for the organics and metals are presented in table 3. It must be remembered that the calculated accumulation rates are based on ponds only receiving runoff from highways and in that case not to compared with other urban detention ponds receiving water from various areas.

![pollutant concentrations](image)

**Fig. 2.** Mean, minimum and maximum pollutant concentration in the pond sediment.
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Table 3. Annual accumulation rates per hectare of impervious catchment in [g yr\(^{-1}\) ha\(^{-1}\)]. The values in the mean column are catchment area weighted mean accumulation rates.

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Pond no.</th>
<th>306.7</th>
<th>302.9</th>
<th>205.4</th>
<th>195.9</th>
<th>187.5</th>
<th>95.3</th>
<th>95.1</th>
<th>92.4</th>
<th>Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>C6H6-C10</td>
<td></td>
<td>43</td>
<td>45</td>
<td>22</td>
<td>25</td>
<td>22</td>
<td>11</td>
<td>6</td>
<td>11</td>
<td>24</td>
</tr>
<tr>
<td>C10-C25</td>
<td></td>
<td>723</td>
<td>683</td>
<td>507</td>
<td>346</td>
<td>402</td>
<td>216</td>
<td>172</td>
<td>372</td>
<td>430</td>
</tr>
<tr>
<td>C25-C35</td>
<td></td>
<td>3033</td>
<td>3195</td>
<td>2131</td>
<td>1396</td>
<td>1900</td>
<td>1035</td>
<td>809</td>
<td>1579</td>
<td>1881</td>
</tr>
<tr>
<td>THC</td>
<td></td>
<td>3835</td>
<td>3927</td>
<td>2673</td>
<td>1765</td>
<td>2307</td>
<td>1264</td>
<td>986</td>
<td>1980</td>
<td>2337</td>
</tr>
<tr>
<td>Fluoranthene</td>
<td></td>
<td>0.47</td>
<td>0.35</td>
<td>0.56</td>
<td>0.24</td>
<td>0.31</td>
<td>0.18</td>
<td>0.16</td>
<td>0.84</td>
<td>0.37</td>
</tr>
<tr>
<td>Benzo(b+j+k)fluoranthene</td>
<td></td>
<td>0.77</td>
<td>0.57</td>
<td>0.74</td>
<td>0.32</td>
<td>0.46</td>
<td>0.20</td>
<td>0.21</td>
<td>1.01</td>
<td>0.51</td>
</tr>
<tr>
<td>Benzo(a)pyrene</td>
<td></td>
<td>0.21</td>
<td>0.17</td>
<td>0.21</td>
<td>0.08</td>
<td>0.12</td>
<td>0.06</td>
<td>0.06</td>
<td>0.27</td>
<td>0.14</td>
</tr>
<tr>
<td>Dibenzo(a,h)anthracene</td>
<td></td>
<td>0.03</td>
<td>0.05</td>
<td>0.06</td>
<td>0.02</td>
<td>0.04</td>
<td>0.02</td>
<td>0.02</td>
<td>0.09</td>
<td>0.04</td>
</tr>
<tr>
<td>Indeno(1,2,3-cd)pyrene</td>
<td></td>
<td>0.29</td>
<td>0.25</td>
<td>0.29</td>
<td>0.14</td>
<td>0.12</td>
<td>0.08</td>
<td>0.08</td>
<td>0.34</td>
<td>0.19</td>
</tr>
<tr>
<td>Sum PAH</td>
<td></td>
<td>1.77</td>
<td>1.38</td>
<td>1.86</td>
<td>0.79</td>
<td>1.06</td>
<td>0.54</td>
<td>0.53</td>
<td>2.56</td>
<td>1.24</td>
</tr>
<tr>
<td>Lead (Pb)</td>
<td></td>
<td>67</td>
<td>51</td>
<td>65</td>
<td>49</td>
<td>59</td>
<td>19</td>
<td>17</td>
<td>45</td>
<td>51</td>
</tr>
<tr>
<td>Cadmium (Cd)</td>
<td></td>
<td>1.8</td>
<td>1.5</td>
<td>0.8</td>
<td>1.3</td>
<td>0.8</td>
<td>0.3</td>
<td>0.2</td>
<td>0.7</td>
<td>1.0</td>
</tr>
<tr>
<td>Copper (Cu)</td>
<td></td>
<td>182</td>
<td>129</td>
<td>218</td>
<td>146</td>
<td>192</td>
<td>70</td>
<td>56</td>
<td>153</td>
<td>156</td>
</tr>
<tr>
<td>Chromium (Cr)</td>
<td></td>
<td>79</td>
<td>59</td>
<td>64</td>
<td>48</td>
<td>40</td>
<td>17</td>
<td>14</td>
<td>43</td>
<td>48</td>
</tr>
<tr>
<td>Nickel (Ni)</td>
<td></td>
<td>69</td>
<td>50</td>
<td>38</td>
<td>40</td>
<td>29</td>
<td>16</td>
<td>10</td>
<td>33</td>
<td>37</td>
</tr>
<tr>
<td>Zinc (Zn)</td>
<td></td>
<td>807</td>
<td>561</td>
<td>734</td>
<td>726</td>
<td>913</td>
<td>615</td>
<td>392</td>
<td>682</td>
<td>709</td>
</tr>
</tbody>
</table>

The calculated relative accumulations (fig. 3) compared to efficiency studies based on inlet and effluent concentrations shows similarities for the metals, but with a slight tendency to show lower relative accumulation than the inlet and effluent based efficiencies does [2], [3], [13] and [16]. For primarily chromium and nickel in some of the ponds the relative accumulations are calculated to value higher than 1. Apparently this seems unrealistic but it reflects the uncertainty especially on the estimated loads from the runoff. However this may give an indication of a high retention. For the organic compounds the relative accumulation are in general much lower (c. 50%) than the efficiencies, likely explained by degradation within the pond sediment. The high relative accumulation for some of the metals indicates that resuspension of sediments may have an insignificant role for the pollutant transport.

Fig. 3. Relative accumulations (Annual accumulation / Annual influx).
The results also show that the accumulation rates for the heavy metals significantly depend on the relative pond area (defined as the pond area divided by the catchment area) (fig. 4). Similar dependencies are shown in [13] but as removal efficiencies as functions of the relative pond area instead. The accumulation rates in this study do not have the same flattening out tendency at a relative pond area of 250 m²/ha as in [13]. For direct comparison the relative accumulation could have been plotted instead. But since the uncertainty in the calculated relative accumulations is high due to the estimated influxes this is not done. The accumulation dependency for the PAHs is not as clear as for the metals, probably due to different degradation possibilities in the very varying ecosystems.

![Fig. 4. Annual accumulation rate as function of relative pond area.](image)

### 5. Conclusion

As expected hydrocarbons, PAH’s and heavy metals accumulate in the pond sediment. The comparison of the accumulation in relation to the load shows that the bulk of the incoming heavy metals can be found in the sediments whereas the organic compounds can only partly be found in the ponds. Although the results have a significant uncertainty the study indicates that 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. The results can also be taken as indication that the resuspension from the ponds can only be of minor importance and that the relation between the pond area and the connected catchment area plays a significant role for the accumulation rates.
6. Acknowledgement

The Danish Road Directorate is acknowledged for their financial support and for helping gathering highway data and other practical help.

7. Reference


14. POLMIT (2002). Pollution from roads and vehicles and dispersal to the local environment, Final Report. Project co-coordinator: Transport Research Laboratory (TRL), UK.


