Controls of Phosphorus Loading and Transport in the Cuyahoga River of Northeastern Ohio, USA

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1. Introduction

Phosphorus (P) is essential to the growth of plants and algae in freshwater ecosystems (Schindler, 1974; Schindler et al., 2008). Excessive P loading from point sources (e.g., effluents from wastewater treatment plants) and diffuse sources such as urban and agricultural runoff often results in cultural eutrophication (Carpenter et al., 1998; Correll, 1998). As a recurring symptom of eutrophication in Lake Erie, blooms of harmful algae (Cladophora spp. and Microcystis spp.) contribute to many water quality degradation problems, including foul odors, poor water clarity, summer hypoxia, and fish kills (Beeton, 1961; Hawley et al., 2005). After years of rigorous management efforts to reduce the total phosphorus (TP) loading from point sources and diffuse sources to the lake, its target tributary loading of 11,000 Mg TP per year was first reached in 1983 and has been maintained more or less since then (Dolan and Chapra, 2012; Dolan and McGunagle, 2005; Schwab et al., 2009). Despite early success from these management efforts, blooms of harmful algae have increased aggressively in western Lake Erie since the mid-1990s (Conroy et al., 2005; Michalak et al., 2013; Stumpf et al., 2012), highlighting a shortcoming of the existing models that were used to establish the guidelines for contemporary P management practices in the basin (Schwab et al., 2009).

Over the last decades, much of the research attention has been focused on the loading of TP from large agricultural watersheds such as the Maumee and Sandusky Rivers in the Lake Erie basin (e.g., Baker and Kramer, 1973; Richards et al., 2009). Since the mid-1980s, the TP loading of these watersheds has been decreasing due to the use of conservation tillage practices (Myers et al., 2000; Richards et al., 2009). While viewed as an effective measure to reduce erosion, such practices have caused P stratification in soil columns (Crumrine, 2009), leading to a substantial increase in the loading of soluble reactive phosphorus (SRP) in agricultural runoff (Daloglu et al., 2012; Michalak et al., 2013; OEPA, 2010). Coupled with favorable hydroclimatic and limnological conditions (e.g., weak lake circulation and prolonged algae incubation) (Michalak et al., 2013), the increased loading of SRP from these watersheds was thought to have triggered the recent resurgence of massive algal blooms in western Lake Erie (Daloglu et al., 2012; OEPA, 2010).

On the other hand, P-bearing effluents from wastewater treatment plants (WWTPs) have repeatedly been reported to have a greater risk to water quality and biological integrity of streams
The Cuyahoga River receives P from a variety of point and non-point sources. Major sources include municipal effluents, combined sewer overflows (CSO), and to a lesser extent agricultural and natural runoffs (OEPA, 1999). There are about sixteen WWTPs and industrial dischargers in the upper Cuyahoga watershed and nine WWTPs in the lower Cuyahoga watershed (seven of them in the Tinkers Creek watershed) (Table 2; OEPA, 2003). Most of these WWTPs are relatively small and release effluent at a flow rate of below 0.22 m³/s. The Akron Water Pollution Control Station (AWPCS) serves a population of 330,000 in the city of Akron and its neighboring communities and releases effluent into the lower Cuyahoga River within reach A at an average discharge rate of 3.42 m³/s (Fig. 1). The Cleveland Southerly Wastewater Treatment Plant (CSWTP) serves a population of 601,000 in the Greater Cleveland area and emits effluent into the river within reach B with an average rate of 5.48 m³/s.

The stream water chemistry changes greatly in the Cuyahoga River from the headwaters downstream. Ca²⁺, Na⁺, and HCO₃⁻ dominate in the upper Cuyahoga River while Na⁺, Cl⁻, and HCO₃⁻ dominate in water of the lower Cuyahoga River (Table 1). The concentration of total dissolved solids (TDS) of the river increases significantly from 255 mg/l at Hiram Rapids to 609 mg/l at Independence though the discharge of stream flow increases fourfold. As a result, the average TDS loading of river water increases over tenfold from 51.5 × 10³ Mg/yr at Hiram Rapids to 592 × 10³ Mg/yr at Independence. The major ion chemistry of Tinkers Creek at Bedford is similar to that of the lower Cuyahoga River at Independence (Table 1).

3. Materials and methods

3.1. Data acquisition

Consideration for selection of sampling sites includes site accessibility, spatial coverage, and availability of real-time daily streamflow data. Among a dozen of water sampling sites selected, nine were along the main stem of the Cuyahoga River and three along Tinkers Creek (Fig. 1). Four sites are close to existing USGS gaging stations (Hiram Rapids, Old Portage, Bedford, and Independence). Five water sampling campaigns were carried out between 2007 and 2008 under three different flow regimes (Fig. 2a). A total of 6 water samples were taken on July 29, 2007, 12 samples on September 3, 2007, and 12 samples on October 30, 2007 under low flow conditions, 12 samples on May 23, 2008 under intermediate flow conditions, and 12 samples on March 15, 2008 under storm flow conditions across the watershed (Fig. 2b).

Water samples were collected by hand-dipping along the river shore at a water depth of 10–15 cm where flowing water was present, using 500 ml high-density polyethylene (HDPE) wide-mouth round bottles. Prior to sampling, HDPE bottles were treated with 1.2 M HCl solution, washed with tap and deionized water at least three times, and re-washed three times in situ using river water. Water samples were frozen and shipped to the National Center for Water Quality Research (NCWQR) at Heidelberg University in Ohio. Analyses of SRP and TP were carried out at the NCWQR by semi-automated colorimetry (version II) in accordance with the U.S. EPA SW-846 Solid Waste method procedures. The method detection limits (MDL) of TP and SRP were determined as 2.3 and 0.8 μg/l, respectively.

Additionally, existing data of stream and effluent flows were gathered from different agencies. Daily stream discharge data of the Cuyahoga River at the four USGS gaging stations (Hiram Rapids, Old Portage, Bedford, and Independence) were downloaded from the National Water Information System (NWIS, 2011). Daily effluent discharge data were provided by the two major WWTPs (i.e.,...
AWPCS and CSWTP). Lastly, we retrieved long-term TP and SRP records of the Cuyahoga River at Independence from the Ohio tributary monitoring program (NCWQR, 2010).

3.2. Loading calculations

In theory, the instantaneous loading \( L_i \) (in g/s) of the river at a specific monitoring station is a function of time \( t \) (in s) and equals to the product of the instantaneous concentration \( C \) (in mg/l) and river discharge \( Q \) (in m³/s), as expressed by

\[
L_i = f(t) = C(t)Q(t)
\]

where \( C(t) \) and \( Q(t) \) are the instantaneous concentration and river discharge at time \( t \). Since the instantaneous \( P \) loading is quite variable, it is always desirable to know the average flux (or loading) of \( P \) traveling through a monitoring station in a specific time interval \((\Delta t = t_2 - t_1)\). The average loading \( \bar{L} \) of the river at a given monitoring station in a time interval of \( \Delta t \) can be estimated by

\[
\bar{L} = \frac{\int_{t_1}^{t_2} f(t)dt}{t_2 - t_1}
\]

Fig. 1. (a) Map showing locations of the Cuyahoga River and Lake Erie. (b) Watershed map showing locations of twelve sampling sites along the main stem of the Cuyahoga River and its main tributary of Tinkers Creek. The 12 sampling sites are West Branch (WB), East Branch (EB), Hiram Rapids (HR), Mantua (M), Kent Bridge (K), Old Portage (OP), Peninsula (P), Independence (I), Harvard Avenue (H), Twinsburg (T), Glennwillow (G), and Bedford (B). The two major effluent emitters are indicated by filled black triangles namely the Akron Water Pollution Control Station (AWPCS) in reach A and Cleveland Southerly Wastewater Treatment Plants (CSWTP) in reach B.

Table 1
Mean flow and major ion concentrations of surface waters in the Cuyahoga River and Tinkers Creek between 2001 and 2007.

<table>
<thead>
<tr>
<th>Gaging station</th>
<th>Flow (m³/s)</th>
<th>pH (S.U.)</th>
<th>Ca (mg/l)</th>
<th>Mg (mg/l)</th>
<th>Na (mg/l)</th>
<th>K (mg/l)</th>
<th>HCO₃ (mg/l)</th>
<th>SO₄ (mg/l)</th>
<th>Cl (mg/l)</th>
<th>TDS (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cuyahoga River</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hiram Rapids</td>
<td>6.4</td>
<td>7.9</td>
<td>34</td>
<td>7.8</td>
<td>28</td>
<td>2.2</td>
<td>104</td>
<td>28</td>
<td>43</td>
<td>255</td>
</tr>
<tr>
<td>Old Portage</td>
<td>15.6</td>
<td>8.0</td>
<td>59</td>
<td>14</td>
<td>58</td>
<td>4.0</td>
<td>149</td>
<td>56</td>
<td>103</td>
<td>451</td>
</tr>
<tr>
<td>Independence</td>
<td>30.8</td>
<td>8.0</td>
<td>67</td>
<td>15</td>
<td>111</td>
<td>5.2</td>
<td>153</td>
<td>72</td>
<td>178</td>
<td>609</td>
</tr>
<tr>
<td>Tinkers Creek</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bedford</td>
<td>4.3</td>
<td>7.9</td>
<td>56</td>
<td>13</td>
<td>117</td>
<td>6.8</td>
<td>140</td>
<td>61</td>
<td>194</td>
<td>596</td>
</tr>
</tbody>
</table>

* Original flow data were taken from USGS National Water Information System (NWIS) and water quality data from USEPA STORET.
In reality, the yearly loading \( (L_a) \) in metric tons or Mg/yr of SRP or TP in a river can be estimated as follows (Baker, 2005).

\[
L_a = \gamma \frac{\sum t_j C_j Q_j}{\sum t_j}
\]

where \( Q_j \) is the average river discharge in the sampling interval (in m³/s), \( C_j \) is the concentration of SRP or TP in the composite water sample collected during the sampling interval (in mg/l), \( t_j \) is the time interval (in days) of the composite sample, and \( \gamma = 31.536 \), is a g/s to Mg/yr unit conversion coefficient.

Alternatively, the average loading \( \bar{L} \) can be approximated by the arithmetic mean of the instantaneous loadings \( L_i \).

\[
\bar{L} = \frac{\sum L_i}{n} = \frac{\sum C_j Q_j}{n} = \bar{C} \bar{Q}
\]

where \( n \) is the number of the instantaneous loadings measured, \( \bar{C} \) is the flow-weighted average concentration, and \( \bar{Q} \) is the average discharge of the river in a given time period. \( \bar{I} \) may be estimated at

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**Fig. 2.** (a) Flow duration curves of the Cuyahoga River at Hiram Rapids, Old Portage, and Independence, and of Tinkers Creek at Bedford. (b) Stream hydrograph of the Cuyahoga River at Independence from July 2007 to May 2008. Three flow regimes are determined by \% time indicated discharge \( Q \) was equaled or exceeded: storm flow \(<5\%\), intermediate flow \(5–60\%\), and low flow \(>60\%\). The five filled circles represent discharge of the Cuyahoga River at Independence on the day when water samples were taken. M – March 15, 2008; M5 – May 23, 2008; J – July 29, 2007; S – September 3, 2007; O – October 30, 2007.

**Table 2**

Estimated P loading from known point sources in Cuyahoga watersheds.²

<table>
<thead>
<tr>
<th>Facility name</th>
<th>Average discharge (MGD)</th>
<th>平均流速 (m²/s)</th>
<th>平均流量 (km³/yr)</th>
<th>TP (mg/l)</th>
<th>TP load (Mg/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cuyahoga River near Kent, Ohio</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Twin Lakes WWTP</td>
<td>0.5</td>
<td>0.02</td>
<td>0.001</td>
<td>1.0</td>
<td>0.7</td>
</tr>
<tr>
<td>Akron WTP</td>
<td>1.6</td>
<td>0.07</td>
<td>0.002</td>
<td>1.0</td>
<td>2.2</td>
</tr>
<tr>
<td>Ravenna WWTP</td>
<td>2.8</td>
<td>0.12</td>
<td>0.004</td>
<td>1.0</td>
<td>3.9</td>
</tr>
<tr>
<td>Franklin Hills WWTP</td>
<td>2.0</td>
<td>0.09</td>
<td>0.003</td>
<td>1.0</td>
<td>2.8</td>
</tr>
<tr>
<td>Kent WWTP</td>
<td>5.0</td>
<td>0.22</td>
<td>0.007</td>
<td>1.0</td>
<td>6.9</td>
</tr>
<tr>
<td>Fish Creek WWTP</td>
<td>5.0</td>
<td>0.22</td>
<td>0.007</td>
<td>1.0</td>
<td>6.9</td>
</tr>
<tr>
<td>Akron Water Pollution Control Station (AWPCS)</td>
<td>7.86</td>
<td>3.44</td>
<td>0.109</td>
<td>0.7</td>
<td>71.8</td>
</tr>
<tr>
<td>Tinkers Creek area</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aurora Westerly Plant</td>
<td>1.4</td>
<td>0.06</td>
<td>0.002</td>
<td>1.0</td>
<td>1.9</td>
</tr>
<tr>
<td>Bedford WWTP</td>
<td>3.2</td>
<td>0.14</td>
<td>0.004</td>
<td>1.0</td>
<td>4.4</td>
</tr>
<tr>
<td>Bedford Heights WWTP</td>
<td>7.5</td>
<td>0.33</td>
<td>0.010</td>
<td>1.0</td>
<td>10.4</td>
</tr>
<tr>
<td>Streetsboro WWTP</td>
<td>4.0</td>
<td>0.18</td>
<td>0.006</td>
<td>1.0</td>
<td>5.5</td>
</tr>
<tr>
<td>Solon WWTP</td>
<td>5.8</td>
<td>0.25</td>
<td>0.008</td>
<td>1.0</td>
<td>8.0</td>
</tr>
<tr>
<td>Twinsburg WWTP</td>
<td>3.4</td>
<td>0.15</td>
<td>0.005</td>
<td>1.0</td>
<td>4.7</td>
</tr>
<tr>
<td>Southerly Wastewater Treatment Plant (CSWTP)</td>
<td>125</td>
<td>5.48</td>
<td>0.173</td>
<td>0.5</td>
<td>86.3</td>
</tr>
<tr>
<td>Total</td>
<td>245.8</td>
<td>10.8</td>
<td>0.340</td>
<td></td>
<td>218.4</td>
</tr>
</tbody>
</table>

² The average discharges from small wastewater treatment plants near Kent and Tinkers Creek areas are the EPA-permitted flow rates (OEPA, 2003). Their TP concentrations are assumed to be 1.0 mg/L.

² MGD: Million gallon per day.
three different time scales, namely daily, monthly, and yearly. The yearly average loading equals to the product of the monthly flow-weighted average concentration and discharge while the monthly average loading equals to the product of the daily flow-weighted average concentration and discharge.

3.3. Mass balances

The mass balance is an application of the law of mass conservation to the analysis of flow and P loading for a river section. Changes in storage ($\Delta S$) of a river section in a time interval ($\Delta t$) is given by

$$\frac{\Delta S}{\Delta t} = Q_u + \Sigma Q_k - Q_d$$

where $Q_u$, $Q_k$, and $Q_d$ are the streamflow discharge in upstream, tributaries, and downstream. Accordingly, changes in the P loading ($\Delta L$) of a given river section may be expressed as

$$\Delta L = L_u + \Sigma L_k - L_d$$

where $L_u$, $L_k$, and $L_d$ are the P loading of a given river section in upstream, tributaries, and downstream.

4. Results

4.1. Riverine phosphorus loadings

Concentrations of TP and SRP as measured on water samples collected from the river exhibit considerable variations, with values ranging from 0.030 to 0.287 mg/l in TP and from 0.004 to 0.175 mg/l in SRP (Fig. 3a and b). There is a clear distinction in the pattern of variations between the upper and lower Cuyahoga River. In the upper basin, TP and SRP were relatively low except some anomalies in the East Branch during low and intermediate flow conditions. In the lower basin (including the Tinkers Creek), however, TP and SRP increased substantially from the upstream downward under the three different flow conditions. Additionally, the ratio of SRP/TP increased substantially from ~0.2 in the upper Cuyahoga River to ~0.7 in the lower Cuyahoga River. Under the storm flow conditions, however, the ratio of SRP/TP was reduced to ~0.1 throughout the river basin.

The loading of TP was fairly low in the upper basin and increased rapidly in the lower basin from the upstream downward (Fig. 4a). Under the storm flow conditions, the loading of TP was extraordinarily high, which increased from 0.6 g/s at Hiram Rapids to 4.4 g/s at Old Portage to 36.8 g/s at Harvard Avenue. The loading of SRP was also low (<0.1 g/s) in the upper basin and increased rapidly in the lower basin under different flow conditions (Fig. 4b). The TP and SRP loadings of Tinkers Creek at Bedford were similar to those of the Cuyahoga River at Old Portage.

4.2. Effluent phosphorus inputs

Over a dozen WWTPs continuously discharge municipal effluents into the river at an average rate of 10.8 m$^3$/s (Table 2), accounting for on average 30% of stream flow as gaged at Independence. Concentrations of the effluent TP from the AWPCS and CSWTP from 2006 to 2008 were 0.7 and 0.5 mg/l, respectively (Table 3). But there were great daily variations in discharge, TP concentration, and TP loading of effluents from the AWPCS and CSWTP. For example, values of the maximal TP loading were one order of magnitude greater than those of the minimal TP loading. In contrast, variations in monthly-averaged discharge, TP concentration, and TP loading of effluents from the two WWTPs were significantly reduced. Moreover, the year-to-year changes in the TP loading of municipal effluents appeared to be minimal. For instance, the difference between maximum and minimum of yearly-averaged TP loading at the CSWTP was only 0.013 Mg/d or 5% of the mean TP loading (Table 3).

4.3. Comparison of riverine and effluent phosphorus loadings

Values of the effluent TP loading from the AWPCS and CSWTP were comparable to those of the riverine TP loading downstream.

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Fig. 3. Concentrations of TP (a) and SRP (b) along the Cuyahoga River and its major tributary of Tinkers Creek under the three different flow regimes, namely the low-flow regime (blue), the intermediate flow regime (green), and the storm flow regime (red). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
under the low and intermediate flow conditions (Fig. 4a). As noted above, values of the riverine TP loading under the storm flow conditions were extremely high and far exceeded those of the effluent TP loading upstream. On the other hand, values of the effluent SRP loading from the two WWTPs were overall larger than those of the riverine SRP loading downstream (Fig. 4b).

Comparison of the monthly-averaged TP loading from the AWPCS with the riverine SRP loading at Independence during a period of 2006–2008 reveals some interesting features (Fig. 5). First, the average value of the effluent TP loading was 0.20 Mg/d, much larger than that of the riverine SRP loading as gaged at Independence (0.12 Mg/d). Second, there was a great deal of similarity between the two records, indicating a great influence of effluent P inputs. Third, there existed some important discrepancies. For example, the moderate TP loading from the AWPCS in December 2007 was apparently inconsistent with the greatest value of the monthly-averaged SRP loading observed at Independence. The effluent TP loading was near or above the average from March to July 2007, whereas the concurrent riverine SRP loading at Independence was far below the average.

4.4. Mass balance analyses of phosphorus loading

Two river reaches (A and B) were selected for mass balances. Reach A stretches from Old Portage to Independence, with a river length of 43.5 km (Fig. 1). It receives effluent from the AWPCS and stream water upstream gaged at Old Portage, and tributary flow from Tinkers Creek gaged at Bedford and many other ungauged small creeks. The ungauged flow ranged from 14% of the stream flow gaged at Independence under the low flow conditions to 48% under the storm flow conditions (Table 4). Although a fair amount of stream flow was ungauged and excluded for the mass-balance analysis, the loading of SRP observed at Independence

---

**Table 3**

Summary of discharge, TP, and TP loading from two major wastewater treatment plants.

<table>
<thead>
<tr>
<th></th>
<th>Discharge (MGD)</th>
<th>TP (mg/l)</th>
<th>TP loading (Mg/d)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>Max</td>
<td>Min</td>
</tr>
<tr>
<td>Akron water pollution control station</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Daily</td>
<td>78.2</td>
<td>232.4</td>
<td>49.2</td>
</tr>
<tr>
<td>Monthly</td>
<td>77.8</td>
<td>134.5</td>
<td>55.8</td>
</tr>
<tr>
<td>Yearly</td>
<td>77.8</td>
<td>80.3</td>
<td>74.9</td>
</tr>
<tr>
<td>Cleveland southerly wastewater treatment plant</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Daily</td>
<td>125.5</td>
<td>380.5</td>
<td>69.4</td>
</tr>
<tr>
<td>Monthly</td>
<td>125.8</td>
<td>218.9</td>
<td>80.7</td>
</tr>
<tr>
<td>Yearly</td>
<td>125.8</td>
<td>128.4</td>
<td>124.0</td>
</tr>
</tbody>
</table>

* Derived from daily monitoring data during the 3-year period (2006–2008) at the two WWTPs.
Table 4
Summary of phosphorus budgetary analyses for the two reaches (A and B) in the lower Cuyahoga River.

<table>
<thead>
<tr>
<th>Low flow</th>
<th>Interim flow</th>
<th>High flow</th>
<th>Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Q (m^3/s)</strong></td>
<td><strong>LSRP (Mg/d)</strong></td>
<td><strong>LTP (Mg/d)</strong></td>
<td><strong>LSRP (Mg/d)</strong></td>
</tr>
<tr>
<td>River reach A: From Old Portage to Independence (L = 43.5 km)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Inputs</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Upstream (OP)</td>
<td>5.00</td>
<td>0.003</td>
<td>0.022</td>
</tr>
<tr>
<td>AWPCS</td>
<td>2.69</td>
<td>0.168</td>
<td>0.184</td>
</tr>
<tr>
<td>Tributary (B)</td>
<td>0.98</td>
<td>0.006</td>
<td>0.015</td>
</tr>
<tr>
<td>Total inputs</td>
<td>8.67</td>
<td>0.177</td>
<td>0.244</td>
</tr>
<tr>
<td>Exports</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Downstream (I)</td>
<td>10.09</td>
<td>0.055</td>
<td>0.132</td>
</tr>
<tr>
<td>AWPCS</td>
<td>3.49</td>
<td>0.206</td>
<td>0.226</td>
</tr>
<tr>
<td>Total exports</td>
<td>13.58</td>
<td>0.261</td>
<td>0.358</td>
</tr>
<tr>
<td>River reach B: From Independence to Harvard Ave (L = 6.1 km)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Inputs</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Upstream (I)</td>
<td>10.09</td>
<td>0.055</td>
<td>0.132</td>
</tr>
<tr>
<td>CSWTP</td>
<td>3.49</td>
<td>0.206</td>
<td>0.226</td>
</tr>
<tr>
<td>Total inputs</td>
<td>13.58</td>
<td>0.261</td>
<td>0.358</td>
</tr>
<tr>
<td>Exports</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Downstream (H)</td>
<td>13.58</td>
<td>0.210</td>
<td>0.343</td>
</tr>
</tbody>
</table>

a: Arithmetic mean of discharge (Q), SRP loading (LSRP), and TP loading (LTP) on the three low-flow sampling dates.
b: Values of the total inputs greater than those of the exports are highlighted in bold fonts.
c: Presumably equivalent to the discharge of total inputs.

5. Discussion

We found multiple lines of evidence indicating that the P loading in the Cuyahoga River came largely from effluent inputs. First, the riverine P loading increased rapidly downstream due to increases in municipal effluents in the lower Cuyahoga River. Second, the ratio of SRP/TP of the Cuyahoga River increased substantially from the upper to lower basin. Third, we found the amount of the effluent TP input was comparable to that of the riverine TP loading, particularly under the low and intermediate flow conditions. Lastly, there was a great deal of similarity between the effluent TP loading record from the AWPCS and the riverine SRP loading record from the Cuyahoga River at Independence. We thus concluded that the lower Cuyahoga River suffered from excessive nutrient loadings from municipal effluents, a conclusion in agreement with the indices of biotic integrity and water quality (OEPA, 1999).

Furthermore, we found that effluent P was highly active and subject to rapid changes or transformations in the Cuyahoga River and that changes in the riverine P loading were affected by streamflow conditions. Comparison of the effluent P loading record from the AWPCS and the riverine SRP loading record indicated that between 2006 and 2009 the average SRP loading of the Cuyahoga River as gaged at Independence was only 60% of the effluent P input, suggesting 30–40% of the reactive effluent P was converted to other forms in this river section. This notion is in line with our mass-balance analyses indicating that 27–77% of the total SRP inputs were lost in reach A. We also noted that this river section retained a fair amount of TP under the low and intermediate flow conditions and released the retained TP during the storm flow conditions, highlighting the role of flow regimes in regulating the P loading and transport across the river.

To address the influence of streamflow conditions, we used the existing long-term tributary monitoring data of the Cuyahoga River at Independence (NCWQR, 2010) to examine the changes in the P loading and transport in relation to hydrological variability in the river on different timescales. As shown in Fig. 6, the concentration of TP increased concurrently with increasing stream discharge during the two consecutive storm events occurred in August 2008. The concurrent increases in the riverine TP also seen in agricultural-dominated watersheds were attributed to increases in P-bearing suspended sediments during storm events (Richards et al., 2001).
On the other hand, the concentration of SRP decreased slightly during the storm events (Fig. 6), presumably attributed to the dilution effect of storm water. But the results from mass-balance analysis show that there was an up to 70% loss of the SRP loading during the storm flow events (Table 4), indicating that the riverine P transformations (e.g., adsorption) were active in the lower Cuyahoga River. It has been repeatedly documented that P released from WWTPs interacts quickly with stream water, sediments, and aquatic communities (e.g., algae, phytoplankton and macrophytes) through a range of physical and biological processes (House, 2003; Marti et al., 2004; Withers and Jarvie, 2008). The degree of the interactions is highly variable, depending on the P retention capacity, saturation rate, and effluent inputs. For instance, the rates of P retention were reported to vary from below 10% to over 30% under a range of flow conditions in the River Swale, northern England (House, 2003) and reach up to 60% under low flow conditions in the River Kennet, England (Jarvie et al., 2002). As to the Cuyahoga River, much uncertainty remains in the dominant processes controlling the quantitative relationship between P retention and stream flow. Nevertheless, our results are broadly consistent with these studies in indicating that riverine retention and processing can lead to changes in the form, quantity, and timing of P transported downstream (Withers and Jarvie, 2008).

Richards et al. (2001) estimated that over 90% of the suspended solids loading in the Maumee and Sandusky Rivers was transported during storm runoff periods which normally accounted for less than a third of the total time. Based on the daily discharge readings from the USGS database (NWIS, 2011) and the daily and sub-daily sampled TP and SRP concentration data of the Cuyahoga River at Independence between 1982 and 2009 (NCWQR, 2010), the percentages of time, discharge, SRP loading, and TP loading were used to evaluate the relative importance of each flow regime. The Cuyahoga River delivered, on average, 53% of river water under the intermediate flow conditions, 27% of river water under the low flow regime

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**Fig. 6.** Variations in stream discharge (solid line), SRP (filled circles) and TP (open circles) concentrations of the Cuyahoga River at Independence before and during two consecutive storm events in August 2007.

**Fig. 7.** Year-to-year variations in percentage discharge (a), percentage number (% N) of days (b), percentage TP loading (c), and percentage SRP loading (d) of the Cuyahoga River at Independence under the three different flow regimes, namely the storm flow (red), intermediate flow (green), and low flow regime (blue). Four paralleled arrows highlight the concurrent increasing or decreasing trends as discussed in the text. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
Analyses of long-term (multidecadal) monitoring data can help develop a useful context of changes in stream chemistry (Yuan and Miyamoto, 2004; Yuan et al., 2007), effectiveness of nutrient management (Bowes et al., 2011; Gustafsson et al., 2012; Howden and Burt, 2008), and trends in suspended sediment and SRP loadings (Daloglu et al., 2012; Richards et al., 2008). We examined the year-to-year changes in the loadings of TP and SRP in relation to changes in streamflow discharge, using the long-term tributary monitoring data of the Cuyahoga River at Independence for water years from 1982 to 2009 (NCWQR, 2010). There were great variations in the annual loadings, with SRP loading ranging from 20 to 105 Mg/yr and TP loading from 150 to 500 Mg/yr (Fig. 8). The loadings of TP and SRP were extraordinarilly large between 1982 and 1985, reflecting the historical P loadings prior to the implementation of stringent P regulations, such as the phosphate detergent ban and 1 mg/l effluent P standard (Hartig et al., 1990). The largest loading of TP occurred in 2003, most likely attributed to low flow conditions in the preceding five consecutive years (1998–2002). There was a robust correlation ($r = 0.86$) between the annual discharge and loading of TP in the Cuyahoga River except the above-mentioned five years (1982–85, 2003) with extraordinarily large loading of TP as enclosed by the dashed line in Fig. 9. This is due in part to that the annual effluent loading is more or less constant. As a result, variations in streamflow discharge are the dominant driver that regulates the annual TP loading of the river.

On the other hand, the annual loading of SRP generally followed the decreasing trend of the TP loading from 1985 to 1989 as a result of the stringent P regulations (Hartig et al., 1990). The loading of SRP remained its minima until 1994, then increased progressively to the maxima in 2005, and declined from 2005 to 2009. It is worth noting that the increasing trend of the SRP loading from 1995 to 2005 was also observed in other watersheds of the Lake Erie basin (Baker, 2007; OEPA, 2010), coinciding with the recent resurge of harmful algal blooms in Lake Erie (Conroy et al., 2005; Michalak et al., 2013). Comparison of the riverine SRP loading with the discharge record revealed there were some degrees of covariability, particularly in the period between 1995 and 2009. This observation suggests that the basin-wide changes in the tributary loading of SRP are related to variations in hydroclimate, e.g., recent increases in storm events across the region (Daloglu et al., 2012).

While the results of this study may contribute to the ongoing efforts to unravel the causes for the resurge of harmful algal blooms in Lake Erie, some uncertainty regarding the tributary P loading and transport still remains. First, our estimated average values of the SRP and TP loadings from our analytical results are comparable to those from the daily to sub-daily resolved samples (Baker, 2007). Our estimated mean loading of TP between 2007 and 2008 was 365 Mg/yr (or 1.002 Mg/d in Table 4), close to the average value of 350 Mg/yr from the long-term tributary monitoring data (Fig. 8), while our estimated mean loading of SRP between 2007 and 2008 was 29 Mg/yr (or 0.079 Mg/d in Table 4), 25% lower than the average value of 42 Mg/yr as derived from the long-term tributary monitoring data (Fig. 8). Concentrations of SRP and TP are highly variable, particularly during storm flow events (Richards et al., 2001). Thus, an extensive sampling scheme would help eliminate some of the uncertainty. Second, our results revealed the

![Fig. 8. Year-to-year changes in stream discharge (Q), TP loading, and SRP loading of the Cuyahoga River near Independence from 1982 to 2009. Horizontal dashed lines represent the long-term mean values of Q, TP loading, and SRP loading. Vertical bars highlight periods with extraordinarily large TP loading.](image1)

![Fig. 9. Linear regression of the annual stream discharge (Q) and TP loading of the Cuyahoga River at Independence. Points within the dashed line represent years with extraordinarily large TP loading as highlighted in Fig. 8.](image2)
presence of P transformations but less detail has been explored to evaluate the relative importance of each of the major biogeochemical processes. Lastly, we had to admit the complexity of the watershed. As described above, the Cuyahoga River also receives P inputs from some diffuse sources such as agricultural runoffs and combined sewer overflows (OEPA, 2003). Changes in the P loading from these sources could affect the tributary loading into Lake Erie. But the magnitude of such changes remains uncertain.

6. Conclusions

This study dealt with a temperate urban river ecosystem to develop a context of P loading and transport in the Cuyahoga River under the three different flow regimes. Although its stream discharge and TP loading changed from reach to reach and from time to time, the river delivered on average nearly 1 km³ of river water and over 300 Mg of TP loading into Lake Erie annually. About 30% of river water was municipal effluent from over a dozen WWTPs across the watershed, contributing at least two thirds of the TP loading present in the lower Cuyahoga River. We found that the loading and transport of TP and SRP were not only affected by the amount of P released from the municipal effluent but also regulated by stream flow regimes. Effluent P was highly reactive and subject to rapid transformations in the river. We found that losses of the loading of SRP in the lower Cuyahoga River occurred most of the sampling occasions but the loading of TP increased substantially in reach A during the storm flow event. The increases in the riverine TP loading appeared to depend on the amount of loss in the TP loading during the low and intermediate flow periods. As a result, most of the TP loading was exported during storm and intermediate flow periods, whereas most of the SRP loading was delivered during low and intermediate flow periods. The results underscored the important role of stream hydrology in controlling the loading and transport of P across the watershed as it dictated the amount, form, and timing of P delivery to Lake Erie. We suggest that an improved understanding of the major biogeochemical processes involved is required in order to develop a better P management practice for restoration of the Cuyahoga River and Lake Erie as well.

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