Accounting for surface roughness in a physically-based urban wash-off model

Stephen B. Shaw\textsuperscript{a,∗}, Jean-Yves Parlange\textsuperscript{a}, Molly Lebowitz\textsuperscript{b}, M. Todd Walter\textsuperscript{a}

\textsuperscript{a}Department of Biological and Environmental Engineering, Cornell University, Ithaca, NY 14853, USA
\textsuperscript{b}Malcolm Pirnie Inc., Kirkland, WA 98033, USA

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\textbf{S U M M A R Y}

To date, urban wash-off models have largely ignored the role of surface roughness in controlling particulate mass loss. We propose a mechanistic model in which particles are ejected by raindrops from surface cavities and travel laterally at the velocity of the overland flow until they are recaptured. In the model, cavities of differing depth and diameter have different ejection rates. The model has a similar form to multiple rate mass transfer models more commonly used to simulate solute transport in groundwater. An analytical solution for a model consisting of two possible cavity geometries is fit to breakthrough curves from sediment wash-off experiments. The experiments are conducted on a 0.8-m flume under artificial rainfall with a surface constructed of casts of asphalt. The experiments use fine sand (\(\sim250\) μm) and rainfall rates equivalent to that from a 2 year, 5-min storm in non-coastal regions of the Northeastern United States. Model parameters can be attributed to specific physical features of the surface cavities, particles, or rainfall rate and can be determined with limited calibration. At the plot scale, the model replicates an initial first flush and then settles to a more gradual loss rate which is noticeably different from the more rapid mass exhaustion implied by use of the common exponential wash-off model. Insights from this model could lead to improved design and placement of water quality management structures in urban landscapes.

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\textbf{Introduction}

With a new focus on using localized management measures to control non-point source pollution in urban areas, further advances in our fundamental knowledge of spatially explicit pollutant generation and transport processes are needed (Potter, 2006). In particular, estimating wash-off of particulate matter still frequently relies on a lumped, catchment scale exponential model or variants (Alley, 1981; Tshihrintzis and Harmid, 1998; Chen and Adams, 2007). While a few spatially distributed models have been developed (Akan, 1988; Deletic et al., 1997), they have a limited physical basis and make no observation of the small-scale, internal catchment processes. Conversely, of the few published plot scale experiments (Sansalone et al., 1998; Vaze and Chiew, 2003), most have little quantitative analysis. As an exception, Shaw et al. (2006) used experiments to evaluate a simple rainfall driven transport model for cases in which shear flow has a negligible role in particle entrainment. However, the experiments were conducted on a uniformly rough surface unlikely to represent the trapping processes associated with the irregular cavity geometries on actual urban surfaces such as asphalt (Deng et al., 2005; Nino et al., 2003).

In this paper, we (1) propose a mechanistic wash-off model that accounts for trapping within surface roughness elements, (2) compare the model to experimental results (indoor, 80 cm flume), (3) evaluate means to parameterize the model a priori based on physical features of the surface, and (4) explore the suitability of the model when applied to a larger 20 m reach scale.

\textbf{Theory}

Similar to Shaw et al. (2006), we assume that particle movement occurs by a sequence of jumps in which particles are either at rest on the rough surface or in motion in the shallow overland flow (Fig. 1). Movement is initiated only by raindrops because cavities on the rough surface shield particles from overland flow shear forces. Our own observations agree with experiments by Nino et al. (2003) which found that rough surfaces shift the threshold for incipient motion upwards, increasing the range of flow conditions in which raindrop initiated movement dominates. We assume particles on the bed surface can fall into multiple cavity geometries or “bins”, each with a different rate of ejection. Thus, the formulation is akin to a simple multiple rate mass transfer (MRMT) model (e.g. Pedit and Miller, 1994; Haggerty and Gorelick, 1995; Wang et al., 2005) or a two site solute transport model (Van Genuchten and Wagenet, 1989), approaches more traditionally applied to solute transport in groundwater. Each bin is considered to occupy a fraction of the surface (\(f\)) characterized by cavities of similar diameter and depth that control ejection at a given rate. Particles enter the shallow flow by raindrop-induced ejection at multiple rates,
Firstly, the capture rate constant \( (k, \text{s}^{-1}) \) proposed by Lisle et al. (1998) assumed a quiescent settling process \( (k = \nu_{set}/d) \) where \( \nu_{set} \) is the particle settling velocity and \( d \) is the average depth of the advecting flow layer (cm). However, more recent work suggests capture may not be due to settling alone and \( k \) may represent an effective settling rate (Shaw et al., 2008a).

**Methods**

Using a small flume situated under an artificial rain machine, we observed the rate of wash-off of particulate “pulses” from two different surfaces under the same upslope flow and rainfall rates.

**Characterization of roughness surface**

Molds of parking lot pavement were made from two sites near Riley-Robb Hall, Cornell University, Ithaca, NY using silicone mold making rubber (Dow Corning HS II). The sites were selected to have different surface roughness characteristics. Lot 2 being newly installed in 2005. From both sites, five 10 cm long, 1 mm wide strips were trimmed from each mold and the cross-sectional profile digitally imaged using a high-resolution scanner (Umax Astra 4000U) (example shown in Fig. 2). For each strip, the width of all crevices was measured at successively deeper 0.5 mm increments.

**Experimental runs**

Laboratory methods closely followed the set-up and approach used in Shaw et al. (2006, 2008a). An 80 cm long, 10.5 cm wide stainless steel flume with a 4% slope was located beneath a computer-controlled rainmaker generating \( \sim 1.6 \text{ mm} \) diameter drops. The rainmaker consisted of hypodermic needles that dispersed raindrops over an approximately 20 cm by 20 cm area. Overland flow was directly applied through a small Plexiglas stilling chamber at the upslope end of the flume. This upslope overland flow constituted approximately 90% of the flow on the flume; direct rainfall contributed the other 10%.

There has been some previous criticism of the experimental set-up (see Kinnell, 2008; Shaw et al., 2008b) based on the fact that the rain machine moves in-line with the direction of movement of the particles. Thus, particles may be subjected to unnatural correlations in rain drop location and frequency not typical of actual rainfall. No doubt, this may add additional experimental uncertainty that may limit the applicability of fitted model parameters to more natural rainfall conditions. However, given that the same rain machine is used in all of our experiments, we do not believe that this potentially unnatural rainfall obscures the influence of the primary factor we are exploring in this paper, the role of impervious surface roughness on particle transport.

![Fig. 2. Profiles of asphalt surfaces from two different parking lots. The mold is shown inverted, as applied to the pavement. The negative space – gray color – would be the pavement with its surface traced by the bold line. The image is enlarged 2x.](image)

**Fig. 2.** Schematic of mass exchange in a multi-bin system. In this case there are three bins – \( M_i \), each covering a different fraction, \( f_i \), of the total surface and with a different ejection rate, \( h_k \), \( k \) is the capture rate of the particles in motion, \( M_s \). Only particles in \( M_i \) can move laterally. The vertical arrows represent fluxes between bins due to either particle ejection (upward) or capture (downward).
A primary difference from Shaw et al. (2006) was the use of smaller particle diameters (225 μm) closer in size to the median observed in wash-off (100 μm, Sansalone et al., 1998) as well as higher up slope overland flow rates (~101 m⁻¹ s⁻¹) equivalent to 144 mm h⁻¹ rainfall accumulated at the end of an impervious 40 m reach. The applied rainfall rate was 0.0040 cm s⁻¹ (144 mm h⁻¹), equivalent to the intensity of a 2 year, 5 min storm in the non-coastal regions of the Northeastern United States (NOAA, 1977).

The flume surface consisted of a plaster-of-paris cast of a 20 cm by 10 cm silicone rubber mold made during the roughness characterization. Runs were carried out on the two different surfaces (herein referred to as Lot 1 and Lot 2) described in the roughness characterization. For each surface, three identical casts of ~20 cm were adjacent to cover a 60 cm length of the flume. The plaster-of-paris was spray coated with a latex paint in order to minimize water seepage into the cast.

We applied 10 g of 225 μm quartz sand particles in a 10 cm long strip within the interval 30–40 cm from the bottom of the flume. This initial particle spatial density of 0.1 g cm⁻² was assumed to be low enough to keep particle from shielding each other from raindrop impacts. Note, this spatial density was different from that necessary to prevent shielding in other experiments (Shaw et al., 2006) due to the different nature of the surface; in the prior experiments, the concave cavities concentrated particles onto a relatively small total area of the flume. Flow off the end of the flume spilled into a stainless steel trough that diverted the sediment-laden water into a funnel fitted with a 100 μm metal screen.

Collection funnels were changed approximately every 45 s. Recovery averaged 90% with any losses assumed to occur uniformly throughout the run. Parameters for each run are summarized in Table 1.

Model implementation

An analytical solution for the $M_i$ loss rate for a two bin MRMT ($i=2$) with initial conditions $M_i(x,0)=\delta(x)$ and $M_i(x,0) = M_j(x,0) = 0$, was found via Laplace Transforms of Eqs. (1) and (2). The solution consists of three terms (as ordered below in Eq. (4)): a convolution in which movement through the bin 2 cavities acts as the response function for movement through the bin 1 cavities, movement through bin 1 cavities alone, and movement through bin 2 cavities alone:

$$M_i(x,t) = H(\zeta)\bar{h}_1 e^{-\zeta} \int_0^t H(\tau_1)H(\tau_2)\exp(-\tau_1 - \tau_2) \frac{sf_1}{\tau_1}\left[2\sqrt{\bar{h}_1f_1 t_1} I_1 \sqrt{\bar{h}_1f_1 t_2} \right] dt' + H(\tau_1)H(\zeta)\bar{h}_1 e^{-\zeta-h_1} \int_0^t H(\tau_1)H(\tau_2)\exp(-\tau_1 - \tau_2) \frac{sf_2}{\tau_2} \left[2\sqrt{\bar{h}_2f_2 t_2} \right] dt'$$

Results and discussion

Modeling the breakthrough curves

Assessing the experimentally observed breakthrough curves, peak loss on Lot 2 (Fig. 3b) is slightly delayed in comparison to Lot 1 (Fig. 3a). Additionally and more significantly, the Lot 2 surface exhibits a greater amount of tailing than Lot 1 with traces of particulate detected after 2000 s. while none is detected after 1000 s. on Lot 1. In terms of the breakthrough time of the center of mass of the pulse, 50% of the applied mass is lost after ~335 s on the Lot 1 surface and 50% is lost after 550 s on the Lot 2 surface. These differences in wash-off behavior correspond to obvious visual differences in the roughness of the two surfaces; the Lot 1 surface has fewer narrow, deep crevices and many more shallow broad crevices in comparison to Lot 2 (Fig. 2).

The breakthrough curves from both surfaces were reasonably fit ($R^2 \sim 0.96$ for Lot 1 and $R^2 \sim 0.98$ for Lot 2) using the solution to the two bin MRMT model, Eq. (4) (Fig. 3). Parameters were manually adjusted to maximize the $R^2$ value. However, a two bin model requires four parameters ($f_1, h_1, h_2$ and $k$), and multiple parameter combinations can produce a similar fit. As in many cases where a model displays equifinality, certain parameter choices are more physically suitable. While not merely calibration parameters, we will demonstrate an underlying physical basis for each of the four parameters and suggest means to identify model parameters a priori in future cases.

Comparison to the Fokker–Planck equation

As a starting point for evaluating the model parameters, we apply the Fokker–Planck equation with $M(x,0)=M_0\delta(t)$ (Fischer et al., 1979, Eq. (2.28)). Note, since we are fitting a breakthrough curve, the standard Fokker–Planck solution is multiplied by $u_{off} \delta(t)$ so as to calculate mass flux and not concentration (see Lisle et al., 1998, Eq. (12)). As a traditional approach to fitting breakthrough curves, the Fokker–Planck equation provides a point of comparison to the two bin model as well as a means to estimate parameters of aggregate movement, effective velocity ($u_{off}$) and dispersion ($D$).

To fit the solution of the Fokker–Planck equation, an experimental $u_{off}$ can obviously be determined from the observed breakthrough curve by taking the quotient of the travel distance, $L$, and the time to peak. An experimental $D$ can be determined from the

<table>
<thead>
<tr>
<th>Run</th>
<th>$q$ (mL s⁻¹)</th>
<th>$P$ (cm s⁻¹)</th>
<th>Length (cm)</th>
<th>$h_1$ (s⁻¹)</th>
<th>$h_2$ (s⁻¹)</th>
<th>$h_3$ (s⁻¹)</th>
<th>$f_1$</th>
<th>$f_2$</th>
<th>$f_3$</th>
<th>$k$ (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lot 1</td>
<td>170</td>
<td>0.0040</td>
<td>35</td>
<td>0.063</td>
<td>0.005</td>
<td>–</td>
<td>0.98</td>
<td>0.02</td>
<td>–</td>
<td>10.0</td>
</tr>
<tr>
<td>Lot 2</td>
<td>173</td>
<td>0.0040</td>
<td>35</td>
<td>0.045</td>
<td>0.003</td>
<td>–</td>
<td>0.96</td>
<td>0.04</td>
<td>–</td>
<td>10.0</td>
</tr>
<tr>
<td>Plot scale</td>
<td>1.6</td>
<td>0.0009</td>
<td>2000</td>
<td>0.075</td>
<td>0.010</td>
<td>0.001</td>
<td>0.70</td>
<td>0.15</td>
<td>0.10</td>
<td>0.056</td>
</tr>
</tbody>
</table>
observed breakthrough curves by manipulating the solution to the Fokker–Planck equation with a delta pulse boundary condition so when $t = L / u_{\text{eff}}$:

$$D = \frac{u_{\text{eff}}^2}{4\pi M_{\text{max}}^2 t}$$

By this approach, the Lot 2 breakthrough is fit with $u_{\text{eff}} = 0.0778 \text{ cm s}^{-1}$ and $D = 0.33 \text{ cm}^2 \text{ s}^{-1}$. While capturing the timing and magnitude of the peak, the width of the peak is slightly exaggerated and, the degree of tailing is underestimated (Fig. 4). We will see below how a fundamentally different model structure is needed to fit these seemingly minor discrepancies.

The $h$ and $k$ parameters in a MRMT can be related to $D$ and $u_{\text{eff}}$ in the Fokker–Planck equation. But, only at long times is the Fokker–Planck equation identical to the MRMT model. With the Fokker–Planck equation and the two bin model in Laplace space (Eq. (A3)), we performed a Taylor Series expansion on terms within the exponential functions. Excising all terms above 2nd order, we found the Fokker–Planck and MRMT formulations were identical. However, since our experiment does not take place at a scale appropriate for a long-time approximation, we can use the Fokker–Planck equation to inform our choice of $h$ and $k$, but we would not expect an identical fit to the observed breakthrough. But, by relating to $D$ and $u_{\text{eff}}$, we gain some insight into how $h$ and $k$ interact to result in aggregate particle behavior.

For a two bin model, we find (see Appendix B for derivation):

$$u_{\text{eff}} = \frac{uh_1h_2}{(h_1h_2 + kf_1h_2 + kf_2h_1)}$$

and

$$D = \frac{u^2(f_1\frac{k_1}{h_1} + f_2\frac{k_2}{h_2})}{\left(1 + \frac{k_1}{h_1} + \frac{k_2}{h_2}\right)^3}$$

Eqs. (6) and (7) will be of some use in constraining $h$ and $k$ as discussed below.

Selecting $f_1$ and $f_2$

Given the fact that $f$ values are constrained between zero and one and $h$ and $k$ values are typically an order of magnitude larger or smaller than one, $u_{\text{eff}}$ and $D$ are relatively insensitive to $f_1$ or $f_2$. Instead, the choice of $f_1$ (or $f_2$ given that $f_1 = 1 - f_2$) mainly controls the magnitude of the peak and the magnitude of the loss in the transition to the tail, features not well captured by $u_{\text{eff}}$ and $D$. The reason for this behavior can be seen in Fig. 3 (dashed lines) where the contribution of the individual terms in the model solution (Eq. (4)) are shown. Adjusting $f_2$ shifts the emphasis on each of the two peaks corresponding to each of the two bins. If there is little tailing, $f_2$ is large ($\sim 1$), the first peak dominates, and the overall breakthrough resembles the first bin’s contribution. If $f_2$ is smaller (i.e. $f_2 = 0.90$, not shown), most particles fall into deep crevices and the second peak dominates such that the overall breakthrough resembles the second bin’s contribution. Distinct features of our observed breakthrough curves arise from overlap between the two bin’s contributions; namely, the asymmetrical, high “shoulder” of the receding breakthrough curve can only be duplicated

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**Fig. 3.** Model simulations fit to breakthrough curves for 225 µm particulate movement on 60 cm asphalt casts from Lot 1 (a) and Lot 2 (b). Symbols indicate observed values (filled and unfilled are replicates); solid line is the model. For both runs, upslope flow ($q$) and rainfall ($P$) were nearly the same. Model parameters are summarized in Table 1. The $R^2$’s for the model runs in 3a and 3b are 0.96 and 0.98, respectively. The dashed lines illustrate the contribution to mass loss from different model components.

**Fig. 4.** Fokker–Planck equation fit (solid line) to Run 2 observed (filled and unfilled symbols indicate different replicates). $D (0.33 \text{ cm}^2 \text{ s}^{-1})$ and $u_{\text{eff}} (0.0778 \text{ cm s}^{-1})$ in the Fokker–Planck equation were determined from inspection of the breakthrough data (see Eqs. (6) and (7)).
with the overlap of the rising second bin’s contribution with the falling first bin’s contribution.

To some degree, \( f_1 \) and \( f_2 \) can be estimated from the physical characteristics of the rough surfaces. We hypothesize that the distinction between a deep and shallow crevice depends on an interaction between average cavity depth and width. From the surface characterization, we can determine the fraction of each surface covered by cavities of a certain depth to width ratio. Evaluating several possible ratios involving the deeper crevices (the deepest was \( \sim 2.5 \) mm), we found Lot 1 and Lot 2 consisted of 3.5% and 5.5%, respectively, of crevices greater than 2 mm deep and less than 8 mm wide. And considering another depth to width ratio, we found Lot 1 and Lot 2 consist of 1.4% and 2.7%, respectively, of crevices greater than 2 mm deep and less than 4 mm wide. This range of depth to width ratios seems to envelop our calibrated \( f_2 \) values of 2% and 4% for Lot 1 and Lot 2, respectively.

Finally, since \( f_1 \) is relatively independent of \( u_{\text{eff}} \) and \( D_f \), \( f_2 \) is also relatively independent of \( h \) and \( k \). With \( k \) constant, one would not be able to compensate for changes in \( f_1 \) with changes in \( h \). But, with \( f_1 \) constant, \( h \) and \( k \) can be used to compensate for one another.

**Balancing \( k \) and \( h \)’s**

With an \( f_1 \) selected as discussed above, one must then narrow the range of \( h \) and \( k \). \( h \) and \( k \) will be linked by Eqs. (6) and (7) – a large \( h \) must be accompanied by a large \( k \). If we can establish the range of either \( h \) or \( k \), we constrain the other. \( k \) relates to the particle capture rate and should be partially dependent on the particle size (in terms of settling velocity) but also potentially on surface characteristics. Recent work suggests that particle capture is not necessarily well modeled as a quiescent settling process (Parsons and Stromberg, 1998; Nino et al., 2003; Shaw et al., 2008a,b), a simplification traditionally assumed in mechanistic erosion models. If the particle capture were solely due to quiescent settling, with a \( v_{\text{set}} \) of 2.83 cm s\(^{-1}\) and an average \( d = 1 \) mm, \( k = 28.3 \) s\(^{-1}\). On a uniformly rough surface consisting of shallow, oblong depressions (not necessarily efficient at trapping), using the same sized particles, Shaw et al. (2008a,b) found \( k = 3.8 \) s\(^{-1}\) from modeling. We consider these values to be reasonable bounds for our \( k \) value (e.g. \( 3.8 \) s\(^{-1}\) < \( k < 28.3 \) s\(^{-1}\)).

With \( k \) and \( f_2 \) selected, the general range of \( h_1 \) and \( h_2 \) can be constrained with Eqs. (6) and (7). We overlayed two-dimensional surfaces (with axis of \( h_1 \) and \( h_2 \)) of the residual error between best-fit \( u_{\text{eff}} \) and \( D \) values (i.e. for Lot 2 \( u_{\text{eff}} = 0.0778 \) cm s\(^{-1}\) and \( D = 0.33 \) cm\(^2\) s\(^{-1}\)) and \( u_{\text{eff}} \) and \( D \) determined from the range of possible \( h_1 \) and \( h_2 \) values. The optimal \( h_1 \) and \( h_2 \) were those that minimized the residual error for both \( u_{\text{eff}} \) and \( D \). Since we can only establish a range of possible \( k \) values, we repeat this determination of \( h \) values several times for different \( k \). Several fits for different \( k \) and the corresponding \( h \) values are shown in Fig. 5. The lowest \( k \) value \( (k = 5 \) s\(^{-1}\)) results in too much dispersion from the leading edge but both \( k = 10 \) and \( k = 15 \) result in physically reasonable fits.

**Relating \( h \) to drop impact area**

While selected largely by calibration thus far, the ejection rate value, \( h \), can also be attributed a physical meaning. As per Eq. (3), \( h \) is the ratio of the impact area \( (A_i) \) of a single rain drop to the drop volume \( (V) \) scaled by the precipitation rate. There are few experiments that measure the impact area of a raindrop on a bed of loose particles in a very shallow flow. However, experiments by Mihara (1952) on bare, wetted sand found that the impact area would be slightly larger than the drop diameter. Additionally, experiments by Macklin and Metaxas (1976) on thin flows found that the splash area in water (for our conditions of flow and drop size) would be about two drop diameters. So, outside of the deep cavities, we would expect the diameter of \( A_i \) to be somewhere near the drop diameter. With \( h_1 = 0.045 \) s\(^{-1}\) for \( P = 0.0040 \) cm s\(^{-1}\) and a \( V = 2.1 \times 10^{-2} \) cm\(^3\) (assuming a spherical drop), we find the diameter of \( A_i \) to be 1.8 mm, nearly the drop diameter. This suggests that shallow cavities do little to constrain the drop impact and that drop effectiveness is largely a function of the drop itself. Conversely, for the deep cavities with high retention \( (h_2 = 0.003 \) s\(^{-1}\)) classified by a diameter \( > 40 \) mm and a depth \( > 2.0 \) mm, the cavity depth appears to combine with the cavity diameter to constrain \( A_i \) to \( \sim 0.45 \) mm. Although the cavity diameter \( (\sim 2.0 \) mm\) is still larger than the drop diameter, the small \( A_i \) for these deep cavities suggests additional energy must depleted for particles to overcome the 2 mm cavity depth. Using this approach, \( h \) values could potentially be estimated a priori in future applications of the model.

**Model predictions for full surface coverage**

A more realistic test of the model would be a larger, plot scale, reach with complete initial particle coverage, not just a pulse. Experiments by Sansalone et al. (1998) reported particle counts/ml for 5 \( \mu \)m particles collected 9, 14, 24, 28, and 47 min after the start of a storm event on a 20 meter reach of roadway, thus providing a suitable data set for validating the model at larger scales. A three bin MRMT model with \( P = 0.0005 \) cm s\(^{-1}\) \( (18 \) mm h\(^{-1}\)), minimal upslope inflow, a length of 20 m, \( V_{\text{eff}} = 0.008 \) cm s\(^{-1}\), and initial mass of 0.001 g cm\(^{-2}\) was compared to the observations (Fig. 6). \( k \) was calculated assuming quiescent settling using the Stokes velocity for a 5 \( \mu \)m particle. \( h \) and \( f_2 \) parameters are summarized in Table 1. The three bin model was implemented using a finite difference scheme in Matlab \( (\Delta t = 15 \) s\). The collection time of the Sansalone et al. data points was shifted forward by 8 min to reflect the start of high intensity rainfall. Also note, since the Sansalone et al. (1998) data were only in terms of particle counts and the three bin MRMT model predicts mass loss, loss rates are reported as the ratio of loss at a given time to the maximum observed loss. For the model, overland flow velocity was estimated using Manning’s Equation with a Manning’s roughness of \( n = 0.03 \) (Anderson et al., 1998), also similar to the 0.025 value used by Cristina and Sansalone (2002) for pavement.
Thus, while not assessing absolute mass loss rates, Fig. 6 shows that the MRMT model is able to replicate the rapid peaking and then gradual tailing of the observed mass loss. We presume that this initial peak results from particles near the bottom of the reach that do not fall into any deep surface cavities before exiting the system. Also shown in Fig. 6, as a point of comparison, a lumped exponential model – traditionally used to predict wash-off – fails to predict the observed pattern of mass loss, greatly overpredicting the time at which the initial surface mass is exhausted. The rapid decline to a near zero loss rate by the exponential model is dramatically different considering we are looking at ratios of loss; the observed rate declines by ~80%, but the exponential declines by nearly 99%, significantly different in terms of actual mass loss.

**Conclusions**

To date, no urban pollutant transport models have addressed the role of surface roughness in retaining and attenuating particles. We used a two bin MRMT model to incorporate the effects of roughness into a physically-based wash-off model and found that model parameters could be related to characteristics of the impervious surface. The concept is demonstrated at the laboratory scale as well as compared to previously published data from a 20 m asphalt reach. With a small fraction of surface area having a long particle retention time, we can explain the dual behavior of a first flush followed by more steady, non-mass limited loss later in the storm, contrary to the behavior of an exponential wash-off model. At larger scales, where shear induced wash-off is more likely to dominate, the exponential model may still be reasonable. These insights could lead to improved design and placement of water quality management structures in urban landscapes.

Additionally, this investigation provides an interesting case study of a situation in which a standard, textbook model appears nearly 99%, significantly different in terms of actual mass loss. Thus, while not assessing absolute mass loss rates, Fig. 6 shows that the MRMT model is able to replicate the rapid peaking and then gradual tailing of the observed mass loss. We presume that this initial peak results from particles near the bottom of the reach that do not fall into any deep surface cavities before exiting the system. Also shown in Fig. 6, as a point of comparison, a lumped exponential model – traditionally used to predict wash-off – fails to predict the observed pattern of mass loss, greatly overpredicting the time at which the initial surface mass is exhausted. The rapid decline to a near zero loss rate by the exponential model is dramatically different considering we are looking at ratios of loss; the observed rate declines by ~80%, but the exponential declines by nearly 99%, significantly different in terms of actual mass loss.

**Appendix A**

*Analytical solution to two bin MRMT model*

For a two bin MRMT model, Eqs. (1) and (2) can be rewritten as:

\[
\frac{\partial M_i}{\partial t} + u \frac{\partial M_i}{\partial x} = -k M_i + h_1 M_1 + h_2 M_2 \quad (A1)
\]

\[
\frac{\partial M_i}{\partial t} = k_f M_i - h_i M_i \quad \text{for } i = 1, 2 \quad (A2)
\]

where \( h_i \) is an ejection rate parameter and \( k \) is a capture rate parameter.

Using a Laplace transform, with an initial condition of \( M_i(x, 0) = \delta(x) \), \( M_i(0) = \frac{\delta(x)}{u} \). A two bin model has the form:

\[
M_i(x,t) = \frac{H(x)}{u} \left( f_{1i} h_1 + \frac{x}{u} h_1 s + 5 \right) \exp \left( \frac{k x f_{1i} h_1}{u} \right) \exp \left( \frac{k x f_{2i} h_2}{u} \right) \quad (A3)
\]

Using the convolution property in combination with the inverse transform (Oberhettinger and Badii, 1973, 5.66):

\[
F(s) : e^{s} - 1 - f(t) : \left( \frac{1}{t} \right) \left[ I_1(2at)^2 \right] \quad (A4)
\]

Eq. (A3) can be inverted to Eq. (4).

**Appendix B**

*Derivation of \( u_{eff} \) and \( D \) in terms of \( h_i \) and \( k \)*

Taking Eqs. (1) and (2) and putting Eq. (1) in terms of \( M_i \) only,

\[
M_i = \frac{1}{h_i} \left( f_i k M_i - \frac{\partial M_i}{\partial t} \right) \quad (A5)
\]

\[
\frac{\partial^n M_i}{\partial t^n} = \frac{1}{h_i} \left( f_i k M_i \frac{\partial^n M_i}{\partial x^n} - \frac{\partial^{n+1} M_i}{\partial x^{n+1}} \right) \quad \text{for } n = 1, 2, \ldots \quad (A6)
\]

Substituting into Eq. (1) and cutting off terms greater than 2nd order:

\[
\left( 1 + \sum_{i=1}^{n} \frac{f_i k M_i}{h_i} \right) \frac{\partial M_i}{\partial t} + u \frac{\partial M_i}{\partial x} = \left( \sum_{i=1}^{n} \frac{f_i k}{h_i^2} \right) \frac{\partial^2 M_i}{\partial x^2} \quad (A7)
\]

One can transform the \( t \) derivative into an \( x \) derivative using the relation:

\[
\left( \frac{\partial}{\partial x} \right)^a = \left( \frac{-1}{u} \sum_{i=1}^{n} \frac{f_i k}{h_i} \right) \frac{\partial}{\partial t} + \frac{1}{u} \sum_{i=1}^{n} \frac{f_i k}{h_i^2} \left( \frac{\partial^2}{\partial x^2} \right)^a \quad (A8)
\]

Resulting, in the equation:

\[
\frac{\partial M_i}{\partial t} + \frac{u}{1 + k \left( \sum_{i=1}^{n} \frac{f_i k}{h_i^2} \right)} \frac{\partial M_i}{\partial x} = \frac{u^2 \left( \sum_{i=1}^{n} \frac{f_i k}{h_i^2} \right)}{1 + k \left( \sum_{i=1}^{n} \frac{f_i k}{h_i^2} \right)} \frac{\partial^2 M_i}{\partial x^2} \quad (A9)
\]

with the scalar of the first order \( x \) derivative analogous to effective velocity, \( u_{eff} \), and the scalar of the second order \( x \) derivative analogous to a dispersion constant, \( D \), similar to Lisle et al. (1998).
References