Transport, Characterization and Control for Storm Water in Coastal Areas

Emerging Technologies, Tools and Techniques to Manage Our Coast in the 21st Century

Cocoa Beach, Florida USA (30 January 2003)

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I would like to acknowledge the research and efforts of all my graduate students, research collaborators, supporting agencies (including University of New Hampshire, CICEET, Sea Grant, LWRRI and USEPA) and reviewers over the last 10 years. Without them this synthesis would not be possible.
The interactions between

- Hydrologic Processes (deterministic & stochastic), i.e.
  - rain-runoff relationships
  - snow-snowmelt relationships
- “Constructed” Environments, i.e.
  - infrastructure, pavement
  - soil, hydraulic modification
- Anthropogenic Activities, i.e.
  - traffic, litter, maintenance
  - inadvertent discharges

result in water quantity, water quality, “control” and beneficial use issues for storm water that are challenging.
**Problem Statement**

- Water quality and quantity, control and reuse of storm water are complex and requires knowledge of:
  1. Hydrologic processes modified by the urban environment
  2. Depositional method, hydraulics, fluxes, spatial location
  3. Chemistry of aqueous solution and solid phase chemistry
  4. Physical-chemical characteristics of particulates and soils
  5. Understanding of Unit Operations, Processes, Hydrodynamics
Objectives

1. Examine storm water science, discuss why storm water is sometimes misunderstood, and demonstrate relationship between quantity and quality (anthrochemical hydrologic cycle),

2. Review aqueous and particulate chemistry and interactions in rainfall-runoff,

3. Present “treatment” or “control” concepts (source ➔ in-situ ➔ regional control),

4. Introduce emerging ideas of: trading, banking, reuse.
Partitioning and distribution of mass (example – Cu)

- Inorganic or organic mass
- Adsorbed (Particulate-Bound) \( f_p \)
- Poorly sampled and often ignored
- Dissolved (aqueous) \( f_d \)
- Ionic
- Complexed
- Colloidal
- Suspended
- Settleable
- Sediment - Floatable

Graph:
- X-axis: Particle diameter (µm)
- Y-axis: Cumulative (%)
- Total Aqueous Cu
- Cu\(^{+2} \)
- Cu DOM
- Concentration (%)
- 0.01
- 0.1
- 1
- 10
- 100

Legend:
- Low
- EMC
- High

Equations:
- \( \text{CuDOM} \)
- \( \text{Cu}^{+2} \)
BACKGROUND and PERSPECTIVE
Compared to Wastewater and Drinking Water:

- Science of drinking water treatment has developed over the last 100 years in the USA; earlier in Europe,
- Science of wastewater has developed over last 80 years in USA,
- Science of urban storm water is young, developing over last 25 years in USA.
Why is Storm Water Control Unique?

Compared to wastewater (WW) control, storm water is:

- Diffuse and stochastic, (in-situ vs. regional control?)
- Physical and Chemical, not Organic or Biological*
- Driven by hydrology, (flows vary by orders of magnitude).

*Roma (2002)

Major source of ancient and modern (up to end of World War I) urban pollution in Europe and USA. Innumerable piles of equine fecal matter (high organic content, high oxygen demand and high fecal organism numbers) deposited on a regular basis in the urban watershed are what helped lead to the concept of a 5-day BOD. It has also, in part, lead to our historical lethargy in relegating BOD, to its proper resting place in history.
Loadings to, disposal of, urban storm water

Before WW-I:
- organic loadings
- biochemical OD
- fecal contamination
- waterborne disease
- transport by horse
- catch basins, sewers
- dilution is solution

After WW-II:
- inorganic loadings
- chemical OD
- metals, xenobiots
- particulates, pathogens
- transport by vehicle
- catch basins, sewers
- treatment control, P3?"
A number of characteristics of the local hydrologic cycle are modified by our constructed environs. The most important are:

- **Infiltration** is significantly *reduced*. Depending on soil characteristics this can be the most important component modification,

- **Evaporation** is significantly *reduced*,

- **Depressional Storage** is significantly *reduced*,

As a result, $Q_p$ and $V$ increase, $t_p$ decreases, temperature increases.
The “Constructed” (i.e., urban) environment modifies 3 primary attributes of the storm water hydrograph compared to the pre-constructed environment:

1. **Peak flow**, \( Q_p \) increases,
2. **Runoff volume**, \( V \) increases,
3. **Temporal behavior**, \( t_p \) of the hydrograph is decreased.

The constructed environment alters the local hydrologic cycle with significant control implications.

- i.e., a 12-hour rainfall-runoff event generating 3 inches (7.6 cm) of runoff over a 200-acre constructed site can generate over 16 million gallons of storm water volume. Consider the treatment infrastructure required to “control” and “treat” such volumes intermittently.
Sources and Loadings

• While it sounds obvious, it is worth remembering that until we know the sources of anthropogenic constituents, we cannot begin to control source loadings
Infrastructure Subject to Leaching of Me^{x+}
(interaction of infrastructure, hydrology and chemistry)
## Traffic-generated constituents in storm water

<table>
<thead>
<tr>
<th>Fuel System</th>
<th>Tires</th>
<th>Pavement</th>
</tr>
</thead>
<tbody>
<tr>
<td>- VOCs</td>
<td>- Zn (3.0 mg/vehicle-km)</td>
<td>- solids (1-10,000+ µm)</td>
</tr>
<tr>
<td>- Petroleum</td>
<td>- Cd (0.02 mg/vehicle-km)</td>
<td>- PAHs (asphalt)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Body/Frame</th>
<th>Tires</th>
<th>Pavement</th>
</tr>
</thead>
<tbody>
<tr>
<td>- Zn, Cr, Fe, Al</td>
<td>- solids (mean dia. = 20µm)</td>
<td>- phenols (asphalt)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Engine</th>
<th>Tires</th>
<th>Pavement</th>
</tr>
</thead>
<tbody>
<tr>
<td>- Zn, Cu, Cr, Mn</td>
<td>- solids (ρs = 1.6)</td>
<td>- thermal (asphalt)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Brakes</th>
<th>Tires</th>
<th>Pavement</th>
</tr>
</thead>
<tbody>
<tr>
<td>- Cu, Pb</td>
<td>- Cd (0.02 mg/vehicle-km)</td>
<td>- PAHs (asphalt)</td>
</tr>
<tr>
<td></td>
<td>- solids (mean dia. = 20µm)</td>
<td>- phenols (asphalt)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Exhaust</th>
<th>Tires</th>
<th>Pavement</th>
</tr>
</thead>
<tbody>
<tr>
<td>- Particulates</td>
<td>- solids (ρs = 1.6)</td>
<td>- thermal (asphalt)</td>
</tr>
</tbody>
</table>

* Metallic particulates can be rapidly leached into storm water as a function of pH, particle size, RTD, hydrodynamics.*
Sources of traffic-generated particulates*
(13,500 mg/m²·day @ ADT = 150,000)

- tire wear: 28 - 31%
- engine/brake wear: 15%
- settleable exhaust: 6%
- background: 3%
- atmospheric deposition: 3%
- pavement wear: 44 - 49%
- tire wear: 28 - 31%

* Metallic particulates can be rapidly leached into storm water as a function of pH, particle size, RTD, hydrodynamics.
Urban Runoff vs. untreated domestic wastewater

Urban data utilized:
- Population: 800,000 (250-Lpd/capita)
- Mean annual rainfall: 1050-mm (C = 0.7)*
- Interstate & arterial road area: 40-km²

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Runoff (M³)</th>
<th>Wastewater (M³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow</td>
<td>3.1 x 10⁹</td>
<td>5.3 x 10⁹</td>
</tr>
<tr>
<td>COD [mg/L]</td>
<td>350</td>
<td>400</td>
</tr>
<tr>
<td>TSS [mg/L]</td>
<td>200¹</td>
<td>220</td>
</tr>
<tr>
<td>ZnT [µg/L]</td>
<td>4500 (232.0 tons)</td>
<td>75 (USEPA, 1993)</td>
</tr>
<tr>
<td>CuT [µg/L]</td>
<td>150 (7.7 tons)</td>
<td>35</td>
</tr>
<tr>
<td>PbT [µg/L]</td>
<td>90 (3.6 tons)</td>
<td>10</td>
</tr>
<tr>
<td>CdT [µg/L]</td>
<td>12 (0.7 tons)</td>
<td>1</td>
</tr>
</tbody>
</table>

¹ TSS: 180-mg/L (81 Urban commercial/residential areas, NURP, 1983)

40-km² as a % of total pavement area of the urban area: 15%
The partitioning and speciation of heavy metals in rainfall-runoff at the upper end of the urban watershed

- Implications for control
  - Physical operations: sedimentation, filtration, C/F
    - The focus is particles
  - Chemical processes: ion exchange, adsorption, precipitation
    - The focus is on solutes
      - Ionic solutes
      - Complexed solutes
    - Ultimately, how control of solutes such as metals is nothing but a mass transfer process
      - Either transfer solutes to entrained particles (i.e. SSC) or fixed media (i.e. engineered media)
<table>
<thead>
<tr>
<th>Location</th>
<th>ADT</th>
<th>Annual Rainfall</th>
<th>Annual Snowfall</th>
<th>Rainfall pH</th>
<th>Runoff pH</th>
<th>Runoff Alkalinity</th>
<th>Volumetric C</th>
<th>Pavement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cincinnati, Ohio</td>
<td>115,000</td>
<td>1050 mm</td>
<td>50 cm</td>
<td>3.5 to 4.5</td>
<td>5.6 to 7.0</td>
<td>30-50 mg/L</td>
<td>0.25 to 0.95</td>
<td>Asphalt</td>
</tr>
<tr>
<td>Baton Rouge, Louisiana</td>
<td>78,000</td>
<td>1460 mm</td>
<td>-</td>
<td>5.5 to 6.5</td>
<td>6.4 to 8.0</td>
<td>40-100 mg/L</td>
<td>0.40 to 0.95</td>
<td>PCC</td>
</tr>
</tbody>
</table>

- Both areas designated as transportation land use and NPDES Phase II areas
- Both areas have mean storm water residence times of less than 15 minutes
- Both areas have initial residence times of less than 30 minutes
- Both areas at upper end of urban watershed where in-situ controls are placed

The geotechnical and environmental characteristics of the highway soil samples were performed to evaluate the spatial distribution of heavy metals and correlate the soil properties to heavy metal concentrations. One objective of this was to correlate geotechnical and environmental indices, which can be easily obtained with readily available equipment, to substitute the expensive and time consuming metals analyses.
Example of partitioning, discharge limits and metals

Chemistry/Hydrology – Baton Rouge:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>SSC</td>
<td>272 - 519</td>
<td>mg/L</td>
</tr>
<tr>
<td>DOC</td>
<td>99 - 138</td>
<td>mg/L</td>
</tr>
<tr>
<td>COD</td>
<td>82 - 1101</td>
<td>mg/L</td>
</tr>
<tr>
<td>pH</td>
<td>6.5 - 8.1</td>
<td>S.U.</td>
</tr>
<tr>
<td>Alkalinity</td>
<td>8 - 107</td>
<td>mg</td>
</tr>
<tr>
<td>Hardness</td>
<td>39 - 43.3</td>
<td>CaCO_3/L</td>
</tr>
<tr>
<td>Rainfall</td>
<td>968 - 1583</td>
<td>mm</td>
</tr>
</tbody>
</table>

Chemistry/Hydrology – Cincinnati:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>SSC</td>
<td>29 - 259</td>
<td>mg/L</td>
</tr>
<tr>
<td>DOC</td>
<td>2 - 25</td>
<td>mg/L</td>
</tr>
<tr>
<td>COD</td>
<td>115 - 332</td>
<td>mg/L</td>
</tr>
<tr>
<td>pH</td>
<td>8.0 - 8.8</td>
<td>S.U.</td>
</tr>
<tr>
<td>Alkalinity</td>
<td>7.8 - 130</td>
<td>mg</td>
</tr>
<tr>
<td>Hardness</td>
<td>18 - 171</td>
<td>CaCO_3/L</td>
</tr>
<tr>
<td>Rainfall</td>
<td>1019 - 1357</td>
<td>mm</td>
</tr>
</tbody>
</table>
Atmospheric Contributions of Pollutants: Rainfall Analysis at Baton Rouge, LA

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>µ</th>
<th>Range</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>TDS</td>
<td>9.4</td>
<td>2.0 – 16.0</td>
<td>mg/L</td>
</tr>
<tr>
<td>COD</td>
<td>0.01</td>
<td>0.0 – 0.4</td>
<td>mg/L</td>
</tr>
<tr>
<td>pH</td>
<td>4.3</td>
<td>3.3 – 5.7</td>
<td>S.U.</td>
</tr>
<tr>
<td>Alkalinity</td>
<td>0.7</td>
<td>0.0 – 5.0</td>
<td>mg/L CaCO₃</td>
</tr>
<tr>
<td>Hardness</td>
<td>0.7</td>
<td>0.05 – 3.0</td>
<td></td>
</tr>
<tr>
<td>Redox</td>
<td>543</td>
<td>134 – 655</td>
<td>mV</td>
</tr>
<tr>
<td>Turbidity</td>
<td>2.7</td>
<td>1.1 – 3.9</td>
<td>NTU</td>
</tr>
<tr>
<td>Conductivity</td>
<td>19.8</td>
<td>3.9 – 28.5</td>
<td>μS/cm</td>
</tr>
<tr>
<td>Temperature</td>
<td>21.6</td>
<td>17.5 – 24.8</td>
<td>°C</td>
</tr>
<tr>
<td>Rainfall</td>
<td>13.6</td>
<td>1.0 – 41.4</td>
<td>mm</td>
</tr>
</tbody>
</table>

Catchment #1: Located at I-10 experimental site, free of obstructions
Catchment #2: Located 5 miles from site in quiescent park-like setting
**Ionic Charge Balance: A Single Instant in Time**

**30-May-02 Storm Event**
- Time = 83 min
- pH = 6.9
- Redox = 428.0 mV
- Ionic strength = 0.01
- Charge Balance = 1.3%

Anions: 3.6e-4 molc/kg

Cations: 3.7e-4 molc/kg

---

### Concentrations

<table>
<thead>
<tr>
<th>Anion</th>
<th>Conc. (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCO₃⁻</td>
<td>10.36</td>
</tr>
<tr>
<td>PO₄³⁻</td>
<td>0.9</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>5.8</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>120.0</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>31.7</td>
</tr>
<tr>
<td>DOC</td>
<td>8.16</td>
</tr>
</tbody>
</table>

### Concentrations (µg/L)

<table>
<thead>
<tr>
<th>Cation</th>
<th>Conc. (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al³⁺</td>
<td>21.4</td>
</tr>
<tr>
<td>Cr²⁺</td>
<td>6.9</td>
</tr>
<tr>
<td>Mn²⁺</td>
<td>251.7</td>
</tr>
<tr>
<td>Fe³⁺</td>
<td>71.6</td>
</tr>
<tr>
<td>Ni²⁺</td>
<td>46.0</td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>50.8</td>
</tr>
<tr>
<td>Zn²⁺</td>
<td>183.3</td>
</tr>
<tr>
<td>As³⁺</td>
<td>4.2</td>
</tr>
<tr>
<td>Cd²⁺</td>
<td>0.8</td>
</tr>
<tr>
<td>Pb²⁺</td>
<td>3.0</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>2869</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>3.5e4</td>
</tr>
<tr>
<td>K⁺</td>
<td>6684</td>
</tr>
<tr>
<td>Ag⁺</td>
<td>0.2</td>
</tr>
<tr>
<td>Ba²⁺</td>
<td>110.9</td>
</tr>
<tr>
<td>Na⁺</td>
<td>7154</td>
</tr>
</tbody>
</table>

---

Anions analyzed by spectrometric methods

Cations analyzed by ICP-MS

---

**Speciation @ t = 83 minutes**

- DOM
- ionic
- CO₃⁻²
- HCO₃⁻
- SO₄²⁻
- OH⁻
Hydrology, Partitioning, and Speciation: Zn

11-April-2002 Storm Event

<table>
<thead>
<tr>
<th>Parameter</th>
<th>µ</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.4</td>
<td>7.3 - 7.4</td>
</tr>
<tr>
<td>Alkalinity [mg/L]</td>
<td>63.6</td>
<td>48 - 83</td>
</tr>
<tr>
<td>SSC [mg/L]</td>
<td>252</td>
<td>101 - 486</td>
</tr>
<tr>
<td>COD [mg/L]</td>
<td>573</td>
<td>474 - 884</td>
</tr>
<tr>
<td>DOC [mg/L]</td>
<td>92.3</td>
<td>66.4 - 138</td>
</tr>
<tr>
<td>Zn T [µg/L]</td>
<td>443</td>
<td>285 - 780</td>
</tr>
<tr>
<td>fD</td>
<td>0.46</td>
<td>0.35 - 0.56</td>
</tr>
</tbody>
</table>

*Indicated species represent 98.0 - 98.6% of total dissolved Zn.
Influences of Hydrograph Intensity on Speciation

Influences of Hydrograph Intensity on Speciation

<table>
<thead>
<tr>
<th></th>
<th>Volume (L)</th>
<th>Rainfall (in)</th>
<th>Qmax (L/min)</th>
<th>PDH (hrs)</th>
<th>ϕ−Cu (µg/L)</th>
<th>ϕ−DOC (mg/L)</th>
<th>ϕ−Alk. (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11-Apr-02</td>
<td>53.6</td>
<td>0.05</td>
<td>5.4</td>
<td>68</td>
<td>101.9-185.0</td>
<td>66.3 - 137.5</td>
<td>48.0 - 83.0</td>
</tr>
<tr>
<td>30-May-02</td>
<td>7336.8</td>
<td>1.63</td>
<td>300.0</td>
<td>306</td>
<td>63.1-129.1</td>
<td>4.1-202.3</td>
<td>5.5- 82.5</td>
</tr>
</tbody>
</table>

ϕ = range
The nature and role of particulate matter transported by rainfall-runoff in the urban watershed
Morphology and Composition of Urban Stormwater F

SEM images for stormwater particles.

Energy Dispersive X-ray Spectrum

- Si
- O
- Al
- Mg
- K
- Ca
- Fe

Energy (keV)

Count

0 1 2 3 4 5 6 7 8 9 10

d = 100 μm
d = 10 μm
The Amphoteric Nature of Anthropogenic Urban Particles

**Point of Zero Charge (PZC)**

**Definition** –
Ph value of a solution at which there is no net charge on the particles (positive and negative surface charges are balanced)

**Measurement** –
- Potentiometric titration
- Ion adsorption
- Zeta potential analysis

Surface potential -
\[
\psi = \frac{RT}{F} \ln \left( \frac{[H_\text{bulk}]}{[H^+]^2} \right)
\]

PZC reflects particle surface mineralogy and surface organic content of particles. The presence of clay minerals will shift the PZC to lower pH value. For urban runoff or snowmelt, PZC is useful in coagulation, surface complexation and sorption studies.
Particulate Agglomeration \((N_t, l_{nv})\) as \(f(pH)\)

- 19 January 2002: \(pH = 6.5\)
- 24 January 2002: \(pH = 5.5\)
- 26 March 2002: \(pH = 8.5\)

\[
N_t = \alpha \ln v,i - \beta
\]
Solid Fractions in Urban Runoff (Baton Rouge)

<table>
<thead>
<tr>
<th>Solid Fraction</th>
<th>(d_{50} = \text{[Mean, Std.Dev]})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Suspended fraction</td>
<td>([1.62, 0.042])</td>
</tr>
<tr>
<td>Sediment fraction</td>
<td>([10.36, 4.686])</td>
</tr>
<tr>
<td>Grit fraction</td>
<td>([649, 96.90])</td>
</tr>
</tbody>
</table>

- Densities of grit are higher than those of clarified sediments across the entire size gradations.
- The difference increases with increase of particle size.

![Density Graph](image)

- Total solids transported by urban rainfall-runoff
- Sediments
- Grit

**Legend:**
- Dashed blue: Suspended solids
- Dashed red: Clarified Sediment
- Solid blue: Grit

**Figure Caption:**

- **Figure:** Solid Fractions in Urban Runoff (Baton Rouge)
- **Legend:**
  - Dashed blue: Suspended solids
  - Dashed red: Clarified Sediment
  - Solid blue: Grit

**Graph Description:**

- The graph shows the density of solid fractions in urban runoff.
- The density ranges from 1.0 to 3.0 g/cm³.
- The particle diameter ranges from 1.0 to 4500 µm.
- The graph includes data for suspended, sediment, and grit fractions.
- The density data for grit fractions is notably higher than that of clarified sediments across the entire size gradations.
- The difference in density increases with the increase of particle size.
Settling Velocity of Non-colloidal Particulates (>180 µm)

- Settling velocities were determined through visual observation of individual particle settling in an experimental settling column.
- Measured velocities agree to the modeled velocities using Newton’s Law assuming Euclidean particles.
Fractal analysis for system of individual primary particles

- Measured perimeter lies above the calculated perimeter assuming Euclidean geometry, indicating slight fractal nature of primary particles in urban rainfall-runoff.
- \( D_1 = 1.0 \) for Euclidean object. \( D_1 \) increases with the irregularity of particle boundaries.
- \( D_1 \) was determined from divider-stepping method in image analysis.
Practical implications: Fractal structures have fundamentally different sedimentation properties and flocculation properties as compared to Euclidian-type particle geometry (or our assumption of such geometry).

$D_2$ is less than 2.0 for primary particulates. In terms of $D_2$, primary suspended particles (<75 $\mu$m) are more fractal than settleable primary particles (> 75 $\mu$m). As $D_2$ decreases, the aggregate become less compact and more amorphous.
The interaction of heavy metals and urban particles

- If our BMPs are effective there will be a need to manage significant quantities of residual solids.
- These residual solids become preferential substrates and potential sources of anthropogenic constituents such as heavy metals.
- Understanding of the nature and interaction between entrained particles, captured particles and urban storm water solutes is critical for long term management strategies.
Clay-size Stormwater Particulate Composition

**Physical Indices:**
- $d_{50}$ (µm): 3.5
- $\rho_s$ (g/cm³): 2.68
- SSA (m²/g): 130
- PZC: 5.8
- $D_2$ (Fractal): 1.93

**Composition:**
- Cu (mg/kg): 210
- Zn (mg/kg): 2160
- Cd (mg/kg): 8.84
- Pb (mg/kg): 728
- Mg (mg/kg): 1510
- Ca (mg/kg): 7610
- Al (mg/kg): 43000
- Fe (mg/kg): 30500
- Mn (mg/kg): 114

**XRD Patterns:**
- M: Montmorillonite 51.4%
- I: Illite 6.3%
- K: Kaolinite 7.6%
- Q: Quartz 6.8%
- A: Anorthite 27.8%

**Intensity (2θ):**
- 4
- 8
- 12
- 16
- 20
- 24
- 28
- 32

**SSA (m²/g):**
- 98.9%
Heavy Metal Adsorption for Urban Stormwater Particles*

Initial Stormwater Concentration:

<table>
<thead>
<tr>
<th>Metal</th>
<th>mM</th>
<th>µg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>(1.5 \times 10^{-3})</td>
<td>100</td>
</tr>
<tr>
<td>Zn</td>
<td>(1.54 \times 10^{-1})</td>
<td>1000</td>
</tr>
<tr>
<td>Cd</td>
<td>(8.9 \times 10^{-5})</td>
<td>10</td>
</tr>
<tr>
<td>Pb</td>
<td>(2.4 \times 10^{-4})</td>
<td>50</td>
</tr>
<tr>
<td>Mg</td>
<td>(8.3 \times 10^{-7})</td>
<td>2000</td>
</tr>
<tr>
<td>Ca</td>
<td>(5.0 \times 10^{-1})</td>
<td>20000</td>
</tr>
</tbody>
</table>

Implications for control in the urban watershed:

- Heavy metal adsorption and precipitation increases with increasing pH
- The adsorption of Pb onto stormwater particles can take place at low pH value
- Pb and Cu have high affinity with and can be accumulated on stormwater solids

* Batch experiments
  - 24 hr contact time
  - 10 g solids/L solution
Cu and Zn Adsorption Isotherms for Urban Storm Water Particles
(Initial Concentration Ratios of Cu : Zn : Cd : Pb of 1 : 10 : 0.06 : 0.15)

\[ q = kC^n \]

<table>
<thead>
<tr>
<th>Symbol</th>
<th>System Component</th>
<th>( k )</th>
<th>( n )</th>
<th>( R^2 )</th>
<th>( k )</th>
<th>( n )</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>+</td>
<td>Cu,Zn,Cd,Pb</td>
<td>0.273</td>
<td>0.410</td>
<td>0.957</td>
<td>0.102</td>
<td>0.330</td>
<td>0.938</td>
</tr>
<tr>
<td>+</td>
<td>Cu,Zn,Cd,Pb,Mg</td>
<td>0.275</td>
<td>0.581</td>
<td>0.989</td>
<td>0.077</td>
<td>0.362</td>
<td>0.956</td>
</tr>
<tr>
<td>•</td>
<td>Cu,Zn,Cd,Pb,Ca</td>
<td>0.276</td>
<td>0.641</td>
<td>0.963</td>
<td>0.065</td>
<td>0.591</td>
<td>0.980</td>
</tr>
<tr>
<td>•</td>
<td>Cu,Zn,Cd,Pb,Mg,Ca</td>
<td>0.268</td>
<td>0.721</td>
<td>0.843</td>
<td>0.036</td>
<td>0.856</td>
<td>0.936</td>
</tr>
</tbody>
</table>
Entrained particulate gradation in storm water

\[ \text{SA}_i = \sum \{ (\text{SSA}_i)(m_i) \} \]

- \( \text{SA}_i \): Incremental particle surface area (m²)
- \( \text{SSA}_i \): Incremental specific surface area (m²/g)
- \( m_i \): Incremental particle mass (g)
Distribution of heavy metal mass across gradation

- **Zn mass**: $R^2 = 0.94$
- **Cu mass**: $R^2 = 0.81$
- **Cd mass**: $R^2 = 0.90$
- **Pb mass**: $R^2 = 0.97$
Particle diameter (µm)

Distribution of metal mass across gradation (1000-g basis)

Site 3SW

Cumulative (%) Cumulative (%)
The concept of a first flush at the upper end of the urban watershed
“First-flush” Transport Is a Function of:

- Hydrology (rainfall and runoff characteristics)
- Previous loadings and deposition
- Event-based loadings and deposition
- Nature and availability of constituent
- Measurement technique (index vs. fundamental)
- Partitioning & phase of constituent (i.e. dissolved vs. particulate)
- Assessment criterion: concentration, mass, toxicity
- Infrastructure and surface characteristics
- Solubility and leachability of a constituent
- Location in the watershed

- Is control based on the “first-flush” or the entire event?
The Concept of the “First Flush”

**Mass-Based First Flush**

\[ \frac{\int_0^t M_i dt}{M_{tot}} > \frac{\int_0^t Q_i dt}{Q_{tot}} > 0.5 \]

Disproportionate Delivery of Mass
80% of Mass Transported in 11% of Flow

**Lack of First Flush**

\[ \frac{\int_0^t M_i dt}{M_{tot}} < \frac{\int_0^t Q_i dt}{Q_{tot}} < 0.5 \]

Proportionate Delivery of Mass
80% of Mass Transported in 75% of Flow
Mass vs. Concentration-Based “First Flush”

- MBFF & CBFF:
  - Mass-Based First Flush
  - Concentration-Based First Flush
  - Mass and concentration delivery disproportionate to hydrograph

- CBFF:
  - Lack of Mass-Based First Flush
  - Concentration-Based First Flush
  - Mass delivery proportionate to hydrograph

- No First Flush:
  - Lack of Mass-Based First Flush
  - Lack of Concentration-Based First Flush
  - Mass and concentration delivery proportionate to hydrograph
Disproportional vs. Proportional Mass Delivery

Incremental Mass
\[ M(t) = \frac{\sum_{i=1}^{n} Q(t_i)C(t_i)\Delta t}{\sum_{i=1}^{n} Q(t_i)\Delta t} \]

Incremental Volume
\[ V(t) = \frac{\sum_{i=1}^{n} Q(t_i)\Delta t}{\sum_{i=1}^{n} \Delta t} \]

Incremental Variables
- \( Q \) = Average flow rate
- \( C \) = Concentration
- \( \Delta t \) = Time increment
- \( n \) = Number of increments

Proportionate Incremental Mass
Proportionate Incremental Volume

Pearson’s Correlation Coefficient
\[ r = \frac{\Sigma xy - \frac{\Sigma x \Sigma y}{N}}{\sqrt{\left(\Sigma x^2 - \frac{(\Sigma x)^2}{N}\right)\left(\Sigma y^2 - \frac{(\Sigma y)^2}{N}\right)}} \]

- \( x \) = Incremental Volume
- \( y \) = Incremental Mass
- \( N \) = Population number

\( r = 1 \)
Perfect Linear relationship between mass and hydrology profiles

\( r = 0 \)
No linear relationship between mass and hydrology profiles
Mass-Limited, High Runoff Volume Events

5 January 2002: SSC

Designation Criteria

1. Low Pearson’s Coefficient: $r < 0.80$
2. High Runoff Volume: $V_{\text{tot}} > \psi_{\text{site}} (702.4-L)$
3. Low VPV ratio: $VPV < \psi_{\text{site}} (2.8-\text{veh/L})$
4. High Stream Power: $P_u > \psi_{\text{site}} (1.6*10^{-2}-\text{W/m}^2)$

\[ P_u = \frac{\gamma m}{b} \int QdA \]

\( \gamma \) = specific weight
\( m \) = pavement slope
\( b \) = pavement width
\( QdA \) = Flow rate

<table>
<thead>
<tr>
<th>$Q_{\text{max}}$</th>
<th>$M_{\text{max}}$</th>
<th>$M_{\text{tot}}$</th>
<th>$C_{\text{max}}$</th>
<th>$t_{\text{max}}$</th>
<th>$r$</th>
<th>$V_{\text{tot}}$</th>
<th>$VPV$</th>
<th>$P_u$</th>
</tr>
</thead>
<tbody>
<tr>
<td>60-L/min</td>
<td>18-gm</td>
<td>1089-gm</td>
<td>631-mg/L</td>
<td>316-min</td>
<td>0.07</td>
<td>10618-L</td>
<td>1.5-veh/L</td>
<td>1.7*10^{-2}-W/m²</td>
</tr>
</tbody>
</table>

*\( \psi_{\text{site}} \) = Site median value
Flow-Limited, Low Runoff Volume Events

19 January 2002: TDS

Designation Criteria

1. High Pearson’s Coefficient: $r > 0.80$

2. Low Runoff Volume: $V_{\text{tot}} < \psi_{\text{site}} (702.4-L)$

3. High VPV ratio: $\text{VPV} > \psi_{\text{site}} (2.8-\text{veh/L})$

4. Low Stream Power: $P_u < \psi_{\text{site}} (1.6*10^{-2}-W/m^2)$

\[
P_u = \frac{\gamma m}{b} \int Q dA
\]

where:
- $\gamma$ = specific weight
- $m$ = pavement slope
- $b$ = pavement width
- $Q dA$ = Flow rate

Total Traffic Volume (# of veh.)
Total Runoff Volume (L)

<table>
<thead>
<tr>
<th>$Q_{\text{max}}$</th>
<th>$M_{\text{max}}$</th>
<th>$M_{\text{tot}}$</th>
<th>$C_{\text{max}}$</th>
<th>$t_{\text{max}}$</th>
<th>$r$</th>
<th>$V_{\text{tot}}$</th>
<th>VPV</th>
<th>$P_u$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6-L/min</td>
<td>1-gm</td>
<td>11-gm</td>
<td>194-mg/L</td>
<td>47-min</td>
<td>0.92</td>
<td>84.9-L</td>
<td>24-veh/L</td>
<td>1.6*10^{-3}-W/m^2</td>
</tr>
</tbody>
</table>

$\psi_{\text{site}}$ = Site median value
Urban water quantity and quality control
What Do We Know?

1. Storm water is a unique and complex water to control as compared to other waters,

2. Urban design (or lack thereof) with respect to rainfall-runoff has increased the storm water quantity and quality problem,

3. Our industrial and urban societies and how we construct the environments we live and work in contribute to quantity and quality problems,

4. Storm water can be a valuable resource, it just depends on our viewpoint.
Perspective: Quantity and Quality Control

• Our reliance on the value of structural storm water BMPs is natural, and in part due to historical developments and choices,

• The original concept of a structural BMP was developed based on storm water quantity control \((Q_p, V, t_p)\),

• There has been strong and valid arguments for the use of structural BMPs for storm water quantity control predicated on proper design and analyses,

• However, the extension of such structural BMP concepts to water quality is problematic and is still not well-understood.

• The magnitude and complexity of the problem is still a fundamental challenge.
Storm Water Quantity and Quality Control – “BMPs”

- A term that has for better or worse made it into the vernacular,
- The problem with BMP is that many structural BMPs may not be “best”, are rarely “managed” and rarely “practiced”,
- BMPs can be non-structural (i.e. P3) or structural (i.e. deflective separators, sand filters or detention basins),
- Storm water quantity and quality interactions are complex as we have seen – therefore so is storm water treatment,
- There is still a fundamental lack of understanding of BMP behavior; however practice and legislation still demands BMPs – practice and legislation are running ahead of the science,
- This fundamental lack of understanding is a major impediment to water quality improvement, concepts such regional controls and mass trading as well as to treatment development.
THE “CONTROL” CONTINUUM

<table>
<thead>
<tr>
<th>Control Classification</th>
<th>Technology &amp; Capitol Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Technology examples</td>
<td>Unleaded Fuels, Porous Pavement, PER, Infiltration, Solids Separation, Detention, Retention, WWTP</td>
</tr>
<tr>
<td>BMP Type</td>
<td>Source Control, In-Situ Control, End-Of-Pipe Control, Centralized Treatment</td>
</tr>
<tr>
<td>Low Cost, High Tech.</td>
<td>High Tech., High Cost</td>
</tr>
</tbody>
</table>
Surficial Cleaning:

- Non-structural BMP
- Street sweepers
- Pavement washers
- Vacuum systems
- Litter gitter

- High-tech system: $500-750K
- < 100 psi to > 2000 psi washing
- Very high recovery efficiencies
- A mobile nonstructural control that allows the constituent to be controlled before having to be removed from storm water.
Process selection diagrams and the power law
Temporal Particulate Agglomeration

Coagulation
Destabilization
(seconds)
Stable particles

Flocculation
Transport/Attachment
(min to hrs)
Unstable “microflocs”

Floc Shearing
Floc Breakup
(min to hrs)
Floc Aggregates

Steady-State Distribution

Particulate Transport Mechanisms

Brownian Diffusion
\[ \text{size} \]

\[ l_nv \]

\[ \kappa T \]

Fluid Shear

\[ \frac{dv}{dz} \]

Fluid velocity gradients

Differential Settling

\[ g, \rho \]

Gravitational & buoyant forces

Particles Agglomeration

\[ f (\text{pH, I, velocity gradients, mixing time, particle properties and concentration}) \]

size number

\[ N_t \]
Coagulation/Flocculation as Storm water Unit Operations

**Example:** Application of Alum for urban stormwater clarification
Alum – Aluminum Sulfate Al$_2$(SO$_4$)$_3$•14H$_2$O (MW=594.4)

**Chemistry of Alum Coagulation:**
*Ionic species:* Charge neutralization, Adsorption; *Insoluble species:* Sweep-floc enmeshment

**Hydrolysis scheme for Al$^{3+}$:**

\[
\begin{align*}
\text{Al}(\text{H}_2\text{O})_6^{3+} & \Leftrightarrow [\text{Al}(\text{H}_2\text{O})_2\text{OH}]^+ \Leftrightarrow [\text{Al}(\text{H}_2\text{O})_3\text{OH}]^- \Leftrightarrow [\text{Al}(\text{H}_2\text{O})_5\text{OH}]^{2-} \Leftrightarrow [\text{Al}_2\text{O}(\text{OH})_3]^{4-} \Leftrightarrow \text{Al}_2\text{O}_3\text{(s)}
\end{align*}
\]

**Graphs:**
- Volume Conc. [µL/L] vs. Particle diameter (µm)
- Time = 0 minutes
- Time = 20 minutes
- LOG PND [#/cm$^3$]
- Removal %
**ADVANTAGES:**
- Quantity control ($Q_p, t_p$, and $V$)
- Quality control w/ proper design
- Passive
- Particulate (TSS, SSC) control
- Potential infiltration, evaporation

**DISADVANTAGES:**
- Safety due to surface water
- Maintenance & Soil contamination
- Moderate cost excluding land area
- Redox issues with low D.O.
- Not effective for soluble fraction
- Repartitioning to dissolved phase

**“Basin-type” BMPs:**
- Settling Basins
- Detention Basins
- Retention Basins
- Water Quality Basins

\[
\frac{ds}{dt} = I - O
\]

Infiltration
Evaporation

$dS/dt$
Gravitational Separation of Urban Anthropogenic Particles

\[ F(t) - F_k = m \frac{dv}{dt} \]

\[ V_i = \frac{4}{3} \frac{g(\rho - \rho_d) d^3}{C_d \rho} \]

- All settling regimes
- Discrete particle sedimentation/flotation

SSC = 85.7 mg/L, T = 23.3 °C, \( \rho_s = 2.5 \text{ g/cm}^3 \)

Pearson r = 0.91, df = 29
**Infiltration BMPs:**
- Structural BMP
- Infiltration trenches
- Infiltration ponds
- Infiltration swales
- Infiltration wells

**ADVANTAGES:**
- Quantity control ($Q_p, t_p,$ and $V$)
- Quality control w/ proper design
- Minimal land area, passive
- No standing surface water
- Solute control w/ proper design
- Particulate (TSS, SSC) control

**DISADVANTAGES:**
- Subsurface and GW contamination
- Clogging & geotechnical concerns
- Maintenance (cannot backwash)
- Redox issues with high GWT
- Maintenance (residual cleanout)
- On relative scale – costs moderate
BTC for GAC and BSPER (flow through capacity)

$C_0 = 5$ mg/L for each of Zn, Cd, Pb and Cu.
Influent pH = 6.5
10% breakthrough BV.

<table>
<thead>
<tr>
<th></th>
<th>Zn</th>
<th>Cd</th>
<th>Pb</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>GAC</td>
<td>45</td>
<td>15</td>
<td>120</td>
<td>350</td>
</tr>
<tr>
<td>BSPET</td>
<td>80</td>
<td>70</td>
<td>420</td>
<td>&gt;600</td>
</tr>
</tbody>
</table>
PER hydraulics (12 June 97 runoff event)

- $\tau_i = 15$ min.
- $\tau_m = 14$ min.
- $\varepsilon = 0.40$
- $K_s \text{(soil)} = 5 \times 10^{-6}$ cm/s.
- $K_s \text{(media)} = 2 \times 10^{-2}$ cm/s.
Filtration mechanisms of porous media (solids separation)

- **Surficial Straining** ($d_m/d_p < 10$)
- **Deep-bed Filtration** ($10 < d_m/d_p < 20$)
- **Physical Chemical** ($d_m/d_p > 20$)

- Coarse size particles: $> 100\mu m$
- Medium size particles: $> 10\mu m$
- Fine size particles: $< 10\mu m$
Example of Media Capacity for an Engineered Design
(Application of PER in Cincinnati, OH)

**PER Loading Inputs**
- Drainage Area (15 x 20 m) = 300 m²
- \( C_{\text{annual}} = 0.5 \)
- Annual rain fall depth = 1000 mm
- EMCs for \( (\text{Me}^{2+})_{\text{aq}} \) [mg/L]:
  - Zn = 1000
  - Pb, Cu = 100
  - Cd = 10
- Annual linear \( Q_{sf} = 20,000 \text{ L/m} \)

**PER System Design**
- \( k_{\text{sat}} \) (media) = \( 10^{-2} \text{ cm/sec} \)
- \( k_{\text{soil}} = 10^{-6} \text{ cm/sec} \)
- Width of PER = 30 cm
- Depth of PER = 90 cm
- Media: \( \eta = 0.40 \)
- Media: \( \rho_s = 2.7 \)

<table>
<thead>
<tr>
<th>Media Type</th>
<th>Capacity (Qsf or years)</th>
<th>[q at C/C₀ = 0.10]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plain filter sand (typical media)</td>
<td>30 L (0.00015 year)</td>
<td>[q = 0.0001 mg/g]</td>
</tr>
<tr>
<td>IOCS (BSPET: 33,000 L)</td>
<td>6,600 L (0.33 yrs)</td>
<td>[q = 0.013 mg/g]</td>
</tr>
<tr>
<td>GAC (( \rho_s = 1.8 ))</td>
<td>57,000 L (2.85 yrs)</td>
<td>[q = 0.19 mg/g]</td>
</tr>
<tr>
<td>MOPM (( \rho_s = 0.95 ))</td>
<td>138,000 L (6.9 yrs)</td>
<td>[q = 0.46 mg/g]</td>
</tr>
<tr>
<td>Uncoated Cementitious Media</td>
<td>198,000 L (9.9 yrs)</td>
<td>[q = 0.66 mg/g]</td>
</tr>
<tr>
<td>MOCM</td>
<td>762,000 L (38.1 yrs)</td>
<td>[q = 2.54 mg/g]</td>
</tr>
</tbody>
</table>
Baton Rouge, LA Experiment Station Schematic

- 80 liter debris separator
- Storm drain collection pipe & gutter (drainage area = 532 m²)
- Overflow valve
- Air inlet line (for backwashing)
- Influent sampling port
- Filtration chamber
- Effluent sampling port
- Submersible pump
- 3500 liter holding tank (completely mixed)
- Bridge deck (total area = 6607 m²)
- Bead bed (v = 14 liter)
- Treated storm water
- pH adjustment
- Primary filtration
- Secondary filtration
- Surface complexation

Bridge deck (total area = 6607 m²)
Turbidity Removal Efficiency

p-values (<0.05 indicates statistical significance)
- Control v Type I: 0.22
- Control v Type II: 0.85
- Type I v Type II: 0.38
Conclusions
What Can We Do?

1. Develop and implement **non-structural** BMPs such as pollution prevention (P3) or street cleaning to address targeted constituents; in many cases proper design and P3s minimize the need for **structural** BMPs,

2. Understand that **non-structural** and **structural** BMPs must be designed and implemented based on choices of quantity and/or quality, targeted constituents and characteristics of such constituents (i.e. mass vs. concentration),

3. Design/implement “controls” (non-structural or structural) given reasonable design standards and outcome objectives. We must ask if objectives are site-based, local or regional?,

4. We should view storm water as a commodity or valuable resource with our thinking focused on beneficial use/reuse.
Conclusions

1. Hydrology (quantity and quality parameters) have a direct impact on transport/partitioning of heavy metals and particulate matter.

2. While storm water constituent loading characteristics have changed over history, our “solutions to pollution” & control concepts tend to lag behind.

3. “Control” must address hydrologic modifications as well as water quality criteria. While regional control is envisioned hydrologic control is in-situ.

4. A “traditional” first-flush may not exist when constituent mass is criterion. Mass is best controlled before it becomes part of hydrologic cycle.

5. If given an equal opportunity for development, non-structural practices and controls have the same potential for equal viability as their structural BMP counterparts for storm water runoff. No one tool solves every problem, both non-structural and structural BMPs should be part of the storm water control toolbox.