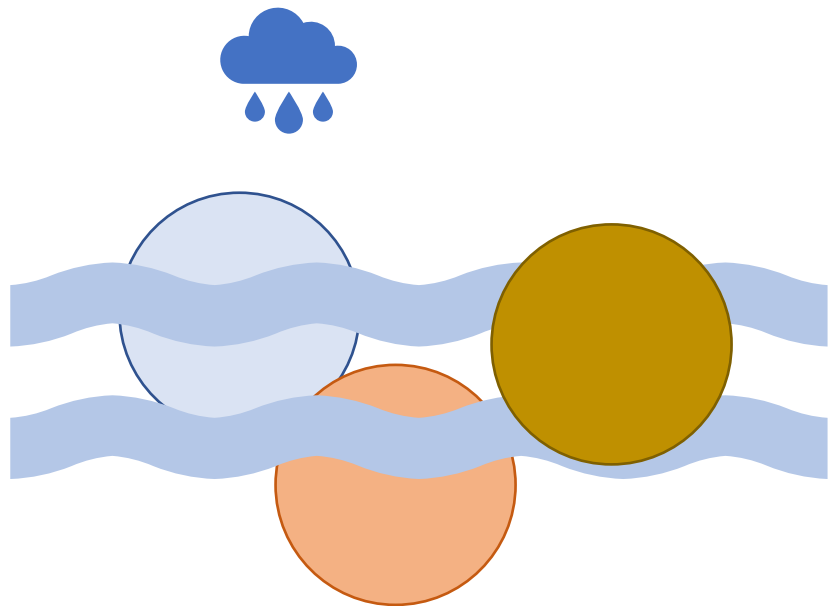


Toxicant Modeling in Flowing Waters



Toxics in Flowing H₂O

1. Reflection: Which toxics may be in movement today in Amherst/Hadley? Are there hotspots?

2. Analytical Solutions

3. Plug-Flow Systems

4. Contaminant Budget

5. Mixed-Flow Systems

6. Numerical Solutions

Analytical Solutions

We now integrate horizontal transport into the toxic modeling scheme emphasizing one-dimensional streams and estuaries.

Some analytical schemes are useful for quick back-of-the-envelope estimation. First, we describe the nondispersive, plug-flow systems applicable to streams and then add dispersion to broaden applications encompassing one-dimensional estuaries and rivers.

Plug-Flow Systems

As in Lec. 40, we develop both solids and contaminant balances for plug-flow rivers and streams.

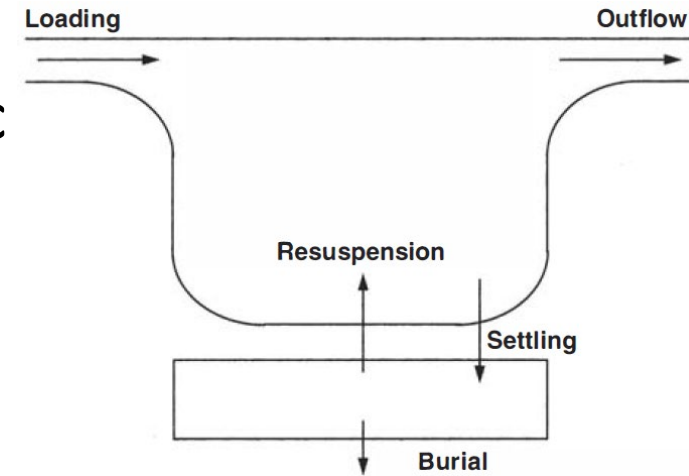
Solids budget: A steady-state solids budget can be written for plug-flow system with constant hydrogeometric characteristics as:

$$0 = -U \frac{dm_1}{dx} - \frac{v_s}{H_1} m_1 + \frac{v_r}{H_1} m_2$$

And for the bottom sediments as

$$0 = v_s m_1 - v_r m_2 - v_b m_2$$

where U = stream velocity (m d^{-1}); m_1 and m_2 = suspended solids in (1) water and (2) sediment layers (g m^{-3}); H = depth (m); v_s , v_r , v_b = settling, resuspension, burial velocities (m d^{-1}).



Plug-Flow Systems

Since sediments do not move horizontally,

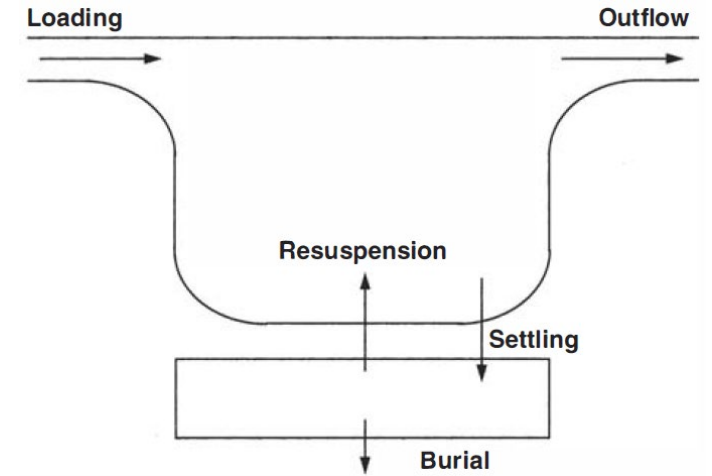
$(0 = v_s m_1 - v_r m_2 - v_b m_2)$ can be solved for:

$$m_2 = \frac{v_s}{v_r + v_b} m_1$$

In other words sediment concentration will be a constant fraction of the concentration in the overlying water. This applies to steady-state contaminant budgets and has beneficial ramifications for time-variable computations.

Substituting $(m_2 = \frac{v_s}{v_r + v_b} m_1)$ into $(0 = -U \frac{dm_1}{dx} - \frac{v_s}{H_1} m_1 + \frac{v_r}{H_1} m_2)$, gives:

$$0 = -U \frac{dm_1}{dx} - \frac{v_s}{H_1} m_1 + \frac{v_r}{H_1} \frac{v_s}{v_r + v_b} m_1$$



Plug-Flow Systems

$$0 = -U \frac{dm_1}{dx} - \frac{v_s}{H_1} m_1 + \frac{v_r}{H_1} \frac{v_s}{v_r + v_b} m_1$$

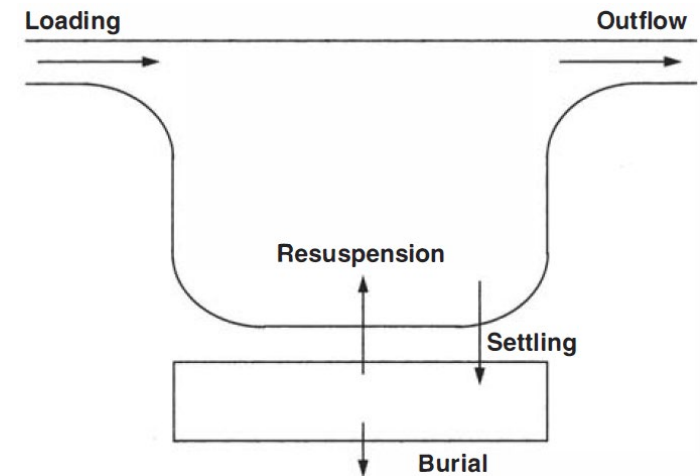
or by collecting terms:

$$0 = -U \frac{dm_1}{dx} - \frac{v_n}{H_1} m_1$$

where v_n = the net settling velocity,

$$v_n = v_s(1 - F_r)$$

in which F_r = ratio of the resuspension velocity to the total purging velocity for the sediment layer = $v_r/(v_r+v_b)$



Plug-Flow Systems

Three general cases can occur for net settling:

$v_n = 0$. In shallow streams, there is often a negligible accumulation of sediments, therefore water solids remain constant as resuspension balances settling.

$v_n > 0$. In deeper streams, sediment will be deposited and there will be net accumulation of sediments. Thus water solids decline (sediment solids build)

$v_n < 0$. Scour will occur and there will be a net loss of bottom sediments. Suspended solids concentration may increase in water w/o external sources.

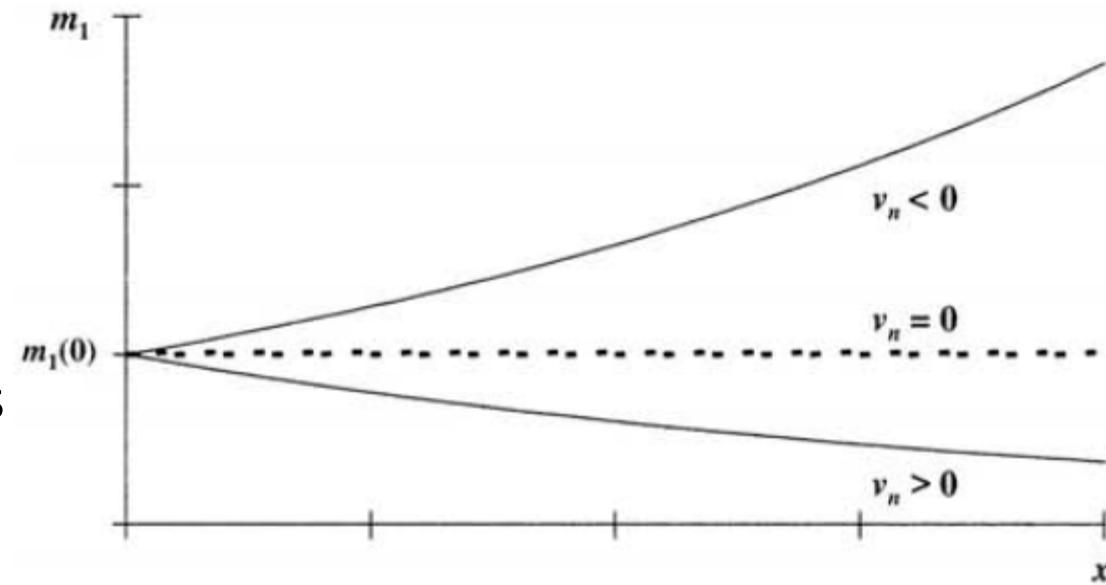
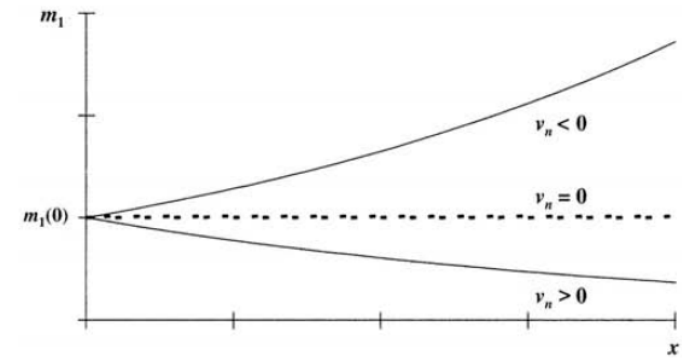


FIGURE 44.1
Suspended solids
versus distance for the
case where sediment
solids concentration is
constant.

Plug-Flow Systems



In the case where sediment solids concentration is a constant over the study stretch, $m_2 = (1 - \phi) \rho$. For this case the solution for the water ($0 = -U \frac{dm_1}{dx} - \frac{v_s}{H_1} m_1 + \frac{v_r}{H_1} m_2$) is:

$$m_1 = m_1(0) e^{-\frac{v}{H_1 U} x} + \frac{v_r (1 - \phi) \rho}{v_s} \left(1 - e^{-\frac{v_s}{H_1 U} x} \right)$$

If the initial solids concentration $m_1(0)$ is small, then the downstream solids concentration should approach a steady value of:

$$m_1(\infty) = \frac{v_r (1 - \phi) \rho}{v_s}$$

The solids profiles could be used to estimate v_r by extrapolating downstream to a stable value of $m_1(\infty)$.

Contaminant Budget

Now we extend the analysis to toxics. Assume the suspended solids are constant across the stretch of interest. A steady-state contaminant budget can be written for a plug-flow system with constant hydrogeometric characteristics as:

$$0 = -U \frac{dc_1}{dx} - k_1 c_1 - \frac{v_v}{H_1} F_{d1} c_1 - \frac{v_s}{H_1} F_{p1} c_1 - \frac{v_d}{H_1} (F_{d2} c_2 - F_{d1} c_1) + \frac{v_r}{H_1} c_2$$

and for the bottom sediments as:

$$0 = v_s F_{p1} c_1 + v_d (F_{d1} c_1 - F_{d2} c_2) - k_2 H_2 c_2 - v_r c_2 - v_b c_2$$

where k = a first-order decomposition rate (d^{-1}) and the F 's are fraction of contaminant in (d)issolved and (p)articulate form in two layers.

Contaminant Budget

where k = a first-order decomposition rate (d^{-1}) and the F 's are fraction of contaminant in (d)issolved and (p)articulate form in two layers.

$$F_d = \frac{1}{1 + K_{d1}m} \quad F_{p1} = \frac{K_{d1}m}{1 + K_{d1}m} \quad F_{d2} = \frac{1}{\phi + K_{d2}(1 - \phi)\rho}$$

Again because the bed does not advect downstream, Eq 44.10 ($0 = v_s F_{p1} c_1 + v_d (F_{d1} c_1 - F_{d2} c_2) - k_2 H_2 c_2 - v_r c_2 - v_b c_2$) establishes a direct relationship between sediment and overlying water concentration,

$$c_2 = R_{21} c_1 = \frac{v_s F_{p1} + v_d F_{d1}}{v_d F_{d2} + k_2 H_2 + v_r + v_b} c_1$$

Contaminant Budget

$$0 = -U \frac{dc_1}{dx} - k_1 c_1 - \frac{v_v}{H_1} F_{d1} c_1 - \frac{v_s}{H_1} F_{p1} c_1 - \frac{v_d}{H_1} (F_{d2} c_2 - F_{d1} c_1) + \frac{v_r}{H_1} c_2$$

in terms of mass-specific sediment concentrations as ($c_2 = (1 - \phi) \rho v_2$):

$$v_2 = \frac{R_{21}}{(1 - \phi) \rho} c_1$$

Eq. 44.12 ($c_2 = R_{21} c_1$) can be substituted into Eq 44.9 to give :

$$0 = -U \frac{dc_1}{dx} - \frac{v_T}{H_1} c_1$$

where v_T = total loss term expressed as settling velocity (m d^{-1}).

$$v_T = k_1 H_1 + v_v F_{d1} + (v_s F_{p1} + v_d F_{d1})(1 - F_r')$$

$$c_2 = \frac{v_s F_{p1} + v_d F_{d1}}{v_d F_{d2} + k_2 H_2 + v_r + v_b} c_1$$

in which F_r' = ratio of sediment feedback to total sediment purging.

$$F_r' = \frac{v_r + v_d F_{d2}}{v_r + v_b + v_d F_{d2} + k_2 H_2}$$

Contaminant Budget

Given the boundary conditions $c_1 = c_1(0)$, we can solve the water balance for:

$$c_1 = c_1(0)e^{-\frac{v_T}{H_1 U}x}$$

Then Eq 44.12 ($c_2 = R_{21}c_1$) can be used to compute sediment concentration,

$$c_2 = R_{21}c_1(0)e^{-\frac{v_T}{H_1 U}x}$$

or in terms of sediment solid concentration,

$$v_2 = \frac{R_{21}}{(1 - \phi)\rho} c_1(0)e^{-\frac{v_T}{H_1 U}x}$$

water concentration follows a simple exponential decay

Discussion

Interactive activities for next week?

- Water body with remediation possibilities (based on PCB pollution)
- Roundtable for Machine Learning in your research

(next year)?

- Running QUAL2E/K (early)
- Fieldtrip to Quabbin Reservoir (excursions to explore out of classroom environments)
- Computer lab set up, extended hours work on current or other models, write up an understanding of model

Critical concentration

An interesting calculation involves computing initial concentration, since the maximum value occurs at the outfall. This concentration represents the critical value upon which assimilative capacity calculations would be based.

Assuming instantaneous mixing at injection point, we compute initial concentration with simple mass balance:

$$c_1(0) = \frac{Q_r c_{1r} + Q_w c_{1w}}{Q_r + Q_w}$$

where subscript w and r designate the waste outfall and receiving river water.

Critical concentration

Toxicant water-quality standards often expressed in terms of mass-specific sediment concentration. The initial value for the sediments can be determined:

$$v_2(0) = \frac{R_{21}}{(1 - \phi)\rho} \frac{Q_r c_{1r} + Q_w c_{1w}}{Q_r + Q_w}$$

Now these can be applied to determine the required loading to meet the standard. We calculate the required waste concentration to attain a desired water concentration $c_1(0)$.

$$c_{1w} = \frac{Q_r + Q_w}{Q_w} c_1(0) - \frac{Q_r}{Q_w} c_{1,r}$$

We could also attain desired sediment concentration $v_2(0)$,

$$c_{1w} = \frac{Q_r + Q_w}{Q_w} \frac{(1 - \phi)\rho}{R_{21}} v_2(0) - \frac{Q_r}{Q_w} c_{1,r}$$

EXAMPLE 44.1. POINT-SOURCE ANALYSIS (PLUG-FLOW). A toxic point source discharges to a stream having the following characteristics:

$$\begin{aligned} Q_r &= 0.99 \text{ m}^3 \text{ s}^{-1} & c_{1,r} &= 0 \text{ mg m}^{-3} & Q_w &= 0.01 \text{ m}^3 \text{ s}^{-1} & c_{1,w} &= 1000 \text{ mg m}^{-3} \\ v_s &= 0.25 \text{ m d}^{-1} & v_v &= 0.1 \text{ m d}^{-1} & U &= 0.1 \text{ mps} & \phi &= 0.8 \\ \rho &= 2.5 \times 10^6 \text{ g m}^{-3} & H_1 &= 2 \text{ m} & & & & \end{aligned}$$

In the water, the toxicant is lost by photolysis at a rate of 0.1 d^{-1} . All other losses are zero and the toxicant associates strongly with solid matter (all F_d 's = 0). Note that the suspended solids in the water is a constant 10 g m^{-3} . (a) Determine the water and sediment concentrations downstream from the source. (b) Calculate the needed inflow concentration so that the maximum sediment concentration is maintained at $250 \mu\text{g g}^{-1}$.

Metals

For metals the model simplifies due to absence of decay/volatilization reaction (except for mercury). If it is assumed that sorption is the same in the water and sediments, sediment-water diffusion can be omitted and steady-state model can be represented by:

$$0 = -U \frac{dc_1}{dx} - \frac{v_T}{H_1} c_1$$

but with the total removal rate simplified to:

$$v_T = v_s F_{p1} (1 - F_r)$$

where

$$F_r = \frac{v_r}{v_r + v_b}$$

Metals

For cases where sediment resuspension is negligible the model simplifies further to:

$$0 = -U \frac{dc_1}{dx} - \frac{F_{p1} v_s}{H_1} c_1$$

If the suspended solids are constant, the solution to the equation is merely ($c_1 = c_1(0)e^{-\frac{v_T}{H_1 U}x}$) with $v_T = F_{p1}v_s$.

When solids are changing the fraction particulate will also change with distance. For this case Mills et al. (1985) provide the following solution,

$$c_1 = c_{10} e^{\left[\ln(K_d m_0 + e^{\frac{v_s x}{H_1 U}}) - \ln(K_d m_0 + 1) - \frac{v_s x}{H_1 U} \right]}$$

EXAMPLE 44.2. FLINT RIVER COPPER. Mills et al. (1985) present the following data for suspended solids and water copper concentrations in the Flint River, Michigan, in August, 1981:

x (km)	1	2.5	7	12	21	30	43	61	63
m (mg L ⁻¹)	11.75 (4–18)	10 (5–15)	10 (7–13.5)	8.5 (6–11)	6.75 (5.3–8)	5.5 (5.3–5.7)	11.5 (3–19.8)	13.5 (10–16.5)	11.75
c_1 (μg L ⁻¹)	3 (2.8–3.4)	4.2 (3.2–5.4)	5.7 (4.5–7)	5.5 (4.9–5.8)	4.2 (2.4–4.8)	4.7 (4–5.2)	8 (4–10)	6 (4.8–7.3)	5.75 (4.5–7)

where the numbers in parentheses represent observed ranges. The river has the following boundary conditions and point sources:

	Kilometers	Flow (cms)	Suspended solids (mg L ⁻¹)	Copper (μg L ⁻¹)
Upstream boundary	0	2.66	13.5	2.9
Flint WWTP	1.3	1.68	4.1	8.3
Ragone WWTP	30.9	0.69	58.7	28.5

The depth and the velocity in the first stretch (km 1.3 to 30.9) are assumed to be 0.5 m and 0.2 m s⁻¹. (a) Use the suspended solids to determine the settling velocity. (b) If copper has a partition coefficient of 0.06×10^6 L kg⁻¹, compute the copper concentration in the stream.

Mixed-Flow Systems

We extend the analysis to systems where dispersion cannot be neglected. If suspended solids are constant, a steady state-contaminant budget can be written for a mixed-flow system with constant hydrogeometric characteristics:

$$0 = E \frac{d^2 c_1}{dx^2} - U \frac{dc_1}{dx} - \frac{v_T}{H_1} c_1$$

where the total removal velocity v_T is defined as previously. The concentration of the underlying sediments can be computed as before:

$$\begin{aligned} c_{1-} &= c_1(0) e^{\lambda_- x} & x \leq 0 \\ c_{1+} &= c_1(0) e^{\lambda_+ x} & x > 0 \end{aligned}$$

where

$$\lambda_{\pm} = \frac{U}{2E} \left(1 \pm \sqrt{1 + \frac{4v_T E}{H_1 U^2}} \right)$$

Subscripts “+” and “-” designate upstream and downstream.

Mixed-Flow Systems

If assumed the waste is much smaller than estuary flow, a mass balance at the outflow can be determined as:

$$c_1(0) = \frac{W}{Q} \frac{1}{\sqrt{1 + \frac{4v_T E}{HU^2}}}$$

and for bottom sediments as:

$$v_2(0) = \frac{R_{21}}{(1 - \phi)\rho} \frac{W}{Q} \frac{1}{\sqrt{1 + \frac{4v_T E}{HU^2}}}$$

Mixed-Flow Systems

The waste concentration required to meet a water standard can be computed in similar fashion to Eq. 44.22 ($c_{1w} = \frac{Q_r + Q_w}{Q_w} c_1(0) - \frac{Q_r}{Q_w} c_{1,r}$). If the upstream flow has negligible toxic concentration:

$$c_{1w} = \frac{Q}{Q_w} c_1(0) \sqrt{1 + 4\eta}$$

where η is the estuary number, which in the present context is defined as $v_T E / (H U^2)$. Alternatively we can calculate the required inflow concentration to attain a desired sediment concentration,

$$c_{1w} = \frac{Q}{Q_w} \frac{(1 - \phi)\rho}{R_{21}} v_2(0) \sqrt{1 + 4\eta}$$

We see that the term $\sqrt{1 + 4\eta}$ reflects the effect of dispersion on the assimilative capacity.

EXAMPLE 44.3. POINT-SOURCE ANALYSIS (MIXED-FLOW). Repeat part (b) of Example 44.1, but assume that the system has an estuary number of 1.

EXAMPLE 44.1. POINT-SOURCE ANALYSIS (PLUG-FLOW). A toxic point source discharges to a stream having the following characteristics:

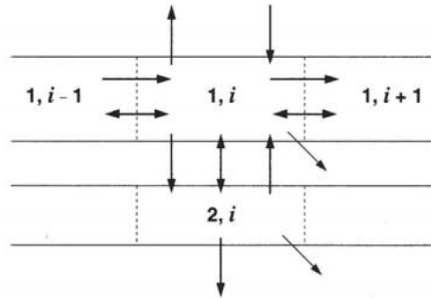
$$\begin{aligned} Q_r &= 0.99 \text{ m}^3 \text{ s}^{-1} & c_{1,r} &= 0 \text{ mg m}^{-3} & Q_w &= 0.01 \text{ m}^3 \text{ s}^{-1} & c_{1,w} &= 1000 \text{ mg m}^{-3} \\ v_s &= 0.25 \text{ m d}^{-1} & v_v &= 0.1 \text{ m d}^{-1} & U &= 0.1 \text{ mps} & \phi &= 0.8 \\ \rho &= 2.5 \times 10^6 \text{ g m}^{-3} & H_1 &= 2 \text{ m} & & & & \end{aligned}$$

In the water, the toxicant is lost by photolysis at a rate of 0.1 d^{-1} . All other losses are zero and the toxicant associates strongly with solid matter (all F_d 's = 0). Note that the suspended solids in the water is a constant 10 g m^{-3} . (a) Determine the water and sediment concentrations downstream from the source. (b) Calculate the needed inflow concentration so that the maximum sediment concentration is maintained at $250 \mu\text{g g}^{-1}$.

Numerical Solutions

The analytical solutions we developed are handy for obtaining a back-of-the-envelope solutions. The numerical approaches provide a more general approach. They provide a means to analyze multiple sources.

The mass balances can be developed for a toxicant in a control volume:



$$\begin{aligned}
 V_{1,i} \frac{dc_{1,i}}{dt} = & W_i + Q_{i-1,i}(\alpha_{i-1,i}c_{1,i-1} + \beta_{i-1,i}c_{1,i-1}) \\
 & - Q_{i,i+1}(\alpha_{i,i+1}c_{1,i} + \beta_{i,i+1}c_{1,i+1}) + E'_{i-1,i}(c_{1,i-1} - c_{1,i}) \\
 & + E'_{i,i+1}(c_{1,i+1} - c_{1,i}) - k_{1,i}V_{1,i}c_{1,i} - v_{v,i}A_{s,i}F_{d1,i}c_{1,i} \\
 & - v_{s,i}A_{s,i}F_{p1,i}c_{1,i} \\
 & + v_{r,i}A_{s,i}c_{2,i} + v_{d,i}A_{s,i}(F_{d2,i}c_{2,i} - F_{d1,i}c_{1,i})
 \end{aligned}$$

and

$$\begin{aligned}
 V_{2,i} \frac{dc_{2,i}}{dt} = & -k_{2,i}V_{2,i}c_{2,i} + v_{s,i}A_{s,i}F_{p1,i}c_{1,i} - v_{r,i}A_{s,i}c_{2,i} \\
 & - v_{b,i}A_{s,i}c_{2,i} + v_{d,i}A_{s,i}(F_{d1,i}c_{1,i} - F_{d2,i}c_{2,i})
 \end{aligned}$$

Numerical Solutions

For the steady state case, these equations can be solved for each volume in a similar fashion to Eq. 44.12 ($c_2 = R_{21}c_1$):

$$c_{2,i} = R_{21,i}c_{1,i}$$

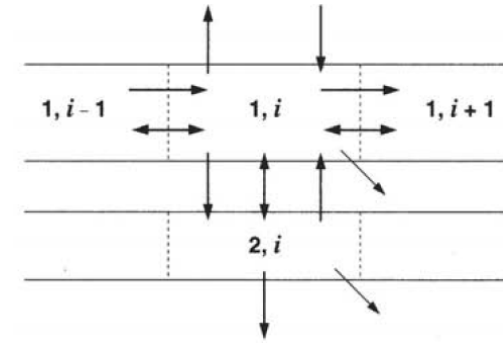
or in matrix form:

$$\{c_2\} = [R_{21}]\{c_1\}$$

where $[R_{21}]$ is a diagonal matrix. Eq. 4.39 ($c_{2,i} = R_{21,i}c_{1,i}$) can be substituted into 44.37 and the result manipulated to yield:

$$\begin{aligned} V_{1,i} \frac{dc_{1,i}}{dt} = & W_i + Q_{i-1,i}(\alpha_{i-1,i}c_{1,i-1} + \beta_{i-1,i}c_{1,i-1}) \\ & - Q_{i,i+1}(\alpha_{i,i+1}c_{1,i} + \beta_{i,i+1}c_{1,i+1}) + E'_{i-1,i}(c_{1,i-1} - c_{1,i}) \\ & + E'_{i,i+1}(c_{1,i+1} - c_{1,i}) - v_{T,i}A_{s,i}c_{1,i} \end{aligned}$$

where v_T is as before.



Numerical Solutions

Equation 44.1 can be written for all the water volumes and expressed in matrix format:

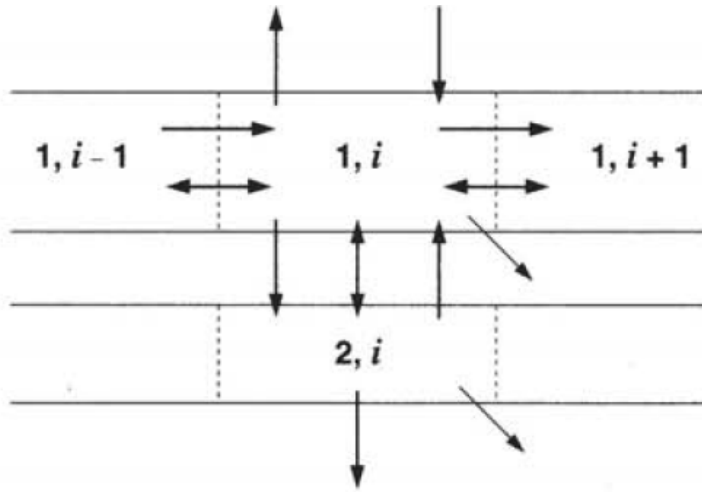


FIGURE 44.2
Segmentation scheme for control-volume approach for toxics.

$$[A]\{c_1\} = \{W\}$$

and solved for:

$$\{c_1\} = [A]^{-1}\{W\}$$

Numerical Solutions

Finally, it can be recognized that the sediment concentration can be determined as:

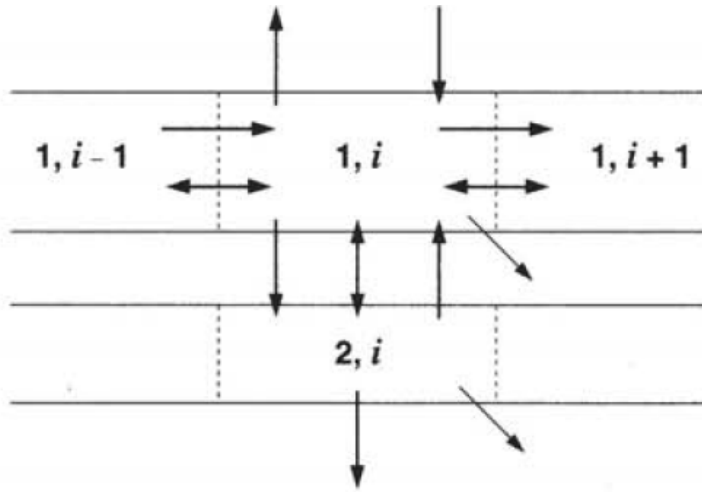


FIGURE 44.2
Segmentation scheme for control-volume approach for toxics.

$$\{v_2\} = \frac{1}{(1 - \phi)\rho} [R_{21}][A]^{-1}\{W\}$$

and collecting terms:

$$\{v_2\} = [S]^{-1}\{W\}$$

where

$$[S]^{-1} = \frac{1}{(1 - \phi)\rho} [R_{21}][A]^{-1}$$

Nonpoint Sources

Though point sources are important, many toxics enter streams and estuaries in a nonpoint or diffuse fashion. Both urban and agricultural runoff can carry toxics in significant concentrations

Low-Flow Nonpoint Sources:

For nonpoint sources that contribute negligible flow, the water mass balance for the plug-flow, constant-parameter case is:

$$0 = -U \frac{dc_1}{dx} - \frac{v_T}{H_1} c_1 + S_d$$

where the total removal velocity v_T is defined as before and S_d is the distributed loading term ($\text{mg m}^{-3} \text{d}^{-1}$).

Low-Flow Nonpoint Sources

The closed form solution is:

$$c_1 = c_1(0)e^{-\frac{v_T}{H_1 U}x} + \frac{S_d H_1}{v_T} \left(1 - e^{-\frac{v_T}{H_1 U}x}\right)$$

The sediment concentrations follow from Eq. 44.12 and 44.13

Flow-Contributing Nonpoint Sources

Although nonpoint sources can contribute negligible flow, it is more likely that they come with significant volumes of water. For such cases a similar setup can be established with a flow balance. . For a steady-state control-volume approach,

$$0 = W_i + Q_{i-1,i}(\alpha_{i-1,i}c_{1,i-1} + \beta_{i-1,i}c_{1,i-1}) - Q_{i,i+1}(\alpha_{i,i+1}c_{1,i} + \beta_{i,i+1}c_{1,i+1}) \\ + E'_{i-1,i}(c_{1,i-1} - c_{1,i}) + E'_{i,i+1}(c_{1,i+1} - c_{1,i}) - v_{T,i}A_{s,i}c_{1,i} + Q_e c_{d,i}$$

where Q_e = distributed inflow for segment i (m^3d^{-1}) and $c_{d,i}$ = concentration of the contaminant in this inflow. This equation can be written for n elements of each reach. Together with appropriate boundary conditions it can be solved for the water concentration in each element.

EXAMPLE 44.4. FLOW-CONTRIBUTING DISTRIBUTED SOURCES OF TOXICS. A demonstration of the model can be developed for the case illustrated in Fig. 44.3. For this simulation a point source marks the beginning of the problem. For

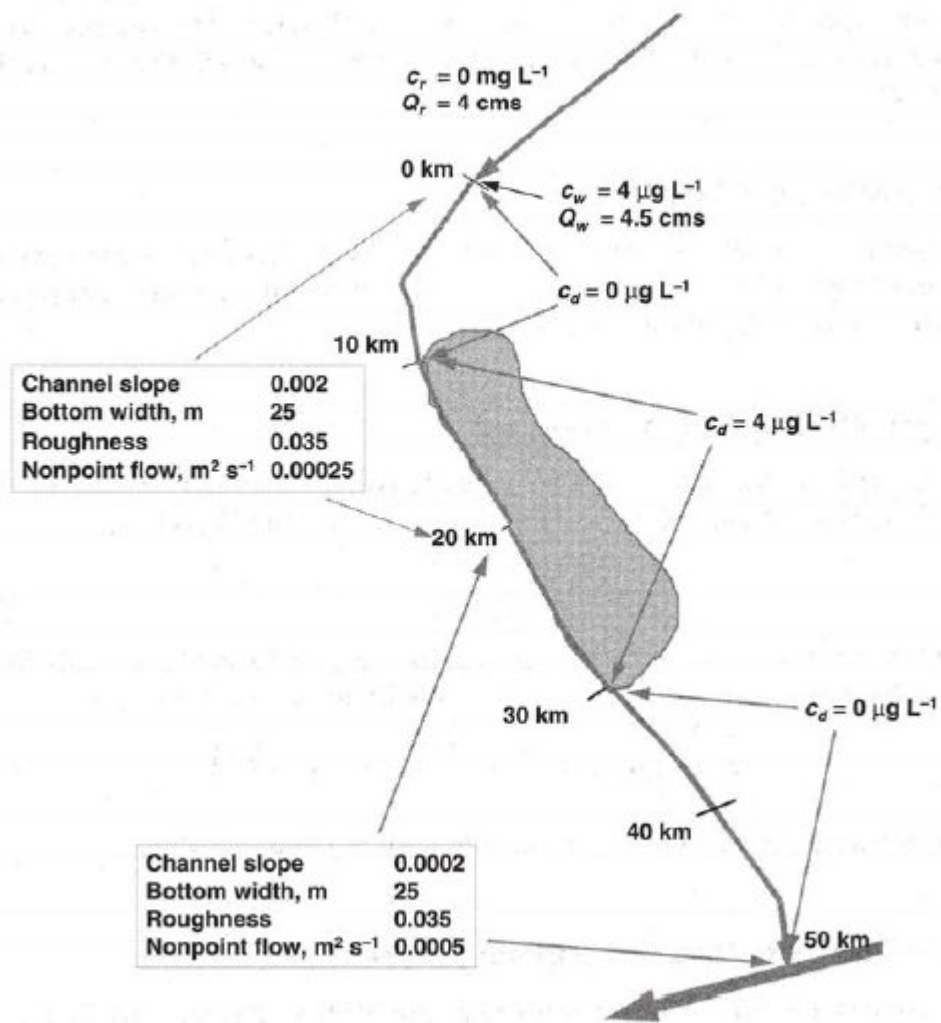


FIGURE 44.3
Example problem.

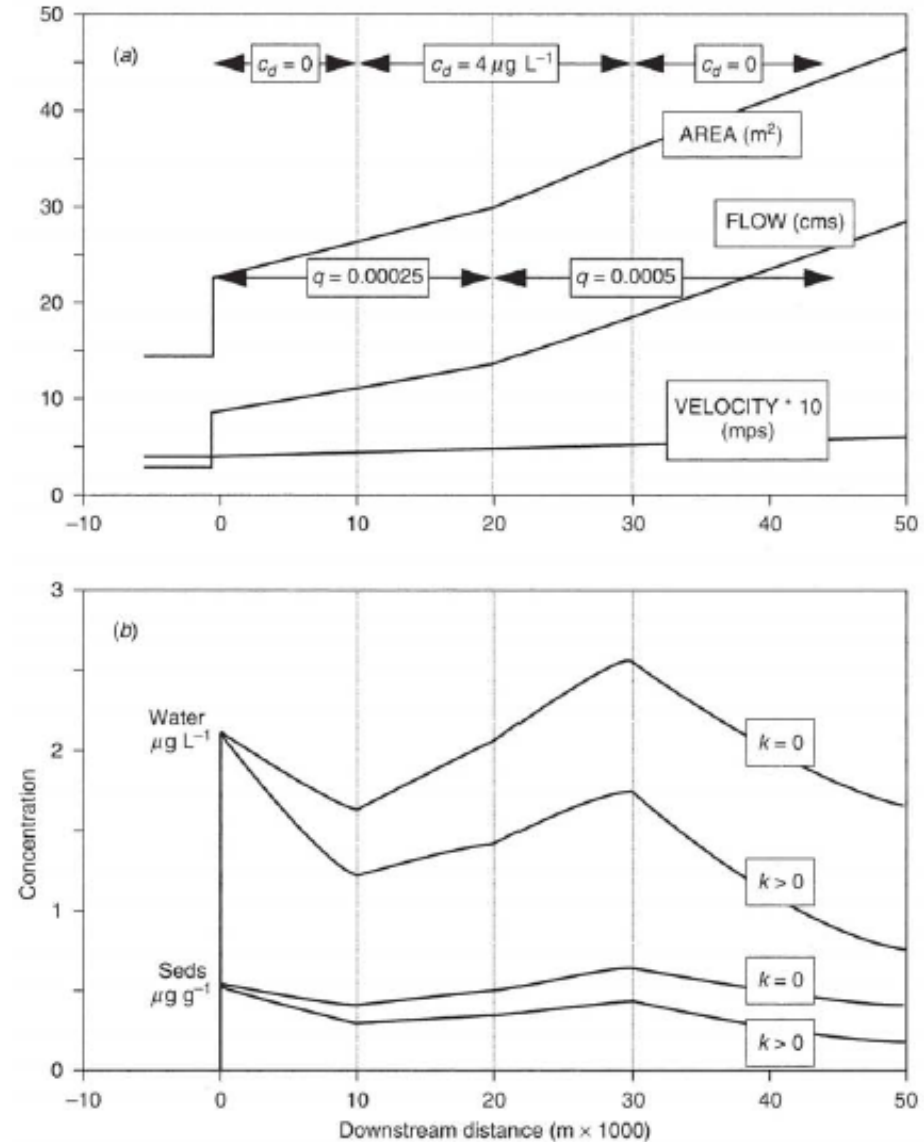


FIGURE 44.4
Simulation results. (a) Hydraulic variables; (b) concentrations.

the next 10 km, there is a constant nonpoint inflow of clean water. Then, in the stretch 10 to 30 km downstream from the point source, runoff from a landfill adds additional toxicant in a diffuse manner. Finally, for the last 20 km, the stream again receives clean water. Other model parameters are $\phi = 0.9$, $\rho = 2.5 \text{ g cm}^{-3}$, $v_s = 0.05 \text{ m d}^{-1}$, $v_r = 0.0006 \text{ m d}^{-1}$, and $v_b = 0.0002 \text{ m d}^{-1}$.