TRACKING A POLLUTANT

An Application of Material Balances

Introduction

A pollutant released to the environment works its way locally or globally through the Earth's major subsystems (the atmosphere, the lithosphere, and the hydrosphere). Questions of obvious importance arise. What is the time- and spatially-dependent history of a pollutant's concentration following its release? What steady-state level will it reach? Given certain corrective action, how long will it take to reduce the concentration to a safe level?

Many such questions can be answered, at least in the form of useful estimates, by applying material balance concepts to mathematical models of the physical system at hand.

An example -- PCBs in the Great Lakes

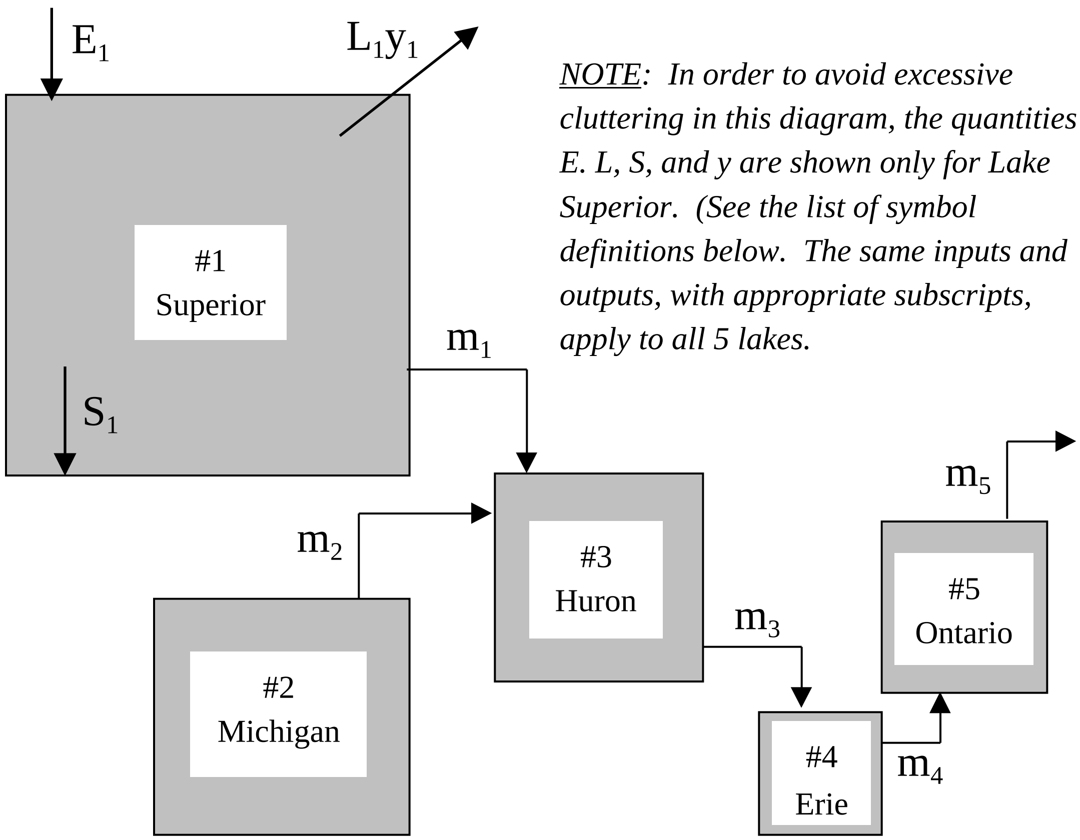
Here we draw example exercises from the case of polychlorinated biphenyls (PCBs) in the Great Lakes system. This case typifies environmental concerns and problems with persistent organic pollutants. Organic chemicals of this type are slow to degrade and dissipate, so that even if banned completely from use, they may be present at harmful levels for generations. Further, as in the PCB case at hand, they often bioaccumulate in fish and other aquatic organisms to the extent that they contaminate a portion of the food web, including foodstuff for human consumption.

PCBs, in commercial use since the 1929, constitute a large family of man-made compounds with varying levels of toxicity throughout the food chain. Once widely used, particularly as coolants and lubricants, their manufacture and use in new products have been banned in the United States since 1976 owing to their bioaccumulation and adverse health effects. Extremely persistent in the environment, they are now known as one of the *bioaccumulative chemicals of concern* targeted by the Great Lakes Water Quality Initiative. A plethora of technical information about PCBs and the history of environmental problems they cause, including their harmful effects on humans and other species, can be found at various Web sites. See, for example, http://www.copa.org.

The model

Consider the Great Lakes system depicted schematically below. Elevation differences cause a bulk lake water flow from Superior and Michigan to Huron, from

Huron to Erie, from Erie to Ontario and finally from Ontario into the St. Lawrence Seaway. Therefore, PCBs that enter Superior or Michigan are transported via bulk flow to the other three. PCBs also enter the lakes through runoff flows from surrounding tributaries and through atmospheric deposits with rainfall or snow. They are lost from the aqueous phase by evaporation and chemical change and also by sedimentation—i.e., by adsorbing to, and settling with, solid material in the lake. PCBs are also removed from the aqueous phase by accumulation in organisms, but the total amount involved is negligible relative to the quantity in the aqueous phase and the amounts exchanged by the other mechanisms



<u>NOTE</u>: In order to avoid excessive cluttering in this diagram, the quantities E. L, S, and y are shown only for Lake Superior. (See the list of symbol definitions below. The same inputs and outputs, with appropriate subscripts, apply to all 5 lakes.

The following list defines the notation used in the diagram above and in the table of data below. The subscript *i* refers to the lake number as identified in the diagram.

E_i mass rate of PCB input from the environment (environmental loading), including atmospheric deposition and runoff from surrounding land and streams.

f_i mass fraction of suspended solids in the lake water.

K — equilibrium constant for PCB distribution between liquid and suspended solids, ratio of mass fraction in the suspended solid to mass fraction in the liquid.

L_i — coefficient for mass rate of PCB losses by evaporation and chemical or biochemical conversion, based on mass fraction driving force.

m_i — total effluent mass flow rate (liquid plus suspended solids).

M_i — total mass of lake contents (liquid plus suspended solids).

S_i — mass rate of solid sedimentation.

x_i — mass fraction of PCB in the suspended solid material.

y_i — mass fraction of PCB in the lake liquid.

Values of Model Constants and Parameters					
	i				
	1	**2**	**3**	**4**	**5**
$E \times 10^{-3}$ (kg PCB/yr)	4.30	4.80	3.40	6.00	2.00
S (tg solids/yr)	4.82	5.59	6.20	27.1	3.16
$K \times 10^{-5}$ (= x/y)	1.00	1.00	1.00	1.00	1.00
$f \times 10^{6}$ (kg solid/kg liq)	3.00	4.00	4.00	20.0	6.00
$m \times 10^{-5}$ (tg/yr)	0.672	0.361	1.61	1.81	2.12
$M \times 10^{-3}$ (pg)	11.9	4.91	3.52	0.470	1.63
L [(pg PCB/yr)/liq mass frac]	2140	1520	1550	677	489

NOTE: *1 teragram (tg) = 10^{12} g = 10^{9} kg*

1 petagram (pg) = 10^{15} g = 10^{12} kg

specific gravity of lake contents = 1.0

These numerical data are based on quantities given in the book by Schnoor: Schnoor, Jerald L., *Environmental Modeling; Fate and Transport of Pollutants in Water, Air, and Soil*, John Wiley & Sons (1996)

Material balance equations

As always, a material balance equation accounts for the conservation of the mass of a substance within a "control volume" by equating its rate of accumulation to the difference between its rates of entering and leaving the volume plus the net rate of its formation within the volume. Ordinarily some assumptions must be invoked, particularly when the concept is employed to construct a mathematical model. Consider, for example, the following material balance on PCBs in Lake Huron. What assumptions are involved in the derivation of this equation?

$$\frac{d}{dt}\left[M_3(1-f_3)y_3 + M_3 f_3 x_3\right] = \\ m_1(1-f_1)y_1 + m_1 f_1 x_1 + m_2(1-f_2)y_2 + m_2 f_2 x_2 + E_3 \\ - S_3 x_3 - L_3 y_3 - m_3(1-f_3)y_3 - m_3 f_3 x_3 \tag{1}$$

where t represents time.

(Notice that each term in the equation has the dimensions of mass of PCB per unit time. However, some conversion factors need to be applied to the quantities in the above table in order to have consistent units.)

What additional assumptions are introduced if Equation 1 is written in the following form?

$$M_3(1+Kf_3)\frac{dy_3}{dt} = m_1(1+Kf_1)y_1 + m_2(1+Kf_2)y_2 + E_3 \\ - S_3 K y_3 - L_3 y_3 - m_3(1+Kf_3)y_3 \tag{2}$$

Finally, the steady-state material balance is obtained simply by setting the left side of Equation 2 to zero.

Problem 1

Using the symbols defined above in these notes and the assumptions incorporated in Equation 2, write the steady-state material balance on PCBs in Lake Michigan. Use the data given in the table to calculate the steady PCB concentration in the liquid and in the suspended solid material. Express your answers in parts per billion (ppb) by mass.

Problem 2

Consider a transient state of Lake Michigan during which the environmental input, E_2, of PCBs gradually decreases -- as it has since the enforcement of a ban on PCB production. To simulate this situation, take the initial mass fraction of PCBs in the liquid to be 2.25×10^{-12} and take $E_2(t) = 4800 \exp(-0.075t)$ kg PCB/yr. (This simulates a 7.5% annual reduction, which was the actual expectation in 1980.) What fraction of the initial PCBs in Lake Michigan will remain after 20 years? . . . after 40 years?

Problem 3

Using the data given in the table, calculate the steady-state PCB concentration (in the liquid and solid) in all five lakes. Express your answers in parts per billion (ppb) by mass.

Problem 4

(a) Taking the steady-state concentrations from Problem 3 as the initial state, and assuming that the values of the environmental inputs, E_i, decrease at an annual rate of 7.5%, obtain curves showing the dissolved PCB concentration, y_i**,** versus time (in years) for all five lakes. For each of the five lakes determine the number of years required to reduce the dissolved PCB level to 0.5 ng/L.

(b) Consider the sediment that forms through this transient period. How would you determine the mass of PCBs sequestered in that sediment, and comment about what might eventually become of those PCBs.

Problem solutions

Solutions to the problems presented in these notes are available to course instructors as Mathcad (Macintosh) files or as copies of those files in pdf format. Copies may be obtained by e-mail request to schmitz.1@nd.edu.

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