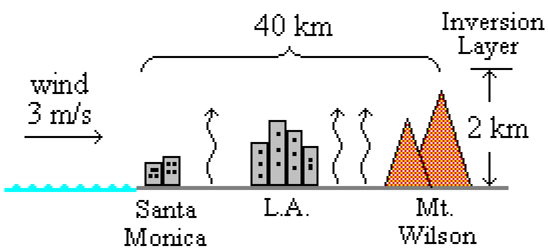
INTERDISCIPLINARY LIVELY APPLICATIONS PROJECT

Air Pollution in Los Angeles

Photochemical smog permeates the Los Angeles basin most days of the year. While this problem is not unique to the Los Angeles area, conditions in the basin are well suited to this phenomenon. As early as 1542, explorer Juan Rodriguez Cabrillo named San Pedro Bay "the Bay of Smokes," because of the heavy haze from native fires that cover the area. The surrounding mountains and frequent inversion layers create the stagnant air that gives rise to these conditions. Automobiles feed the basin with the primary pollutants of hydrocarbons (RH) and nitrogen dioxide (NO_2). The ample sunshine drives atmospheric reactions that create the strong oxidants of ozone (O_3) and peroxyacetylnitrate (PAN). These oxidants are particularly destructive to human health, vegetation, and materials.

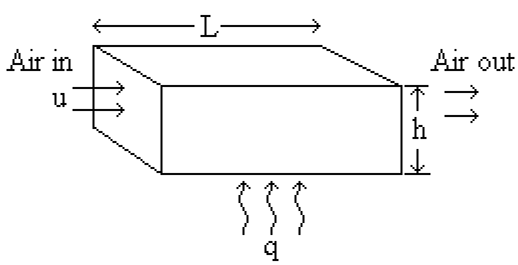
Consider the following conditions.



Pollutants entering per square meter:

Hydrocarbons (RH) = 1.08×10^{-4} moles/m^2 min
Nitrogen Dioxide (NO_2) = 2.24×10^{-5} moles/m^2 min

Using a "box model" approach, we can determine the steady state concentrations of the elements involved in the reaction between the pollutants and the sunshine. The "box model" considers the air volume defined by the area of the basin and the height of the inversion layer. Air enters at one end at the wind speed given, and exits at the other end. We assume that air in the "box" is perfectly mixed. As such, the above conditions can be represented by the following "box model."



Let: u = wind speed = 3 m/sec = 180 m/min
L = length of the box = 40,000 m
h = height of the box = 2,000 m
q = pollutants measured in moles/m^2 min

The steady state concentrations of the pollutants involved are determined by $C_{element} = \frac{qL}{uH}$, expressed in units of moles per liter of air. As such, the concentration of NO_2 is:

$$C_{NO_2} = \frac{(2.24 \times 10^{-5}\ moles/m^2\ min)(40{,}000\ m)}{(180\ m/min)(2{,}000\ m)} \times \frac{1\ m^3}{100\ L} = 2.49 \times 10^{-9}\ moles/L$$

and the concentration of RH is:

$$C_{RH} = \frac{(1.08 \times 10^{-4}\ moles/m^2\ min)(40{,}000\ m)}{(180\ m/min)(2{,}000\ m)} \times \frac{1\ m^3}{100\ L} = 1.20 \times 10^{-8}\ moles/L.$$

The sun provides energy to the Los Angeles basin on a clear day at a maximum rate of $E_{max} = 5.0 \times 10^4$ J/m^2 min (i.e., at noon). Since we recognize that the sun will not always radiate its maximum energy, we determine the average energy radiated by $E_{ave} = 2.5 \times 10^4$ J/m^2 min. The energy from the sun, E, starts the following series of simplified reactions:

$$NO_2 \xrightarrow[k_1]{E} NO + O$$

$$O_2 + O \xrightarrow[k_2]{} O_3$$

$$O + RH \xrightarrow[k_3]{} R^O \qquad \textbf{(a hydrocarbon radical)}$$

$$O_3 + RH \xrightarrow[k_4]{} R^O$$

$$NO_2 + R^O \xrightarrow[k_5]{} PAN$$

On the basis of these reactions and the original concentrations of the pollutants involved, the concentration of each element can be calculated at each time step (i.e. at discrete intervals). To simplify the problem, we will consider the concentrations of NO_2, O_2, and RH constant because they are continuously being replenished in the atmosphere (C_{NO_2} and C_{RH} were given previously). Also, we will let $x = C_O$, $y = C_{O_3}$, $z = C_{R^o}$, and $w = C_{PAN}$. Given that the change in concentration of an element is equal to the concentration of the element CREATED due to reactions minus the concentration of the element CONSUMED due to reactions minus the concentration of the element LOST with exit from our "box model", we can determine the concentration of oxygen (C_o), for example, by the following equation:

$$x(n+1) - x(n) = k_1 E_{AVE} C_{NO_2} - k_2 C_{O_2} x(n) - k_3 C_{RH}\, x(n) - \frac{u}{L} x(n)$$

which simplifies to

$$x(n+1) = \left(1 - k_2 C_{O_2} - k_3 C_{RH} - \frac{u}{L}\right) x(n) + k_1 E_{AVE} C_{NO_2}$$

We can also determine the concentration of the hydorcarbon radical (C_{R^o}), for example, by the following equation:

$$z(n+1) - z(n) = k_3 C_{RH}\, x(n) + k_4 C_{RH}\, y(n) - k_5 C_{NO_2} z(n) - \frac{u}{L} z(n)$$

which simplifies to

$$z(n+1) = k_3 C_{RH}\, x(n) + k_4 C_{RH}\, y(n) + \left(1 - k_5 C_{NO_2} - \frac{u}{L}\right) z(n)$$

Since the oxidants involved, ozone (O_3) and peroxyacetylnitrate (PAN), are harmful to humans as well as the environment, it is important for the city to determine when these elements reach levels that will seriously effect those within the area. Using the techniques that you have studied, complete the following requirements:

Requirement 1:

a. Using the concentration of oxygen difference equation as an example, write the equations that will determine the concentrations of ozone, y (C_{O_3}) and peroxyacetylnitrate, w (C_{PAN}).

b. Write the system of four difference equations generated, and express them using matrix notation.

Requirement 2: Given the following constants and initial values:

$\boldsymbol{C_{NO_2} = 2.49 \times 10^{-9}\ moles/L}$	$\boldsymbol{C_{RH} = 1.20 \times 10^{-8}\ moles/L.}$
$\boldsymbol{C_{O_2} = 0.0085\ moles/L}$	$\boldsymbol{k_1 = 2.0 \times 10^{-6} m^2/J}$
$\boldsymbol{k_2 = 1.5\ L/moles\ min}$	$\boldsymbol{k_3 = 5.0 \times 10^4 L/moles\ min}$
$\boldsymbol{k_4 = 3.0 \times 10^5 L/moles\ min}$	$\boldsymbol{k_5 = 1.0 \times 10^6 L/moles\ min}$

and initial values of $x, y, z,$ and w ($\boldsymbol{C_O}$, $\boldsymbol{C_{O_3}}$, $\boldsymbol{C_{R^o}}$, and $\boldsymbol{C_{PAN}}$) are zero at sunrise ($n = 0$).

a. Use Derive to find the characteristic values (eigenvalues) and the characteristic vectors (eigenvectors) of the coefficient matrix for the system you developed in requirement one. (NOTE: Keep your work in scientific notation; don't round to the fourth decimal place.)

b. Give a general solution to the system of dynamical equations. What happens to the concentrations of oxidants O_3 and PAN after a long period of time? Verify your conclusions by iterating the system on Quattro Pro.

c. Make a graph of the concentrations of O_3 and PAN during a 12 hour day. Use discrete intervals of one minute.

Requirement 3: A high cloud layer attenuates half of the sunlight. How does this affect the long term behavior of the oxidants? Be quantitative in your analysis.

Requirement 4: A weather system reduces the height of the inversion layer to 1,000 meters. What is the impact on the long term behavior of the oxidants? Be quantitative in your analysis. (HINT: you will need to recalculate the concentrations of RH and NO_2.)

Requirement 5: Comment on the validity of the model. Is the assumption that the concentrations of NO_2 and RH are constant reasonable? What is the impact on your model and your ability to solve it if these concentrations are not constant?

Partial Solution to Requirement 1. The system of equations that model the concentration of pollutants in the Los Angeles basin is

$$C_O(n+1) - C_O(n) = k_1 E_{AVE} C_{NO_2} - k_2 C_{NO_2} C_O(n) - k_3 C_{RH} C_O(n) - \frac{u}{L} C_O(n)$$

$$C_{O_3}(n+1) - C_{O_3}(n) = k_2 C_{O_2} C_O(n) - k_4 C_{RH} C_{O_3}(n) - \frac{u}{L} C_{O_3}(n)$$

$$C_{R^o}(n+1) - C_{R^o}(n) = k_3 C_{O_2} C_O(n) + k_4 C_{RH} C_{O_3}(n) - k_5 C_{NO_2} C_{R^o}(n) - \frac{u}{L} C_{R^o}(n)$$

$$C_{PAN}(n+1) - C_{PAN}(n) = k_5 C_{NO_2} C_{R^o}(n) - \frac{u}{L} C_{PAN}(n)$$

Rearranging the equations gives us

$$C_O(n+1) = k_1 E_{AVE} C_{NO_2} + C_O(n) - k_2 C_{NO_2} C_O(n) - k_3 C_{RH} C_O(n) - \frac{u}{L} C_O(n)$$

$$C_{O_3}(n+1) = k_2 C_{O_2} C_O(n) + C_{O_3}(n) - k_4 C_{RH} C_{O_3}(n) - \frac{u}{L} C_{O_3}(n)$$

$$C_{R^o}(n+1) = k_3 C_{O_2} C_O(n) + k_4 C_{RH} C_{O_3}(n) + C_{R^o}(n) - k_5 C_{NO_2} C_{R^o}(n) - \frac{u}{L} C_{R^o}(n)$$

$$C_{PAN}(n+1) = k_5 C_{NO_2} C_{R^o}(n) + C_{PAN}(n) - \frac{u}{L} C_{PAN}(n)$$

Simplifying these, we have

$$C_O(n+1) = \left(1 - k_2 C_{NO_2} - k_3 C_{RH} - \frac{u}{L}\right) C_O(n) + k_1 E_{AVE} C_{NO_2}$$

$$C_{O_3}(n+1) = k_2 C_{O_2} C_O(n) + \left(1 - k_4 C_{RH} - \frac{u}{L}\right) C_{O_3}(n)$$

$$C_{R^o}(n+1) = k_3 C_{O_2} C_O(n) + k_4 C_{RH} C_{O_3}(n) + \left(1 - k_5 C_{NO_2} - \frac{u}{L}\right) C_{R^o}(n)$$

$$C_{PAN}(n+1) = k_5 C_{NO_2} C_{R^o}(n) + \left(1 - \frac{u}{L}\right) C_{PAN}(n)$$

Our matrix equation is

$$\begin{bmatrix} C_O(n+1) \\ C_{O_3}(n+1) \\ C_{R^o}(n+1) \\ C_{PAN}(n+1) \end{bmatrix} = \begin{bmatrix} \left(1-k_2C_{NO_2}-k_3C_{RH}-\frac{u}{L}\right) & 0 & 0 & 0 \\ k_2C_{O_2} & \left(1-k_4C_{RH}-\frac{u}{L}\right) & 0 & 0 \\ k_3C_{O_2} & k_4C_{RH} & \left(1-k_5C_{NO_2}-\frac{u}{L}\right) & 0 \\ 0 & 0 & k_5C_{NO_2} & \left(1-\frac{u}{L}\right) \end{bmatrix} \begin{bmatrix} C_O(n) \\ C_{O_3}(n) \\ C_{R^o}(n) \\ C_{PAN}(n) \end{bmatrix} +$$

$$\begin{bmatrix} k_1E_{AVE}C_{NO_2} \\ 0 \\ 0 \\ 0 \end{bmatrix}$$