CHAPTER VI

NUMERICAL MODEL OF ATMOSPHERIC POLLUTANTS FOR AN AREA SOURCE OF STEADY EMISSION WITH THE REMOVAL MECHANISMS, TRANSFORMATION PROCESS, VARIABLE WIND VELOCITY AND EDDY-DIFFUSIVITY OF PRIMARY POLLUTANTS

6.1 INTRODUCTION

In this chapter, we study the effect of removal as well as transformation processes of primary pollutants on concentration distribution in an urban area. Primary pollutants are those which are emitted directly into the atmosphere such as SO$_2$, CO and NO$_2$. In addition to the adsorption (impaction) processes, considered in the previous chapter, there are other significant natural mechanisms at work in the atmosphere, namely absorption process. In the natural absorption process, particulates or gaseous pollutants are collected in rain or mist, and then settle down with that moisture. This phenomenon, known as washout takes place below the cloud level. Both large and small particles can be caught by rain falling from higher levels and can be cleansed from atmosphere by washout. The potential for scavenging gases and particulates depends on many factors, including the intensity of rainfall and the nature of the contaminants being scavenged. Under ordinary circumstances, only a fraction of the particles in the path of descent of a raindrop will be collected. Also, washout may be negligible for particles less than 1µm in diameter gases may be dissolved without being chemically changed.
Rainout is another natural atmospheric cleansing process involving precipitation. Whereas washout occurs below the cloud level when falling raindrops absorb pollutants. Rainout occurs when submicron particulates serve as condensation nuclei around which drops of water may form. This phenomenon has resulted in increased rainfall and fog formation in urban area. Also, with a strong uprison air flow contaminants may be carried into the stratospheric region that is leakage of some amount of pollutants through the upper boundary of the mixing layer which is another removal mechanism and characterized by leakage velocity and has been considered in this model.

Moreover, gases may be dissolved and enter into chemical reactions with rainwater. For example, SO$_2$ gas may react with rain water to form H$_2$SO$_3$ (Sulfurous acid) or H$_2$SO$_4$ (Sulfuric acid) mists, known as “acid rain”, which is potentially far more harmful than the original SO$_2$. Rainfall through uncontaminated air has a pH of 5.6 to 6.0 values may fall as low as 2. This low pH of rainfall can have far-reaching effects, such as extensive erosion of some surfaces (notably limestone) and can change the pH in streams and rivers, thereby influencing aquatic environment.

Therefore, in addition to physical aspects of the transport, diffusion and removal of pollutants without considering properties of an individual pollutant, one has to consider the loss or transformation of individual pollutants through chemical reactions. To formulate, chemically reactive dispersion models, we must ideally account for all the reactions, reactants, products, reaction rates and meteorological conditions involved in a chemical system. Our current knowledge of atmospheric chemistry is insufficient to completely specify this entire system. Thus, the formulation of reactive pollutants
requires compromises, particularly in determining the important reactions to model and valid parameterizations of the reaction rate phenomena.

**Reaction Rates:** Often an exponential chemical decay rate is assumed with time constant

$$\tau, \frac{c(t)}{c(0)} = e^{-\tau}.$$  

The residence time of a pollutant is the time required to empty a system of that pollutant,

i.e., $\tau = \frac{M}{R}$,

where, $M$ - mass of the pollutant in the system and

$R$ - is the mass removed per unit time.

The above equation assumes that there is no inflow of pollutants into the system. Then, if the reaction or removal rate is of the first order,

$$R = kM,$$

Where $k$ is the turnover constant, then

$$\tau = \frac{M}{R}$$ Implies, $\tau$ is independent of $M$.

In the case of no reverse reaction the turnover constant is more or less equivalent to the first order reaction rate constant for the chemical reaction.
\[ A \rightarrow B \]

Then \( \frac{dA}{dt} = -kA \) and \( k \) is equal to the fraction loss per unit time.

On integration,

\[ \int_{A_0}^{A} \frac{dA}{A} = \int_{0}^{t} kdt \]

\[ \frac{A}{A_0} = \exp(-kt) = \exp(-t/\tau) \]

Where, \( \tau = 1/k \) is the time required for the original concentration \( A_0 \) to be depleted to 1\( /e \) i.e. 0.378, of its original value.

If, in the absence of catalytic surfaces in the free atmosphere, the depletion rate of SO\(_2\) to sulfate is less than 0.1 percent/hour. This means that the turnover constant is 0.001/hour. And the residence time of SO\(_2\) is roughly 1,000 hours or forty days.

The theoretical treatment of wet deposition is often divided into rainout (within cloud scavenging) and washout (below cloud scavenging). In practical applications the two processes are generally lumped together since they can be modeled similarly, Hosker (1980) and Shun (1981). There are two methods of modeling this problem. In the first the concentration \( C \) is assumed to decrease exponentially with time.

\[ C(t) = C(0)e^{-\lambda t}, \]
Where $\Lambda$ is scavenging coefficient and $t$ is time since precipitation began. This method is applicable only to particles of a single size and to highly reactive gases. Also, $\Lambda$ scavenging coefficient is independent of both space and time. However, in modeling process, $\Lambda$ is often allowed to vary with position to account for changes in precipitation over the region of interest.

Other method called wet removal modeling, uses the so-called washout ratio ($w_r$). Let $k_0$ and $C_0$ be the concentration of effluent in the precipitation (e.g. rain drops) and in the air, respectively, at some reference height. Both the quantities are measured in unit of mass per volume.

$$w_r = \frac{k_0}{C_0}.$$  

Then, $w_r = \frac{k_0}{C_0}$.

Note that a value of $\Lambda$ ranging from $10^{-5}$ to $10^{-3}$/sec, implies half-life for wet removal processes ranging from about 2 hour to 1 day. The use of scavenging coefficients for wet removal modeling is probably best regarded as an order-of-magnitude estimation procedure, which is particularly true when empirical values of $\Lambda$ are unavailable or inappropriate for the conditions at hand; thus theoretical estimates of $\Lambda$ must be used.
6.2 FORMULATION/MODEL DEVELOPMENT

The basic equation of conservation of species in the presence of turbulence diffusion, using K-theory approach is given by,

\[ \frac{\partial C}{\partial t} + U \frac{\partial C}{\partial x} + V \frac{\partial C}{\partial y} + W \frac{\partial C}{\partial z} = \frac{\partial}{\partial x} \left( K_x \frac{\partial C}{\partial x} \right) + \frac{\partial}{\partial y} \left( K_y \frac{\partial C}{\partial y} \right) + \frac{\partial}{\partial z} \left( K_z \frac{\partial C}{\partial z} \right) + R_i(C,t) \] (6.2.1)

where, C is the mean pollutant concentration in the air at any location \((x,y,z)\) and time \(t\). U,V and W are the components of the mean wind velocity, the x-axis of the Cartesian co-ordinate system is aligned in the direction of actual wind near the ground surface (East), y-axis is oriented in the horizontal cross wind direction (North/South) and the z-axis is chosen vertically upwards where \(K_x, K_y\) and \(K_z\) are eddy diffusivity coefficients in x, y, z directions respectively.

We assume that

1. Pollutants undergo precipitation scavenging i.e., wet deposition (rainout/washout)
2. Leakage of pollutants through the top of the boundary layer, i.e., leakage velocity.
3. Pollutants are chemically reactive, transformation process with first order chemical reaction rate.

Under the above assumptions made in Chapter III the governing Partial differential equation becomes,

\[ \frac{\partial C}{\partial t} + U(z) \frac{\partial C}{\partial x} = \frac{\partial}{\partial Z} \left( K_x(z) \frac{\partial C}{\partial z} \right) - (k + k_m)C \] (6.2.2)
The initial and boundary conditions are:

\[ C = 0 \quad \text{at} \quad t = 0, \quad \text{for} \quad 0 \leq x \leq L, \text{and} \quad 0 \leq z \leq H \]

\[ C = C_B \quad \text{at} \quad x = 0, \quad \text{for} \quad 0 \leq z \leq H, \text{and} \forall t > 0 \]

\[ K_z \frac{\partial C}{\partial z} - W_z C + V_d C = Q, \quad \text{at} \quad z = 0, \quad 0 \leq x \leq l, t > 0 \]

\[ K_z \frac{\partial C}{\partial z} - W_z C + V_d C = 0, \quad \text{at} \quad z = 0, \quad l \leq x \leq L, t > 0 \]

\[ K_z \frac{\partial C}{\partial z} + \gamma C = 0, \quad \text{at} \quad Z = H, \quad x > 0, t \geq 0, \]

Where,

\( k_w \) - Washout coefficient

\( k \) - First order chemical reaction rate coefficient for transformation

\( \gamma \) - Leakage velocity of pollutant at \( Z = H \)

\( V_d \) - Dry deposition velocity.
6.3 METEOROLOGICAL PARAMETERS

To solve equation (6.2.2), it is essential to know the profiles of eddy diffusivity and wind speed for various atmospheric stability conditions and also for various meteorological parameters such as stability length, friction velocity, net heat flux, surface roughness etc., precisely. These are discussed in Chapter-III in detail and the same has been used in this model. To determine the wind speed and eddy diffusivity as accurate as possible, near the ground, two layers are considered: the surface layer and the planetary boundary layer. The surface layer extends up to 100m, sometimes much lower depending on the stability and roughness parameter, and the planetary boundary layer, which extends up to 1000m or so. It is assumed that the surface layer terminate at

\[ z = 0.1k \frac{u_*}{f} \]  

For neutral stability condition,

Where \( k \) - Karman’s Constant \( \approx 0.4 \)

\( f \) - Carioles parameter

\( u_* \) - Friction velocity.

For stable case, the surface layer extends up to \( z = 6L \), where \( L \) is the Monin-Obukhov parameter. The boundary layer extends up to mixing height, \( z = H \), for both the cases.
In the surface layer, logarithmic profiles are used for neutral stability with 
\[ z < 0.1k \frac{u^*}{f}. \]

\[ U = \frac{u^*}{k} \ln \left( \frac{z + z_0}{z_0} \right), \text{(Within surface layer)} \]

For stable flow with \( 0 < \frac{z}{L} < 1 \),

\[ U = \frac{u^*}{k} \left[ \ln \left( \frac{z + z_0}{z_0} \right) + \frac{\alpha}{L} z \right]. \]

For stable flow with \( 0 < \frac{z}{L} < 6 \),

\[ U = \frac{u^*}{k} \left[ \ln \left( \frac{z + z_0}{z_0} \right) + 5.2 \right]. \]

In the planetary layer, above the surface layer, power law scheme has been used.

\[ U = (u_t - u_d) \left( \frac{z - z_{ul}}{z_{ul} - z_d} \right) + u_d, \]

Where,

\[ u_t \quad \text{Geotropic wind} \]

\[ z_{ul} \quad \text{Top of the surface layer} \]
\( u_{sl} \) - wind at \( z_{sl} \)

\( z_m \) - mixing height, H

\( p \) - An exponent which depends upon the atmospheric stability.

Jones et al (1971) suggest the values of the exponent \( p \), obtained from the measurements made from urban wind profiles, as follows:

\[ p = 0.2 \text{ for neutral condition} \]

\[ p = 0.35 \text{ for slightly stable flow} \]

\[ p = 0.5 \text{ for stable flow} \]

And the following eddy-diffusivity profiles are used for the entire boundary layer (surface layer and planetary boundary layer)

\[ K_z = 0.4u_z e^{-4z/H}, \text{ For neutral case} \]

For stable condition, Ku et al (1987) used the following form of eddy-diffusivity,

\[ K_z = \frac{ku_z z}{0.74 + 4.7z/l} \exp(-b\eta). \]

\[ b = 0.91, \quad \eta = z/(L\sqrt[3]{\mu}), \quad \mu = u_\ast L/fL \text{ and } f = 10^{-4}, \text{carioles parameter}. \]
We have used the value of

\[ k_w = 10^{-4} / \text{sec} \] (Fairly insensitive to rainfall rate)

\[ k = 0.035 / \text{hour} \]

\[ \gamma = 0.001 m / \text{sec} \]

\[ V_d = 0.01 m / \text{sec}, \text{ (In the model).} \]

### 6.4 NUMERICAL SOLUTION AND VALIDATION

We have used Crank-Nicolson implicit finite difference method for the solution of the equation (6.2.2),

The governing partial differential equation (6.2.2) is

\[
\frac{\partial C}{\partial t} \bigg|_{ij}^{n+1/2} + U(z) \frac{\partial C}{\partial x} \bigg|_{ij}^{n+1/2} = \frac{\partial}{\partial Z} \left( K_z(z) \frac{\partial C}{\partial z} \right) \bigg|_{ij}^{n+1/2} - (K + K_w) C \bigg|_{ij}^{n+1/2}
\]

This can be approximated as,

\[
\frac{\partial C}{\partial t} \bigg|_{ij}^{n+1/2} + U(z) \left[ \frac{\partial C}{\partial x} \bigg|_{ij}^{n} + \frac{\partial C}{\partial x} \bigg|_{ij}^{n+1} \right] = \frac{1}{2} \left[ \frac{\partial}{\partial Z} \left( K_z(z) \frac{\partial C}{\partial z} \bigg|_{ij}^{n} \right) + \frac{\partial}{\partial Z} \left( K_z(z) \frac{\partial C}{\partial z} \bigg|_{ij}^{n+1} \right) \right] - \frac{(K + K_w)}{2} \left[ \frac{\partial C}{\partial z} \bigg|_{ij}^{n} + \frac{\partial C}{\partial z} \bigg|_{ij}^{n+1} \right]
\]
Using

\[ \frac{\partial c}{\partial t} \bigg|_{ij}^{n+1/2} = \frac{C_{ij}^{n+1} - C_{ij}^{n}}{\Delta t} \]  

(Forward difference)

\[ U(z) \frac{\partial C}{\partial x} \bigg|_{ij}^{n} = U_{j} \left[ \frac{C_{ij}^{n} - C_{ij-1}^{n}}{\Delta x} \right] \]  

(Upwind difference)

\[ \frac{\partial}{\partial Z} \left( K_{z}(z) \frac{\partial C}{\partial z} \right) \bigg|_{ij}^{n} = \frac{1}{2\Delta z^{2}} \left[ (K_{j+1} + K_{j}) (C_{ij}^{n} - C_{ij+1}^{n}) - (K_{j} + K_{j-1}) (C_{ij}^{n} - C_{ij-1}^{n}) \right] \]  

(Central difference)

\[ (K + K_{w}) \frac{\partial C}{\partial Z} \bigg|_{ij}^{n} = \frac{C_{ij+1}^{n} - C_{ij}^{n}}{\Delta z}, \]  

(Forward difference)

Substituting all these equations in the equation (6.2.2) and rearranging we get,

\[ A_{j} C_{i-1j}^{n+1} + B_{j} C_{ij-1}^{n+1} + D_{j} C_{ij}^{n+1} + E_{j} C_{ij+1}^{n+1} = F_{j} C_{i-1j}^{n} + G_{j} C_{ij-1}^{n} + M_{j} C_{ij}^{n} + N_{j} C_{ij+1}^{n} \]

Where,

\[ A_{j} = \frac{-U_{j} \Delta t}{2\Delta x}; \]

\[ F_{j} = \frac{U_{j} \Delta t}{2\Delta x}; \]

\[ B_{j} = \frac{-\Delta t}{4\Delta z^{2}} (K_{j} + K_{j-1}); \]

\[ G_{j} = \frac{\Delta t}{4\Delta z^{2}} (K_{j} + K_{j+1}); \]
\[ D_j = \left\{ 1 + U_j \frac{\Delta t}{2\Delta x} + \frac{\Delta t}{4\Delta z^2} (K_{j-1} + 2K_j + K_{j+1}) + \left( \frac{K + K_w}{2} \right) \Delta t \right\}; \]

\[ M_j = \left\{ 1 - U_j \frac{\Delta t}{2\Delta x} - \frac{\Delta t}{4\Delta z^2} (K_{j-1} + 2K_j + K_{j+1}) - \left( \frac{K + K_w}{2} \right) \Delta t \right\}; \]

\[ E_j = -\frac{\Delta t}{4\Delta z^2} (K_{j+1} + K_j); \]

\[ N_j = \frac{\Delta t}{4\Delta z^2} (K_{j+1} + K_j); \]

\[ \{ i = 2,3,4,.....(i_{\text{max}})_l,.....(i_{\text{max}})_r, \]  

For each, \[ j = 2,3,4,.....(j_{\text{max}}) \]  

\[ n = 0,1,2,3,............. \]

And for \[ j = 1 \]  and \[ j = j_{\text{max}} \]  and \[ n = 0,1,2,3,.... \]  lower and upper boundary

Conditions equations are, at \[ j=1 \]  and \[ j=j_{\text{max}} \], the boundary conditions are:

\[ \left\{ 1 + V_d \frac{\Delta z}{K_j} \right\} C_{ij}^{n+1} - C_{ij+1}^{n+1} = -\frac{Q \Delta z}{K_j} \quad \text{For} \quad j = 1, i = 2,3,4,.....(i_{\text{max}})_l, n = 0,1,2,3,..... \]

\[ \left\{ 1 + V_d \frac{\Delta z}{K_j} \right\} C_{ij}^{n+1} - C_{ij+1}^{n+1} = 0 \quad \text{for} \quad j = 1, i = (i_{\text{max}})_l + 1....(i_{\text{max}})_r, \text{and} \quad n = 0,1,2,3,..... \]

\[ C_{ij_{\text{max}}-1}^{n+1} - \left( 1 + \gamma \frac{\Delta z}{k_j} \right) C_{ij_{\text{max}}}^{n+1} = 0 \quad \text{for} \quad j = j_{\text{max}}, \quad n = 0,1,2,3,..... \]

The above system of equations gives a tridiagonal structure and has been solved by Thomas algorithm. The ambient air concentrations of chemically reactive pollutants were obtained for various atmospheric conditions and for the values of dry
deposition, wet deposition, leakage velocity and chemical reaction rate constant, by a computer program. The result of this model has been validated with the results of Chapter III.

6.5 RESULTS AND DISCUSSION

A numerical model for the computation of the ambient air concentration emitted from a steady area source undergoing various removal mechanisms and transformation process is presented.

The effects of dry deposition on the GLC distribution for both stable and neutral conditions are shown in Fig. 6.2. It reveals that with the inclusion of dry deposition GLC distribution increases considerably for the stable case. This is because the pollutants being absorbed at the ground due to the surface terrain thereby the pollution concentration is more nearer to the ground. The same phenomenon is observed for the case of neutral condition also. But the magnitude of the maximum concentration is less in the case of neutral condition than the stable condition. The decrease in concentration is more in stable condition than the neutral case when dry deposition is included. The influences of leakage velocity on GLC distribution for stable and neutral cases are depicted in Fig 6.3. From this figure we observe that there is no significant difference between the concentration profile with and without the inclusion of leakage velocity.

Similarly the effect of wet deposition as well as first order chemical reaction does not show any significant difference in the concentration profiles for both neutral and stable cases (Figs. 6.4 and 6.5). Although there is quantitatively small change in the
concentration distribution, the same cannot be visualized graphically. Fig. 6.6 depicts the effect of all the removal mechanisms and transformation process for stable and neutral cases. One can see that for the combined effect, GLC distribution is less than that shown in the Fig. 6.2 where we have considered only one removal mechanism that is dry deposition. Figs. 6.7-6.8 variation of ground level concentration with respect to distance of the primary pollutant with different values of dry deposition for the stable and neutral case is analyzed. As the deposition velocity increases the concentration of the primary pollutant decreases. Figs. 6.9-6.10 variation of ground level concentration with respect to height of the primary pollutant with different values of dry deposition for the stable and neutral case is studied. As the deposition velocity increases the concentration of the primary pollutant decreases rapidly with respect to the height.
Fig. 6.1: Physical Layout of the Model

\[ K_z \frac{\partial C}{\partial z} + \gamma C = 0, \quad x > 0 \quad \text{for} \quad t \geq 0 \]

\[ \text{k} \text{ Chemical Reaction (first order)} \]

Leakage Velocity (y)

Mixing Height

Planout \( (K_w) \)

Washout \( (K_w) \)

Dry Deposition \( (V_d) \)

Steady Emission

No Emission

Urban Area

Out Skirt
Fig. 6.2: Effect of Dry Deposition of GLC for Stable and Neutral cases
Fig. 6.3: Effect of Leakage Velocity on GLC for Stable and Neutral cases
Fig. 6.4: Effect of Wet Deposition of GLC for Stable and Neutral cases
Fig. 6.5: Effect of First order chemical reaction
Fig. 6.6: Effect of Removal mechanisms and Transformation
Fig. 6.7: Effect of Dry Deposition of GLC for Stable and Neutral cases
Fig. 6.8: Effect of Dry Deposition of GLC for Stable and Neutral cases
Fig. 6.9: Concentration at various heights for Stable and Neutral cases
Fig. 6.10: Concentration at various heights for Stable and Neutral cases.