Mathematical Models for Predicting Concentrations of Non-Reaction and Reacting Air Pollutants from Point Source

Asira, Enim Enim & Njan, N.N.
School of Science
College of Education, Akamkpa, Cross River State

ABSTRACT
The atmosphere is unabatedly bombarded with numerous substances released from natural and anthropogenic sources. When these substances are in concentrations higher and duration longer than normal, they tend to cause injury to life or property or interfere with comfortable enjoyment of life or property, repose, health and safety, they tend to constitute pollutants. Their levels and lengths of exposure are determined by air quality impact assessment (AQIA). In this study, the air quality impact assessment procedure used are the mathematical models of plume dispersion(Gaussian profile), atmospheric, meteorological and topographical conditions to evaluate pollution sources and concentrations of non- reacting substances, and thermodynamics and reaction kinetics models for reacting substances . Knowledge and understanding of these models would help in predicting concentrations of air pollutants in the atmosphere, and provide a picture of possible damage to vegetation, organisms and the environment, with a view to arriving at solutions for reduction if not complete elimination of pollutants in the atmosphere, and prevent disastrous consequences of pollutants from newly planned industries.
Key words: Mathematical models, prediction, reacting, non-reacting and substances.

Introduction
All year round, millions of substances are generated and released into the atmosphere that envelops the earth surface from sources that could best be described as, natural or anthropogenic, point or non-point, and primary or secondary. This substances exist in form of gaseous (Co_x, SO_x, NO_x and H_2S); vaporous (H_2SO_4, HNO_y aerosols, and halogens); particulate matter (metals, dust, soot and organics); radioactive (radon, progeny and radionuclides), and thermal or mechanical (greenhouse effect, ozone depletion and noise). When these substances are present in the atmosphere in such concentration higher than normal and duration likely to the injurious to life, property or interfere with the comfort and enjoyment of life or property, health, repose and safety, pollution of the atmosphere arises (stern, *et al,* 1984). The concentration air pollutants in a particular place is primarily dependent on specific sources as mentioned above, meteorological conditions, land topography and utilization patterns of the resources (Scorer, R. C. 1968). The levels of pollution and lengths of exposure are established by air quality criteria (Harrison and Perry, (1984). These are determined by air quality impact assessment (AQIA).

In air quality impact assessment procedures, mathematical models of plume dispersion, and atmospheric, meteorological and topographical conditions are applied to evaluate pollution sources, to arrive at providing solutions for the reduction of air pollution. While the mathematical model for prediction of concentrations of non-reacting air pollutants from point source are based or plume dispersion (Gaussian type) and availably meteorological data, prediction of air pollution due to reacting substances in addition to the above models, are based on application of principles of thermodynamics and reaction kinetics' (Narayana, 2006).

PREDICTION OF AIR POLLUTION DUE TO NON-REACTING SUBSTANCES

Air Pollution Dispersion Model: The goal of air quality dispersion model is to estimate pollution's concentration at a point source downward of one or more emission sources. Dispersion models are useful tools for detecting potential concentration impact from sources: The commonly used models for dispersion of non-reacting gaseous air pollutant are based on Gaussian profile. This models assumes an ideal steady state of constant meteorological condition over a long distance. Dispersion is a process by which pollutants disperse in the air by convection and plume spreads over an area. It is dependent on turbulence, wind speed and atmosphere and terrain conditions (Narayana, 2006).

Turbulence: Turbulence is the irregular air movement in which wind constantly varies in speed and direction. Turbulence MIxes and enhances the dispersion of pollutants. The stronger the turbulence, the more pollutants are dispersed. It decreases the concentrations of pollutants inside the plume and increases their concentrations outside the plume. It is dependent on the concentration of the pollutants and temperature.

Concentration effect: The concentration of a pollutant at distance from the source A is given by the equation.

$$C_s = \frac{Q}{\pi u 6y63} \exp \frac{y2}{z6y2} - \frac{z2}{z6z}$$

Where Q = source of strength

6 = standard deviation in x, y and z direction

u = average wind speed

Correlating concentration to diffusion coefficients, the speed of the pollutant horizontally, laterally and vertically can be estimated as follows;

$$C = \frac{Q}{4\pi \ DyDz} \exp \left(\frac{-u}{4x} \right) \quad \left(\frac{y2}{Dy} + \frac{z2}{Dz} \right)$$

Where $= \sqrt{x^2} + y^2 + z^2$

D_y and D_z = diffusion coefficients in lateral and vertical wind.

Effect of temperature: Temperature inversion is a major cause for atmospheric pollutants getting concentrated. Pollutants travel with wind and inversion layer (ie a layer of warm air above cooler air) suppresses the vertical mixing of pollutants and make them spread horizontally. Under normal conditions as the warm air rises, it expands adiabatically and cools due to decrease in atmospheric pressure with height. Since pressure decreases with height, there is upward pressure gradient force. The buoyant force is the difference between upward and gravitational force. The accelerator (a) of the air pollutant under this force in vertical direction is given as;

$$a = g \left(\frac{Tr - Te}{Ti} \right)$$

where T_r = temperature of the ambient air (kelvin)

T_e = temperature of the surrounding environment

g = acceleration due to gravity.

But the density of air is affected by moisture in the air. This is related to thermodynamic parameters.

$$P = \partial^{RT}: \Delta H = C_p + \Delta T - V.\Delta P$$
$$C_p = R + C_P$$

Where P = Density of air, R = gas constant

ΔH = enthalpy change, V = volume

C_P = specific heat at constant pressure

C_v = specific heat at constant volume

The plume rise (diffusion of hot gas can be explained using

Fick's law of diffusion

$$\frac{dc}{d} = -\frac{Dudc}{dx} + V_z \frac{dc}{d3}$$

Where C = concentration of pollutant u = horizontal wind,

D = diffusion coefficient, V_z = wind speed in vertical direction.

In case of stable atmosphere, the stability parameter is determined by the equation below:.

$$S = \Delta g \left(\frac{dT}{d3} + 1\right)$$

Where $1 = \frac{dt}{d3}$ adiabatic

For neutral (adiabatic ambient) atmosphere

$$\frac{dT}{d3} = -1 \text{ and } S = 0$$

For stable atmosphere, $\frac{dT}{d} > 1, S > 0$

For unstable atmosphere, $\frac{dT}{d3} < 1; S < 0$

Mechanical and thermal effect: Turbulence is due to a combination of both mechanical and thermal factors. Normal condition allows for gradual temperature decrease with increase in height in the atmosphere. The Richardson number is used to characterize mechanical and heat convention.

$R_i = \underline{\text{Turbulence by buoyancy}}$

Turbulence by mechanical shear

$R_i = 0$; mechanical turbulence occurs

$R_i < 0.05$, Heat convection occurs

$R_i > 0.25$ inversion (no vertical mixture)

The amount of wind turbulence can be classified a Pasquill stability classes, A,B,C,D,E and F.

Class D = most turbulence

Class F = least turbulence

Class A B and C = unstable atmosphere (extensive mixing of air)

Classes E and F = stable air, thermal stratification dampens
mechanical turbulence.

Topographic effect: Low and high – pressure environments have varied ventilation characteristics. Low – pressure environment covered relatively small area and are usually accompanied by cloudy skies that could be a source of pollutants, while high – pressure environment covers large area and experiences stagnation when ventilation rate is low. Topographic effect is felt in mountain – valley situation, where fogs sit in the valley and

stabilize inversion by preventing the sun from warming the valley floor, thus prolonging the pollution episodes (see diagram).

PREDICTION OF AIR POLLUTION DUE TO REACTING SUBSTANCES:

When pollutants are released into the atmosphere, they undergo chemical reactions to produce secondary pollutants. The principles of thermodynamics and reaction kinetic are used to predict the rate of formation and distribution of the reacting pollutants (Hammes, G.C, 2000).

Principle of thermodynamics: Many particles obey general laws called laws of thermodynamics which address phenomenological properties of material bodies characterized by macroscopic parameter. It is deals with reaction states (initial and final). These laws are:

1st law: statement of energy conservation

2nd law: state of direction of the spontaneous process

3rd law: relates to experimental approach to absolute zero temperature.

The first law of thermodynamics describes the quantitative relations between the quantities that characterize a system, while the state of the system changes.

$$\Delta u = \Delta Q + \Delta W$$

Where Δu = change in internal energy

ΔQ = change in heat

ΔW = change in work done.

Entropy: The first law does not determine the nature of the processes and direction of the changes, hence there the need for the 2nd law

The second law of thermodynamics indicates the direction of a spontaneous process. It is defined in terms of state function, called entropy.

$$ds > \frac{\partial Q}{T}$$

$$S > K_j \ln z$$

Where, K_j = Boltzmann constant

Z_i = statistical probability of the ith state.

Entropy is determined by the logarithm of the number of microscopic states. The longer the number of microscopic states in a system, the larder the number of microscopic states, the more disorder will be the system.

Free energy: The free energy of a system is a property of the system at whose expense the system does work. In a reversible processes, the 2nd law of thermodynamics assumes

$$Tds = \partial Q = du + dw$$

$$\partial W_{nax} = d(U - TS)$$

$A = U + TS$ (Hemoltz, free energy) at Constant volume. However, Gibb's free energy, (G) gives the work done at constant pressure

$$\partial W = (dW)_{useful} = (dW)_{nax} - W_{pv}$$

$G = A - W_{pv}$

$G - U - TS + PV = H - TS$ (Gibb's free energy)

$\Delta G = \Delta H - T\Delta S$

$\Delta G < O$ The reaction is spontaneous and reacting substances become very disorderly.

$\Delta G >$ The reaction is not spontaneous.

Reaction kinetics: Knowledge of the rates of reacting substances (pollutants) is important in understanding and controlling the chemical and biodegradation processes, and for the evaluation of the persistence of pollutants and to assess exposure of human and other living things. Reaction kinetics formalism quantitatively describe the dependence of the reaction rate on the concentrations of the components of the reaction system. Reaction rate is defined as the change with time in the concentration of the components in a reaction and is given as:

$$V = \frac{d[A]}{dt} - \frac{d[B]}{dt} + \frac{d[C]}{dt} + \frac{d[D]}{dt}$$

However, for many simple, irrevocable reactions, the reaction rate is

$$V = K[A]^a [B]^b$$

Where a and b are reaction order with respect to substances A and B, K = rate account.

APPLICATION OF REACTION ORDER ON REACTING SUBSTANCES IN THE ATMOSPHERE

Zero order reactions: In zero – order processes, the rate is independent of the concentration of the reacting substances. When the concentration is plotted against time, the concentration decreases at constant rate in zero – order process.

When n = o, a = o, and b = o

$$-\frac{d[A]}{dt} = K$$

1ST order reactions: This is also called half – life kinetics because half the chemical is degraded in time t. The concentration of reacting substances falls quickly initially and thereafter slowly in 1st order processes. Here the rate of reaction is proportional to the concentration of one reactants only.

$a A + bB \longrightarrow$ Product

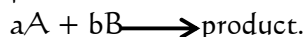$$-\frac{d[A]}{dt} = K_A [A]$$

$$\frac{dA}{[A]} = -K_a dt$$

$$[A] = [A_o] \exp (-K_A t)$$

Where A_o = initial concentration

K_A = rate constant (no equilibrium constant).

2ND order reaction: In the 2nd order of reaction, the rate of reaction is proportional to the 2nd power of concentration

$aA + bB \longrightarrow$ product.

This order of reaction is important in reaction kinetics where catalytic and combustion reaction prevail. Catalytic reactions are systems of two – step reaction in which the catalyst reacts with one of the reacting substances to from an intermediate complex in the rate determining step (1st step).

$$C + S \underset{K_{-1}}{\overset{K_1}{\rightleftarrows}} M, \qquad M + R \xrightarrow{K_2} P + C$$
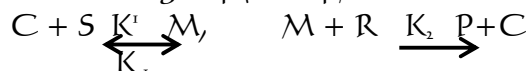
Where C = Catalyst S = substrate, M = intermediate complex

R = reactant, K, K-1 and K$_2$ = rate constants. Under such condition, where the intermediate is a component of the reaction process, the reaction kinetics is expressed as follows:
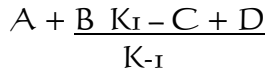
$$A = \underset{K_{-1}}{\underline{K_1 M}} + C$$

$$M + B \xrightarrow{K_2 product}$$
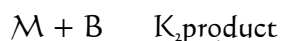
Molar concentration and the reaction rate are expressed by:

$$[M] = \frac{K_1 [A]}{K_{-1}[C] + K_2 [B]}$$

$$Rate = \frac{K_1 K_2 [A] [B]}{K_{-1} [C] + K_2 [B]}$$

3RD order reaction: The rate of reaction in the 3rd order is proportional to the 3rd power of concentration and products of a reaction can react to produce the original reactants.

$$A + \underset{K_{-1}}{\underline{B \; K_1 – C + D}}$$

$$- \frac{d[A]}{dt} = K_1[A] [B] = L_{-1} [C] [D]$$

A decrease in [A] depends on forward and backward reaction

3rd order (n = 2, a = 3 or 2, b = 0 order

$$- \frac{dA}{dt} = K[A]^3 \text{ or } K[A]^2 \; [3]$$

Kinetic reaction mechanisms are applied in the determination of reaction rate involving molecules, ions, radical and the rate of reaction determined by rates of decomposition of intermediates (Hamme, 2000).

CONCLUSION
The atmosphere is constantly washed with substances produced and released by natural and anthropogenic phenomena. These substances, when in concentration higher than normal and duration longer than necessary in the atmosphere, result in pollution. Hence there is need to adopt model of predicting their sources , direction of transport and sinks with a view to proffering solutions where necessary to mitigate pollution. One of these models are Gaussian profile for dispersion of non-reacting substances; and thermodynamics and reaction kinetics for reacting substances in the atmosphere.

REFERENCES

Hammes, G. C; (2000) "Thermodynamics and Kinetics for Biological Sciences. Wiley Interscience: New York.

Harrison, R. M and Party, R.; (1984) "Handbook of air Pollution analyst (2nd ed., Chapman and Hall London.

Narayan, P., (2000). Environmental Pollution: Principles Analysis and control CBS Publishers and Distributors PVT Ltd. New Delhi (India) 3:50 – 69.

Scorer R., (1968). "Air Pollution". Pergamum Press: Oxford.

Stern, A. C., (1984)."Fundamentals of Air Pollution" (2nd ed.), McGraw – Hill: New York.