Geographically Based Models for Surface and Estuarine Waters and River/Aquifer Interfaces

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1 INTRODUCTION

The mathematical modeling of chemical fate in surface waters has four purposes: (1) description of the problem; (2) parameter identification; (3) prediction of time evolution problem; and (4) management. The mathematical models are categorised in two families according to scale: global and local. Global models are further subdivided into black box and grey box.

Black box models represent the water body as a system with no assumed physical structure, considering only inputs and outputs which are mathematically related usually by a convolution equation or by an ordinary differential equation (e.g., a mass balance dilution equation). These oversimplified models generally provide a first approach to the phenomenon. Grey box models represent the water body as a system with a few structural properties. An example of such a model is a sequence of reservoirs with various mixing properties.

The local models are structural, accounting for the various features of contaminant transport and physico-chemical transformations and interactions:

(1) convection (or advection) of contaminants (i.e., its movement with the mean flow);

(2) dilution of contaminants with inflowing water;

(3) removal of pollutants in particulate form by sedimentation;

(4) dissolution of gases or of soluble parts of contaminants;

(5) biochemical or physico-chemical reactions of contaminants with their environment (biodegradation by microorganisms, adsorption/desorption on sediments, chemical transformation, precipitation when the solubility threshold is exceeded, coprecipitation of secondary components with the primary precipitate when the newly formed precipitate provides a large reactive surface for simultaneous adsorption of these components); and

(6) radioactive decay.

Local models are usually based on a set of partial differential equations; sometimes they consist of a mixture of structural and grey box models.

The choice of a model depends upon the objectives of the study, its

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constraints (financial, technical, time) and the available data (scarcity, accuracy). We shall describe various recent models in both families and try to estimate their limits of use.

2 GLOBAL MODELS

The basis of global models is the mass conservation principle relating inputs and outputs of the system, taking into account the reactions within the system that either increase or decrease contaminant concentrations or masses. Most models are adapted from Streeter-Phelps equations predicting the biochemical oxygen demand (BOD) and dissolved oxygen (DO) concentrations or deficits resulting from the discharge of biodegradable organic wastes into river systems, and completed by simple decay, dilution or sedimentation models for other contaminants.

2.1 DO AND BOD MODELS

Under the assumptions that, for most flowing streams, diffusion effects are negligible and that conditions change slowly enough over time compared to reaction rates that the concentrations remain close to their current steady state, Streeter-Phelps steady state equations are used, the general form of which is

$$\frac{\mathrm{d}D}{\mathrm{d}t} = u\frac{\mathrm{d}D}{\mathrm{d}x} = (K_1 + K_3)\,L - K_2D \qquad (1)$$

where D represents the oxygen deficit at the downstream distance $x(D =$ oxygen at saturation $-$ actual oxygen content), K_1 the BOD reaction rate determined in the laboratory, K_2 the reaeration coefficient, K_3 the coefficient expressing the effects of organic settling and other parameters, L the oxidisable organic matter (ultimate BOD) present at any time t, u the mean stream velocity, $(K_1 + K_3)L$ the rate of deoxygeneration and $-K_2\,D$ the rate of reoxygenation.

The second member of this equation can be completed by terms expressing addition or removal of oxygen, such as the difference between photosynthetic oxygen production and respiratory demand by algae and other plant life, benthal oxygen demand or ultimate nitrifying oxygen demand.

Simple in its form, this equation is subject to difficulties due to the estimation of its parameters: Of the reaction rates, only K_1 can be accurately determined in the laboratory by the BOD tests; K_2 is usually estimated by one of a number of different formulas relating the physical characteristics of the stream (velocity, depth, etc.) to reaeration and giving different results; K_3 is usually uncertain and often assumed to be zero; these coefficients will vary over distance along the stream (30 to 35 percent average variation (Harrison, 1980)).

The usual modeling technique consists in (1) obtaining DO, BOD, flow values in the stream and other parameters like NH_3 for some dates and at some sampling stations; (2) assuming values for K_1, K_2, and other variables such as the sedimentation/resuspension situation and the nitrification situation; and (3) verifying the assumed values on a second set of data. The model is then considered ready for forecasting (Whipple and Hunter, 1981).

The estimation of coefficients K_1, K_2 and K_3 is a subject for investigation. Among recent methods (Wen *et al.*, 1981) which, when applied to tidal and nontidal streams, enabled the identification of five water quality parameters (the reaeration coefficient K_2, the coefficient K_3, the rate of organic addition to the overlying water from the bottom deposits as well as local run-off, the oxygen production rate by photosynthesis, and the longitudinal dispersion coefficient when the stream velocity, the downstream distance, the stream water temperature, the BOD and DO at each sampling station and K_1 are known).

The uncertainty of the coefficients K_1, K_2, K_3 will be treated either by a sensitivity analysis of the Streeter Phelps model with its coefficients and initial conditions varying within known bounds (Harrison, 1980) or by assuming that the model is probabilistic, i.e., a random differential equation with random coefficients and initial conditions (Padgett, 1978 in Harrison, 1980).

Because of fluctuations in time of the reactions adding or removing oxygen the steady state models are not accurate, and a more general mass balance equation can be introduced. For instance Deb and Bowers (1983) modeled the diurnal change of DO (in a stream where photosynthetic activities of plants are prominent, the DO concentration of stream water changes with the hour of the day) by the equation:

$$\frac{\partial c}{\partial t} + u\frac{\partial c}{\partial x} = K_2(C_s - c) - K_1\,L(x) - K_nN(x) + P(x, t) - R(x) - S(x) \quad (2)$$

where c is the DO concentration, C_s the DO saturation value, $L(x)$ the carbonaceous BOD, K_1 the BOD reaction rate, K_2 the reaeration coefficient, K_n the coefficient of nitrogenous oxidation, $N(x)$ the nitrogenous BOD, $P(x, t)$ the algal photosynthetic oxygen production rate, $R(x)$ the algal respiration rate, and $S(x)$ the benthic bacterial respiration rate. $P(x, t)$ is a periodic function of time, expanded in a Fourier series; the upstream diurnal variation of DO, represented by a Fourier series, is taken as a boundary condition.

Because of the difficulties related to the Streeter Phelps model, alternate global models have been investigated. For instance, a model based on a multiple linear correlation approach has been derived by Wang *et al.* (1979) as

$$Y = a_0 + a_1X_1 + a_2X_2 + a_3X_3 \tag{3}$$

where Y is the dissolved oxygen deficit, X_1 the combined BOD loads upstream, X_2 the temperature of stream water, and X_3 the stream flow.

The coefficients a_0 to a_3 can be determined by solving the linear set of four equations, ΣY, ΣYX, ΣYX_2, ΣYX_3 where the sum Σ is taken over N sets of data. According to the authors, such a model could be used in stream pollution control, but it seems that field experience is still lacking.

Another approach, adopted by Whipple and Hunter (1981), is to consider that the lack of knowledge of the Streeter Phelps coefficients is such that a rough estimate of BOD and DO will be as significant as a so-called more refined but illusory estimate; they use the BOD decay relationship, independent of K_2:

$$\frac{\mathrm{d}L}{\mathrm{d}t} = -K_rL \tag{4}$$

which yields

$$\frac{L_t}{L_0} = \exp(-K_rt) \tag{5}$$

where L_t is the BOD at time t, L_0 the initial BOD, t the time of travel of the water from the initial point, K_r the total rate of removal of BOD from the water, including both the effect of BOD decay and the net effect of sedimentation suspension ($K_r = K_1 + K_3$). The main advantage of this equation is that it can be solved with a hand-held calculator.

2.2 MODELS FOR VARIOUS CONTAMINANTS

DO or BOD models can be used to represent water quality related to various contaminants, with the contaminant concentrations as unknowns.

In particular, the random nature of the hydrological variables, like rainfall and runoff, can be accounted for by using random mass balance models, i.e., models with random inputs. For instance, a random dilution model meant to study the behaviour of substances at locations downstream of the point of complete vertical and lateral mixing, but upstream of locations where removal and other mechanisms have a significant impact, has been introduced by Di Toro (1984) as:

$$C_T = \frac{Q_S}{Q_S + Q_R}C_S + \frac{Q_R}{Q_S + Q_R}C_R \tag{6}$$

where C_T is the downstream concentration, C_R, C_S, Q_R, Q_S respectively the mean runoff and upstream concentrations and flow rates which are jointly lognormally distributed. To determine the probability distribution of C_T, a more accurate numerical method has been used, and the model has been checked for COD, lead, and phosphorus data.

As a basis for an economic model, a deterministic mass balance model of phosphorus dilution in stream systems has been derived by Jeng *et al.* (1983), who divide the stream into a series of reaches, or boxes where dilution of phosphorus from tributaries and from point and non-point (urban, agricultural) sources at point "A" take place according to the relationships:

$$\begin{aligned} Q_{ki} &= Q_{k,i-1} + Q^P_{ki} + Q^u_{ki} + Q^g_{ki} + Q^t_{ki} \\ P^a_{ki}\, Q_{ki} &= P^b_{k,i-1}\, Q_{k,i-1} + PX_{ki}(I - X_{ki})Q^P_{ki} + PY_{ki}(I - Y_{ki})Q^u_{ki} \\ &\quad + PZ_{ki}(I - Z_{ki})Q^g_{ki} + PT_{ki}Q^t_{ki} \end{aligned} \tag{7}$$

where $Q_{k,\, i-1}$ and Q_{ki} are the stream flows in the $(i-1)$ and ith reach of the kth tributary; Q^P_{ki}, Q^u_{ki}, Q^g_{ki}, Q^t_{ki}, respectively, the sewage treatment plant flow, the urban runoff flow, the agricultural runoff flow, the tributary flow; p^a_{ki} the total phosphorus concentration in the ith reach of the kth tributary immediately downstream of point A, $p^b_{k,i-1}$ the total phosphorus concentration at the downstream end of the $(i-1)$th reach of the kth tributary, PX_{ki}, PY_{ki}, PZ_{ki} the total phosphorus concentrations without treatment of respectively point source, urban runoff, agricultural runoff, PT_{ki} the total phosphorus concentration of tributary sources; X_{ki}, Y_{ki}, Z_{ki}, respectively, the fractional efficiencies of total phosphorus removal for the ith reach of the kth tributary from municipal sewage treatment plants, and urban and agricultural sources.

The variations of phosphorus concentration P_{ki} in a given reach are governed by the equation:

$$\frac{\partial P_{ki}}{\partial t} = \frac{Q_{ki}}{A_{ki}} \frac{\partial P_{ki}}{\partial x} \pm K_{ki} P_{ki} \tag{8}$$

where A_{ki} is the average cross-sectional area, K_{ki} a first order source or sink rate of total phosphorus, x the distance downstream of point A, and t the time.

This model has been applied with success to a small lake system. A similar dilution model has been introduced by Paulson *et al.* (1984) to study the behaviour of dissolved metals (Cu, Cd, Fe, Mn) in a river partly influenced by tides, distinguishing physical mixing processes from biogeochemical reactions like adsorption or desorption. The discrepancies between the concentration values obtained from the mass balance equation (assumed to apply to conservative situations) and the concentrations measured in the water body indicate the occurrence of biogeochemical reactions; for instance, it has been confirmed that the main stream was the siege of conservative mixing (i.e., no significant reactions), while the estuary was an area of significant chemical reaction.

While the models presented above are global in the sense that they describe river reaches or even whole rivers, larger scale models are sometimes introduced to simulate non-point source pollution at the level of a watershed. For instance, they can consist of a classical watershed hydrological model (giving runoff from rainfall, soil moisture, and subsurface recharge of stream channels), where quality aspects are introduced by assigning monthly concentrations of pollutant loads to sediments or runoff according to land use (Hartigan *et al.*, 1983; McTernan *et al.*, 1981); for example, the model will consist of the hydrological equations:

$$\begin{aligned} Q &= \frac{(P - 0.02\,S)^2}{P + 0.8\,S} \\ S &= \frac{2540}{\mathrm{CN}} - 25.4 \\ q_s &= 11.8(q_p Q)^{0.56}\,\mathrm{LS}\,.\,K\,.\,C\,.\,\mathrm{P}_r \end{aligned} \tag{9}$$

where q_{p} is the peak flow, q_{s} the sediment delivered; C, K, LS, P_r are factors accounting for cover, soil erosion, length-slope, practice; CN is the curve number combining soil hydrological properties and land use/cover features; q is the flow volume; P is the storm precipitation; Q is the direct storm runoff; S is the maximum soil moisture retention. The pollutant load is related to q_s through a potency factor (ratio of pollutant mass to sediment mass).

Of course, such models are very global, subject to uncertainties about hydrological parameters; they probably can be of some help in the first approach of a non-point source pollution problem in a rather large area, especially to help formulate smaller scale programmes.

2.3 TRANSFER FUNCTIONS

An important parameter of pollution transport, conditioning chemical reactions among other factors, is the residence time of a pollutant in the water body. For instance, this residence time can be the basis for management decisions concerning the delay of intervention after an accident.

An interesting way of estimating the residence time is the transfer function method which consists in defining the water body as a black box and analysing the input u to output y relationship as a convolution, where $h(t)$ is the impulse-response of the system assumed to be linear and stationary.

$$y(t) = \int_{-\infty}^{+\infty} u(\gamma)\, h(t - \gamma)\mathrm{d}t \tag{10}$$

Distribution of residence times or $h(t)$ is the probability that a water particle stays in the system during some time between t and $t + \mathrm{d}t$; if $C(t)$ is the output concentration of a tracer, then

$$h(t) = \frac{C(t)}{\int_{-\infty}^{+\infty} - C(t)\mathrm{d}t} \tag{11}$$

3 LOCAL MODELS

The local or structural models, accounting for the various mechanical and physico-chemical phenomena listed in the introduction, are based on a set of equations describing water flow and contaminant transport. They usually consist of three equations: conservation of total mass, conservation of momentum, and dispersion-convection. In the particularly simple case of one dimension, they can be written:

$$\frac{\partial A}{\partial Q} + \frac{\partial Q}{\partial x} = q \tag{12}$$

$$\frac{\partial Q}{\partial t} + \frac{\partial (uQ)}{\partial x} + g\,A\,\frac{\partial h}{\partial x} = g\,a(S_0 - S_f) + q\,u_q \tag{13}$$

$$\frac{\partial (AC)}{\partial t} + \frac{\partial (QC)}{\partial x} = \frac{\partial}{\partial x}\left(EA\,\frac{\partial c}{\partial x}\right) + S_i) \tag{14}$$

where A is the cross-sectional area of the stream, C the contaminant concentration, E a dispersion coefficient, g the gravity, h the flow depth, Q the flow discharge, q the lateral inflow per unit channel length entering the river, S_f the friction slope, S_i sources and sinks, S_0 the mean bed slope, t the time, u the mean velocity of flow, u_q the velocity component of the lateral inflow that is parallel to the river.

The first two equations describe the hydrodynamics with or without contaminant and the last one the transport of contaminant as a generalised equation of contaminant mass conservation based upon an analogy of Fick's law describing dispersion due to differential convection and turbulent diffusion. Its form is

$$\frac{\mathrm{d}m}{\mathrm{d}t} = EA\,\frac{\mathrm{d}C}{\mathrm{d}l} \tag{15}$$

where dm is the quantity of matter travelling during the period dt between two sections of areas A at a distance dl and displaying a difference in concentrations dC, and E being the dispersion coefficient.

For freshwater streams, the convective flux is significantly larger than the mass flux due to longitudinal dispersion: sometimes dispersion is neglected, and a Streeter Phelps type model may be sufficiently precise. In a tidal river, the convective and dispersive fluxes are both significant. In an estuary, turbulent diffusion is due mainly to tidal currents, wind-induced waves, and friction on the boundaries; whereas, dispersion related to differential convection is due to the topography, bends and variations in depth of the estuary, Coriolis force, weather conditions, and salinity.

The general model is three-dimensional but, because of numerical difficulties involved, users attempt to simplify it in 2-D or 1-D under various assumptions subject to discussions. The sink and source terms take various forms: for example, $S_i = -KC$ with K being a decay constant of the pollutant.

3.1 EXAMPLES OF MODELS

3.1.1 Estuary Flow

Transport and mixing in estuaries are influenced by oscillation of flow due to tidal action, changes in bottom topography, curvature of the estuary in the longitudinal direction, effects of the aspect ratio in a 3-D model, variation in phase of velocity across the cross-section, buoyancy, and salinity effects (Allen, 1982). Usually only a few of these parameters are accounted for by the models.

A theory of oscillatory flow has been established by Jimenez and Sullivan (1984), based on a probabilistic formulation of the streamwise dispersion of contaminant molecules in time dependent flow between parallel plates and in tubes; however, a simpler and more practical model has been proposed by Allen (1982) to describe this dispersion in steady and oscillatory turbulent shear flow in a two-dimensional channel, based on a random walk approach: The pollutant source is represented by a larger number of particles followed by computer as they move through the fluid, their velocities following a generated random distribution. The domain is divided into grid squares, and the number of particles per grid square is the concentration. In steady flow, the velocity has a logarithmic profile; and in oscillatory flow, it is a superposition of a logarithmic and a sinusoidal profile. The various statistical properties of the concentration are computed (mean, variance, skewness) and the dispersion coefficient is defined classically as:

$$E = \frac{1}{2}\frac{d\sigma_x^2}{dt} \tag{16}$$

where σ_x^2 is the variance of the longitudinal concentration distribution.

Because of the heterogeneous distribution of concentration in a cross-section, Wang *et al.* (1980) considered the general convection-dispersion equation:

$$\frac{\partial c}{\partial t} + u\frac{\partial c}{\partial x} + v\frac{\partial c}{\partial y} + w\frac{\partial c}{\partial z} = \frac{K}{\partial x}\left(K_x\frac{\partial c}{\partial x}\right) + \frac{\partial}{\partial y}\left(K_y\frac{\partial c}{\partial y}\right) + \frac{\partial}{\partial z}\left(K_z\frac{\partial c}{\partial z}\right) \quad (17)$$

where K_x, K_y, K_z are the dispersion coefficients and u, v, w the mean velocity components. They assume that K_x, K_y, K_z are constant, that the only flow is in the longitudinal direction ($u = w = 0$), that u is constant in the longitudinal direction ($u = f(y)\ g\ (z)$) and zero on the boundaries (no slip-flow condition).

But most authors will introduce a 1-D equation of dispersion by averaging the 3-D equation over a transverse cross-section A to obtain equation (14). For instance, Curran (1981) models various non-conservative parameters of interest in that way, namely BOD, ammonia nitrogen (NH_3-N), nitrate nitrogen (NO_3-N), DO, with the following equations:

$$\frac{d}{dx}(QL) = \frac{d}{dx}\left(EA\frac{dL}{dx}\right) + m - k\,AL \quad (18)$$

$$\frac{d}{dx}(QM) = \frac{d}{dx}\left(EA\frac{dM}{dx}\right) + m_M - k_N\,AM \quad (19)$$

$$\frac{d}{dx}(QN) = \frac{d}{dx}\left(EA\frac{dN}{dx}\right) + k_N\frac{AM}{N} + m \quad (20)$$

$$\frac{d}{dx}(QD) = \frac{d}{dx}\left(EA\frac{dD}{dx}\right) + k_a A\left(D_s - D\right) - k\frac{AL}{L} - 4.57\,k_N\,AM + m \quad (21)$$

where m is the addition of solute per unit length of estuary, k the reaction rate describing the depletion of s solute, k_a the reaeration coefficient, D and D_s the concentration and saturation concentration of DO, L, M, N the respective concentrations of BOD, ammonia nitrogen, nitrate nitrogen, and Q the upstream total freshwater discharge.

3.1.2 Stream Flow

Bujon (1983) introduced a general 3-D model, assuming that the flow velocities decrease linearly transversally and vertically from a maximum velocity located at the free surface and along the longitudinal flow axis:

$$u = u_0 + G_y y + G_z \quad (22)$$

$$E_x \frac{\partial^2 c}{\partial x^2} + E_y \frac{\partial^2}{\partial y^2} + E_z \frac{\partial^2 c}{\partial y^2} - u \frac{\partial c}{\partial x} = \frac{\partial c}{\partial t}$$

where u_0 is the velocity on the axis, G_y and G_z linear decay coefficients (<0). Assuming a fast vertical homogenisation, this equation can be reduced to 2-D, neglecting the y-terms.

Starting with a two-dimensional model written in an orthogonal curvilinear coordinate system in which the x-axis follows the meander of the river, then using the cumulative discharge to replace the transverse distance coordinate, Lam Lau and Krishnappan (1981) represent steady, two-dimensional mixing with a stream tube model:

$$\frac{\partial c}{\partial x} = \frac{1}{Q^2} \frac{\partial}{\partial \eta} \left(D_z(x, \eta) \frac{\partial c}{\partial \eta} \right) \tag{23}$$

where η is a dimensionless cumulative discharge (ratio of the cumulative discharge q_c to the total discharge Q of the channel; $\eta = q_c/Q$) and D_z the dispersion coefficient.

One-dimensional models are frequently introduced. For instance, Medina *et al.* (1981) describe the DO deficit D by the steady state equation:

$$E \frac{\mathrm{d}^2 D}{\mathrm{d}x^2} - u \frac{\mathrm{d}D}{\mathrm{d}x} + K_1\, L_0\, \mathrm{e}^{mx} - K_2 D = 0 \tag{24}$$

where K_1 is the deoxygenation constant of carbonaceous BOD, K_2 the atmospheric reaeration coefficient, L_0 the remaining carbonaceous BOD concentration at $x = 0$, $m = (u/2E)\,(1 - \sqrt{1 + [(4\, K_1\, E)/U^2]})$ for $x > 0$.

This type of model can be extended to the unsteady state by adding a term $\partial D/\partial t$ (Medina and Buzun, 1981). Orhon and Goneng (1982) introduce one-dimensional equations to represent the fate of ammonia nitrogen in rivers, taking into account both transport and biochemical conversion (i.e., the influence of nitrifying micro-organisms):

$$\begin{aligned} D_L \frac{\partial^2 c}{\partial x^2} - u \frac{\partial c}{\partial x} - \frac{\partial c}{\partial t} - r_s = 0 \\ D_L \frac{\partial^2 n}{\partial x^2} - u \frac{\partial n}{\partial x} - \frac{\partial n}{\partial t} - r_n = 0 \end{aligned} \tag{25}$$

where c is the ammonia-nitrogen concentration, n the concentration of nitrifying bacteria, D_L the longitudinal turbulent diffusion coefficient, u the average stream velocity, r_s and r_n substrate and biomass reaction rates per unit volume (represented for instance by a Monod type kinetic equation

$$\tau_n = \frac{\partial n}{\partial t} = \hat{\mu} = \frac{cn}{k_s + c}$$

with $\hat{\mu}$ the maximum growth rate and k_s the saturation coefficient).

For a river where the flow changes continuously due to downstream tidal effects, Tucci and Moretti (1982) have used the group of equations (12), (13), and (14) to represent BOD and DO; while for a small river with stable bottom influenced by storm conditions Bedford *et al.* (1983) also use the same system but consider that, due to increased cross-sectional mixing, longitudinal dispersion can be neglected, thus reducing equation (14) to:

$$\frac{\partial(AC)}{\partial t} + \frac{\partial(QC)}{\partial x} = \gamma q + S_i \qquad (26)$$

where γ is the contaminant concentration in the lateral inflow. Equations (12) and (13) are solved simultaneously, yielding flows, areas, topwidths, depths and water surface elevations for an entire flood event, and the output of these equations is used to solve equation (14).

An important factor of pollution behaviour is the interaction with sediments influencing the uptake and release of dissolved and particulate elements. Somlyody (1982a) has taken this factor into account in his study of cadmium behaviour in a stream by using equations (12) and (13) and adding descriptions of adsorption, coprecipitation, settling velocity, and the probability coefficient for deposition. This study also addressed wind-induced sediment/water interaction in a lake based on a depth-integrated transport equation.

Onishi (1981) used a sediment/contaminant transport model, representing seperately the transport of sediment (convection-dispersion, fall velocity and cohesiveness, deposition on the river bed, erosion from the river bed, sediment contributions from point/non-point sources and subsequent mixing), the transport of dissolved contaminant (convection-dispersion, adsorption of dissolved contaminants by both moving and stationary sediments or desorption from the sediments into water, chemical and biological degradation or radionuclide decay, contaminant contribution from point/non-point sources and subsequent mixing), the transport of particulate contaminant (convection-dispersion, adsorption of dissolved contaminants by sediment or desorption from sediment into water, chemical and biological degradation or radionuclide decay, deposition of particulate contaminants on the river bed or erosion from the river bed, contaminant contribution from point and non-point sources and subsequent mixing). The resulting equations are all three of the same type, two-dimensional dispersion equations (integrated vertically over the river depth) with various sink and source terms to account for the phenomena listed above. This model has been applied to the transport of a pesticide, Kepone, in a stream and near an estuary.

3.2 RESOLUTION METHODS

Mathematical methods are used to solve the equations, usually simplified in some way, to compare the mathematical results with the experimental data, and to calibrate the model, taking into account uncertainties of the data and the models themselves. A wide range of mathematical methods exists; they belong to the fields of functional analysis, numerical analysis, probability and statistics, vector and tensor analysis, and matrix algebra.

The following is a brief account of the most commonly used methods. Analytical solutions can be handled easily on mini computers; they are usually difficult to obtain except in some particular cases of strong simplifying assumptions. For instance, Wang *et al.* (1980), using the method of Gill, approximated the general dispersion equation with one having constant coefficients by expanding the concentration in a kind of Taylor series and averaging it; the classical elementary exponential solution is then obtained.

Chapman *et al.* (1982) introduce a semi-analytical solution by a convolution of the elementary solution with time and a space integration by taking all sources into account. Such a solution is also recommended by Bujon (1983), and extended to represent the finite distance boundary effects.

Yet only numerical methods like finite differences, finite elements, or characteristics can fully account for complex boundary conditions. The methods of characteristics, although free from numerical difficulties like numerical diffusion or overshoot, are cumbersome to programme; and for practical applications, modelers usually introduce either finite difference methods, sometimes with varying time steps and spatial grids (Lam Lau and Krishnappan, 1981; Somlyody, 1982b; Bedford *et al.*, 1983; West and Lin, 1983) or finite element methods like Galerkin (Curran, 1981).

3.3 THE DISPERSION COEFFICIENTS

A most important parameter of local models is the dispersion coefficient. It is related to turbulent diffusive transport and to the local variations in velocity, influenced by bottom friction, curvature, and shape of the river. In estuaries, a tidal mean dispersion coefficient is usually introduced by accounting for vertical and transverse oscillatory shears and circulation mechanisms, like the gravitational circulation associated with saline water intrusion, the wind stress at the water surface, the bottom topography, the flow rate of fresh water, or the influence of the Coriolis force.

The dependence of the dispersion coefficients on these parameters is generally unclear, and various formulas have been derived, which may differ greatly from one another according to the assumptions used. For instance, under the assumption of a steady turbulent velocity close to the time-average tidal velocity over a half-tidal cycle, Harleman gives

$$E = 77n\bar{H}^{5/6}\,\bar{U}_t \quad \text{(Ozturk, 1981)} \tag{27}$$

where n is the Manning's roughness coefficient, H the mean flow depth and U_t the mean tidal velocity, while Bowden finds

$$E = 0.295\bar{H}\bar{U}_t \quad \text{(Ozturk, 1981)} \tag{28}$$

and Holley uses

$$E = \frac{\Gamma T^2 \bar{H}}{b^2} \quad \text{(Smith and Tukhan, 1981)}$$

with Γ a function of time and space, assumed to be constant in a first approximation, b the width at the surface, T the tidal period.

A review of the various formulas currently used for estuary conditions, obtained either from theoretical considerations or determined empirically from experimental results, is provided by West and Broyd (1981). This review illustrates the wide variety of formulas owing to the diversity in assumptions and methods of averaging the solute mass transport equation. A major difficulty in the use of local models based on the dispersion equation thus appears to lay with dispersion coefficients, whose dependence on the various flow parameters is unclear, whose values can usually be determined for given conditions by calibration, but are difficult to use for prediction when the flow and domain conditions change. An illustration of such difficulties is the observed difference in magnitude between computed coefficients by means of formulas in laboratory channels and field measurements of these coefficients.

4 LIMITATIONS OF THE MODELING

The mathematical modeling of pollution fate in surface waters is limited by the basic adequacy of the models to represent the phenomena, the difficulties of identifying the parameters and performing field experiments, and the mathematical and numerical problems related to the solution of the equations.

4.1 BASIC ADEQUACY OF THE MODELS

The field models of dispersion are based on a generalisation of Taylor's approach, which assumes the validity of a diffusion equation at the microscopic scale, and averages it into another diffusion equation at a larger scale under the rather strong assumptions that a sufficiently long time has elapsed since release of a contaminant; furthermore, the cross-sectional area is independent of x and t, the turbulence is stationary in time, and the contaminant is passive.

Various studies conclude that a dispersion process is not necessarily of the diffusive type and that the emergence in the field of a diffusive regime is related to sufficient spatial averaging, conditioned by good mixing.

To cope with non-Gaussian distributions of field dispersion in the early stages of the movement, various solutions have been suggested. For instance, it is assumed that the dispersion is represented by a diffusion equation for very large times only (asymptotic time) and that the transient states can be represented at given times by a diffusion type equation with a time-dependent diffusion coefficient (Lee and Gill, 1980) or by a delay-diffusion equation which can be applied to oscillatory flow in estuaries (Smith, 1982). Another approach consists of assuming that the non-Gaussian distribution is largely due to the effects of dead zones, i.e., zones of temporary entrapment of portions of a contaminant in bottom and side irregularities of the stream (Nordin and Troutman, 1980; Beer and Young, 1983); the models are then a combination of diffusion and reservoir models. Random walk techniques are also a way to cope with the non-observation of Taylor's assumptions, by tracking pollutant particles as they jump randomly through the water according to some probability law (Allen, 1982); in particular, the variation with time of the variances σ^2 will be indicative of a diffusive behaviour. Naturally most of the authors will seek to estimate a minimum asymptotic time, i.e., a finite time such as when the behaviour of the contaminant appears reasonably Gaussian.

4.2 PARAMETER IDENTIFICATION

The determination of the dispersion coefficients is usually delicate. Because of the great variety of assumed relationships between these coefficients and the more basic parameters, it seems illusory in practice to compute them from experimental values of these basic parameters; their identification is rather an inverse problem, consisting of estimations using diffusion equations.

From equation (16), we see that, when concentrations and velocities are known, the dispersion coefficients verify a first order partial differential equation. The problem is not mathematically well posed: small errors in C will create severe oscillations in K and, conversely, small changes in C erase the influence of large variations in K; furthermore, the boundary conditions on K are usually not well known.

In general, identification will be obtained either by trial and error fitting of measured and computed concentrations or by direct substitution of measured concentrations into the governing equation. An illustration of the latter case is given by West and Broyd (1981) who evaluate the gross tidal mean dispersion coefficient K_{AT} with the formula:

$$K_{AT} = \frac{QC_{AT}}{A_T \dfrac{\partial C_{AT}}{\partial x}} \tag{29}$$

where C_{AT} is the tidal mean concentration, A_T the tidal mean cross-sectional area and Q the river discharge; this formula is obtained by integrating the intertidal steady state equation.

$$\frac{\partial}{\partial t}(QC_{AT}) = \frac{\partial}{\partial x}\left(K_{AT}A_T\frac{\partial C_{AT}}{\partial x}\right) \tag{30}$$

Field values of the transverse dispersion coefficient for various rivers are given by Lam Lau and Krishnappan (1981), and field values of the tidal mean dispersion coefficient for some estuaries are given by West and Broyd (1981). In general, the experimental determination of field parameters, even when it is more straightforward than the determination of dispersion coefficients, as in the case of velocities or geometrical parameters of the stream, is difficult and expensive because the heterogeneities of field situations require a multiplicity of measurements to cover large domains adequately. It implies the introduction of mathematical methods, like statistical analysis, to estimate the uncertainties on the predicted concentrations from the uncertainties on the parameters; the probabilistic approach of transport is then certainly useful.

As a result of experimental difficulties, the scarcity of data influences the choice of a model. A sophisticated model can be meaningless if the number and quality of data are not sufficient; for example, Whipple and Hunter (1981) use a very simple BOD decay relationship instead of a DO equation more complex but not more accurate because of the lack of data.

4.3 NUMERICAL DIFFICULTIES

Some difficulties are related to parameter identification by inverse methods or deconvolution, like the instabilities. The non-linearity of the diffusion equation, when density variations have to be accounted for as for salt water intrusion, is another possible mathematical difficulty. More specific numerical difficulties exist in the resolution of diffusion and convection equations, for instance, numerical diffusion, smearing the computed concentration front, or overshoot characterised by oscillations in the computed concentration profiles. They are a subject of current research, although there are methods of taking care of them, like the method of characteristics, but they may be very cumbersome to operate.

The dispersion model is usually simplified in a two-dimensional model, considering a lateral homogeneous distribution of pollutant. Yet this approach is sometimes not justified, and three-dimensional models have to be used (Wang *et al.*, 1980; Somlyody, 1982b) with all the numerical difficulties they involve.

5 GROUNDWATER/SURFACE WATER RELATIONSHIPS

While some consideration has been given to the pressure transfer between surface water and groundwater, little work has been performed on mass transfer.

The analysis of mass transfer between rivers and aquifers is made along the following lines of thought: to consider the surface water as a boundary condition of the hydrogeological model expressed in terms of fluxes of water or of sources and sinks, and by simple dilution of the contaminant in the corresponding input or output flows to transform the water flow conditions into contaminant flow conditions of the equations of mass transfer in the aquifers. For instance, the dispersion equation in an aquifer is written as follows for a given species:

$$\frac{\partial c}{\partial t} = \mathrm{div}(K\mathrm{grade}) - \mathrm{div}(uc) + wc' \tag{31}$$

with K the dispersion tensor, u the mean pore velocity, c' the concentration of the species in the source/sink flow, c the concentration of the species in the aquifer, w the volumetric flow rate per unit volume of porous medium of a source/sink. This equation is coupled to the flow equation (the hydrogeological model), derived from Darcy's law, which can be written for the case of a confined aquifer:

$$\mathrm{div}(T\,\mathrm{grad}\,h) = S\frac{\partial h}{\partial t} + w \tag{32}$$

where h is the piezometric head, T the transmissivity, S the storage coefficient and w has been defined above.

The last equation is related to the surface water flow equation. In an example of Pinder and Sauer (1971) of one-dimensional unsteady stream flow in a channel of constant cross-section partially penetrating the aquifer, the surface water flow is expressed by

$$z\frac{\partial v}{\partial l} + v\frac{\partial z}{\partial l} + \frac{\partial z}{\partial t} = (q_l + q_g)/b$$

$$v\frac{\partial v}{\partial l} + g\frac{\partial z}{\partial l} + v\frac{q_l + q_g}{bz} + \frac{\partial v}{\gamma t} = g(S_0 - S_f) \tag{33}$$

where b is the channel width, g the gravity, l the space coordinate, q_l the lateral inflow per unit length over the channel banks and from tributaries, q_g the flow into the channel per unit length through its wetted perimeter, S_0 the slope of the channel bottom, S_f the friction slope, v the flow velocity, z the flow depth, t the time.

The groundwater flow equation becomes

$$\operatorname{div}(T \operatorname{grad} h) = S \frac{\partial h}{\partial \mathrm{d}t} + W + \frac{q_g}{b + 2z} \tag{34}$$

and vertical flow from the aquifer to the stream is given by

$$\frac{q_g}{b + 2z} = K_p \frac{z + z_0 - h}{\Delta z'} \tag{35}$$

where K_p is the hydraulic conductivity of the bottom sediments of the channel, z_0 the elevation of the stream bottom measured from the same datum as h, z' the thickness of the bottom sediments along the wetted perimeter of the channel.

Let us quote a study along the same lines by (Price *et al.*, 1983): to consider the system river–aquifer as a black box and analyze the response of the aquifer to a contaminant input from the river (or conversely) by a statistical correlation method, for instance, or by a convolution relationship as used in signal processing. An example of the latter is given by (Collongues *et al.*, 1980), who study the mass transfer of sodium chloride from the Rhine into the underlying aquifer by considering that the system consists of a sequence of N linear identical reservoirs defined by the equation

$$\begin{gathered} u(t) - y(t) = \frac{\mathrm{d}R(t)}{\mathrm{d}t} \\ R(t) = k\, y\, (t) \end{gathered} \tag{5.6}$$

where k is the storage coefficient, R the system reserve, u the input concentration in the river, y the output concentration in the aquifer. The system is globally defined by the function h verifying:

$$y(t) = \int_{\mathbb{R}} h(t - x)\, u(x)\, \mathrm{d}x \quad \text{and} \quad h(t) = \frac{1}{k} \mathrm{e}^{-t/k}$$

and for the N reservoirs $h(t) = \dfrac{1}{\Gamma(N) k^N} t^{N-1} \mathrm{e}^{-t/k}$ where $\Gamma(N)$ is the gamma function.

The impulse response h of the system (i.e., k and N) is a characteristic of the medium determined by calibration and deconvolution. The applicability of the method is limited by the consistency of the time series in the river and in the aquifer used to determine the impulse response, by the randomness in time of the input and by the chemical behaviour of the chemical when it is not conservative.

6 CONCLUSIONS

A large variety of models exists, built around relatively few basic concepts: either structural models trying to describe all aspects of the phenomena or black or grey box models describing the evolution with time of one parameter only without any physical assumption on the system. Because they rely on many data points, the structural models are necessarily local, while the others will be used on a global scale, sometimes as a first approach to a given problem.

The global models rely mostly on a general mass conservation equation without consideration for the flow characteristics and introducing bulk coefficients to account for the various inputs or outputs; a good illustration of these models are the Streeter Phelps equations for BOD and DO and their various improvements.

Local models are also based on a mass conservation equation, accounting for the movement of the contaminant particles inside the system and their physico-chemical behaviour through various complementary relationships; they usually consist of a system of partial differential equations describing the flow of the receiving water and the dispersion-convection of the contaminant within the receiving water and its interactions with the surrounding environment like the bottom sediments. Although local at field scales, the dispersion-convection equations are derived by a change of scale procedure analogous to the procedure used in the study of molecular diffusion, i.e., an averaging in some way of very local velocities and concentrations and the introduction of macroscopic coefficients, the dispersion coefficients, by a phenomenological relationship between averaged quantities.

Global models are simple to use but of limited predictive capability, because they do not account for the changes affecting the conditions that prevail when their transfer functions are derived.

Local models are more complex, may be closer to reality but are not necessarily more accurate. The governing phenomena are not always clearly understood; the validity of the equations and the meaning of the dispersion coefficients are not well established; the solutions of the models depend on the approximations made on the equations and boundary conditions as well as on mathematical and numerical procedures used; the gathering of the correct data in sufficient quantity at the proper places and according to the appropriate time series is neither obvious nor inexpensive.

For these reasons, although modeling is certainly the only methodological tool enabling progress in the study of contaminant behaviour in surface water and especially allowing the transfer of knowledge from laboratory to field, there are no automatic rules for model use. The choice of a model depends on the advancement of the study, the number and quality of the data, knowledge of the various mechanisms and phenomena, the time required for providing a solution, and the skill and competence of the modeler. It should be remembered that although mysterious in some way, the models are just tools and if, the output product reflects the quality of the tool, it depends mainly on the skill of the modeler.

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