CHEMICAL TRANSPORT IN RIVERS

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Contents

Summary

Due to human activities water pollution has become a widespread phenomenon. An understanding of the behavior and fate of chemicals, which are discharged to the aquatic environment as a result of these activities, is essential to the control of water pollution. In rivers the basic physical movement of pollutant molecules is the result of advection, but superimposed upon this are the effects of dispersion and mixing with tributaries and other discharges.

Some of the chemicals discharged are relatively inert, so their concentration changes only due to advection, dispersion and mixing. However many substances are not conservative in their behavior and undergo changes due to chemical or biochemical processes like oxidation, photolysis, etc.

River models are mathematical representations of the pattern of concentrations in space and time. A variety of techniques are employed, especially finite difference, to segment the movement of the chemicals through a spatial grid in steps 2-dimensional grid in space and time.

Such basic models have been extended to deal with particular problems. For example pollution control legislation is generally framed in a probabilistic manner (e.g. in terms of a 90 percentile concentration), so the corresponding models contain a stochastic element to generate frequency distributions of concentration. River models have also been formulated to simulate diffuse inputs, or deal with lateral variation of concentration in wide rivers.

The lower reaches of rivers are generally subject to tidal influence. Such estuarine reaches are hydraulically much more complex, and require specialized models.

1. Introduction

Water quality models attempt to simulate changes in the concentration of pollutants as they move through the aquatic environment. There are some pollutants that are sufficiently inert for their concentration to be regarded as unchanging, except by hydraulic processes like advection and dispersion. These are referred to as conservative substances and are often employed in the calibration/validation of water quality models. The basic mechanism involved in advection and dispersion is discussed in Section 2 since this affects both conservative and non-conservative substances.

Superimposed upon these mass transfer mechanisms, for the majority of pollutants, are physical, chemical and biological processes which also cause changes in concentration.

The kinetic processes responsible for pollutant decay are discussed in Section 3.

The fate of a pollutant is the resultant of the interaction between mass transfer and kinetic processes. The principal factors determining the fate of a chemical after discharge, are the nature of the chemical and the nature of the environment. Even in a relatively self contained system like a river there are interactions with the atmosphere, the ground water and at the river mouth, the sea.

Idealized reactors are often used to represent the fate of chemicals as they pass through a river system. Two types of reactor – CSTR and Plug Flow are described in Section 4.

Section 5 discusses the ways in which mathematical models of river water quality have been formulated. It includes a brief mention of models for particular types of situation but does not extend to estuaries, as the pattern of water movements are so complex as to require specialized models.

Section 6 discusses the trends in river modeling.

In modeling the fate of chemicals in the environment, it is essential to define a specific control volume for the model which must have a clearly defined boundary. The inputs and outputs that move across the boundaries should be known as estimated by numerical or empirical formulation. Besides these, the characteristics of transport within the controlled volume and across the boundaries are necessary for modeling. Furthermore, the reaction kinetics and rate constants of the model within the controlled volume play important roles in the models.

A controlled volume can be as small as infinitesimally thin slice of water in a rapidly flowing stream or as a large as an ocean. No matter how large it is, the important point is that the boundary of it must be clearly defined so that the volume is known and mass transport flux across the boundaries can be determined.

Generally speaking, at least four elements are necessary to successfully formulate a mathematical model of polluting chemicals:

1. reliable field data on chemical concentration and mass fluxes information,

2. a mathematical model formulation that can adequately reflect the real dynamic and transport condition,
3. appropriate rate constants and kinetic coefficients for the model, and
4. the criteria with which to assess the model performance.

2. Hydraulic Mechanisms

It is important to appreciate that not all pollutants mix freely with water. There are some chemicals which are immiscible and others which may have particle sizes and density differences which cause them to rise or sink. However the majority of pollutants which are in true solution, colloidal solution or in fine suspension, are carried along and mixed by the movement of the water. The processes involved are advection and dispersion, respectively.

Advection may be defined as mass transport in the aquatic environment at the velocity of the bulk liquid. Any factors that influence flow would also affect the advective transport. Dispersion refers to the spreading of a pollutant from a region of high concentration to other regions of lower concentration. It is brought about at the molecular level, over long time scales by Brownian Motion (i.e. random movement of solute and solvent molecules), but at the macroscopic level and in much smaller time scales it is due to eddy diffusion (i.e. transport due to random variations in the advective velocity).

Chemical transport due to advection and dispersion can be described by the principle of mass conservation and Fick's law as following

$$\frac{\partial C}{\partial t} = -U_i \frac{\partial C}{\partial X_i} + \frac{\partial}{\partial X_i}\left(K_i \frac{\partial C}{\partial X_i - R_i} \right) \tag{1}$$

Where C = concentration, U_i = average velocity in the i-th direction, X_i = distance in the i-th direction and R = reaction transformation rate. K_i is the diffusion coefficient in the i-th direction, and it is assumed to be constant.

The three dimensional advection-diffusion equation can be written as

$$\frac{\partial C}{\partial t} = -U \frac{\partial C}{\partial x} - V \frac{\partial C}{\partial y} - W \frac{\partial C}{\partial z} + K_x \frac{\partial^2 C}{\partial x^2} + K_y \frac{\partial^2 C}{\partial y^2} + K_z \frac{\partial^2 C}{\partial z^2} - R \tag{2}$$

Where U, V, W = average in x, y, z direction, respectively, and K_z, K_y, K_z = diffusion coefficient in x, y, z direction, respectively.

The modeling of chemical transport, based on (1) and (2) may be from zero-dimensional to three-dimensional, as detailed in the following.

Some lakes or reservoirs in which strong turbulence exists and concentration of chemicals is considered uniform, zero dimensional models are appropriate for such lakes and reservoirs.

Most rivers in practice are considered as horizontal linear networks of segments or volume elements, especially for long, narrow and shallow rivers. A one dimensional transport model is appropriate to these rivers.

A one dimensional model can be applied to narrow estuaries while some estuaries are conceptually composed of multiple inter-connecting one-dimensional channels.

In modeling the hydrodynamics and water quality of relatively shallow estuaries, the crucial assumption involves vertically well-mixed layers that allows for vertical integration of the continuity, momentum, and mass transport equations (Benelmouffok and Yu, 1989).

The two dimensional laterally average models require the hypothesis of uniform lateral mixing in the cross channel direction. These models are the standard simulation techniques for reservoirs or estuaries which have considerable variations of density and water quality condition in the vertical and lateral directions.

For those lakes and estuaries in which chemical transport is caused not only by advection but also by dispersion in the whole environment, three dimensional models are normally used.

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Bibliography

Bencala, K.E. (1984) Interactions of Solutes and Streambed Sediment. *Water Resources Research* **20(12)**, pp 1804-1814.

Bennel Mouffok, D.E. and Yu, S.L. (1989) Two Dimensional Modelling of Hydrodynamics and Pollutants Transport in a Wet Detention Pond. *Water Science and Technology*, **21(8/9)**, pp 727-738.

Clifforde, I. (1991) Urban Pollution Management. *Water and Waste Treatment* **35(2)**, pp 22-40.

Czernuszenko, W. (1987) Dispersion of Pollutants in Rivers. *Hydrological Journal* **32(1)**, pp 59-67.

Daniel, T.M. and Wundke, A.D. (1993) Neural Network Assisting in Water Quality Modeling. *2nd Australasian Conference on Computing for the Water Industry*, Melbourne, Australia. NATL CONF PUBL INST ENG AUST., No. 93, part 2, pp 51-57.

Ditoro, D.M. (1969) Stream Equations and Methods of Characteristics. *Proc. ASCE Sanitary Eng. Div. Journal*, **95**, SA4, pp 699-703.

Elliott, D.J. (1993) River Models. *Chapter 6 in An Introduction to Water Quality Modelling*, edited by A. James. Wiley, Chichester.

EPA (1987) Rates, Constants and Kinetics: Formulations in Surface Water Quality Modelling. 2nd edition, *U.S. Environmental Protection Agency Report No. EPA/600/3-85/040*. Athens, Georgia, U.S.A.

Falconer, R.A., Liu, S.W. and Chen, Y. (1992) *Application of High Order Accurate Schemes for*

Advective Transportation in a 2-*D Model*. Ashgate Publishing Ltd., University Press, Cambridge.

Fischer, H.B. (1981) *Transport Models for Inland and Coastal Waters*. Academic Press, London.

James, A. (1984) *An Introduction to Water Quality Modelling*. Wiley, Chichester.

Leonard, P.B.A. (1979) A Stable and Accurate Convective Modelling Procedure Based on Quadratic Upstream Interpolation. *Computer Methods in Applied Mechanics and Engineering*, **19**, pp 59-98.

Luk, G.K.Y., Lau, Y.L. and Watt, W.E. (1990) Two-Dimensional Modelling in Rivers with Unsteady Pollutant Source. *Journal of Environmental Engineering*, **116(1)**, pp 121-124

Manson, J.R. and Wallis, S.G. (2000) Conservative, Semi-Lagrangian fate of transport model for fluvial systems. *Water Research,* **34(15)**, pp 3769-3777.

McBride, G.B. (1982) Modelling Advection and Longitudinal Dispersion. *Proceedings of River and Estuarine Mixing Workshop*, edited by J.C. Rutherford, New Zealand Water and Soil Organization, Wellington, New Zealand.

McBride, G.B. and Rutherford, J.C. (1984) Accurate Modelling of River Pollutant Transport. *Journal of Environmental Engineering* **110(4)**, pp 808-827.

McDonnell, R.A. (2000) Heirarchical modelling of environmental impacts of river impoundment based on GIS. *Hydrol. Processes*, **14(11)**, pp 2123-2142.

Orlob, G.T. and Beck, M.B. (1983) *Mathematical Modelling of Water Quality*. Wiley, Chichester.

Rajar, R. and Cetina, M. (1995) Hydrodynamic models as a basis for water quality modelling. 3*rd* *International Conference on Water Pollution*. Computational Mechanics Inc., Billercia, MA 01821 (USA), pp 199-211.

Raunch, W., Henze, M., Koncos, L., Reichert, P., Shanahan, P., Somlyody, L. and Vanrolleghem. P. (1998) River Water Quality Modelling. The State of the Art. *Water Science & Technology* **38(11)**, pp 237-244.

Reichert, P. and Wanner, O. (1991) Enhanced One-Dimensional Modelling of Transport in Rivers. *Journal of Hydraulic Engineering,* **117(9)**, pp 1165-1183.

Rodda, H.J.E., Shankar, U. and Demuth, S. (1999) Application of GIS to Water Quality Modelling in New Zealand. *International Association of Hydrological Sciences*, Publication No. 254, pp 243-251.

Scarlatos, P.D. (1996) Estuarine Hydraulics. Chapter 9 in *Environmental Hydraulics,* edited by Singh, V.P. and Hagar, W.H. Published by Kluwer Academic Publishers, London.

Streeter, V.L. and Phelps, (1925) *A study of the pollution and natural purification of the Ohio River Bulletin No. 146*, U.S. Public Health Service.

Thomann, R.V. (1972) *Systems Analysis and Water Quality Management*. Environmental Research and Applications Inc., New York.

Valentine, E.M. and Wood, I.R. (1977) Longitudinal Dispersion. *Journal of Hydraulics Div.,* ASCE 93, HY9, pp 975-990.

Ven der Perk, M. (1998) Calibration and identifiability analysis of a water quality model to evaluate the contribution of different processes to the short term dynamics of suspended solids and dissolved nutrients in the surface water of a rural catchment. *Hydrological Processes* **12(5)**, pp 683-699.

Van Rijn, L.C. (1896) Mathematical Modelling of Suspended Sediment in Non-Uniform Flows. *Journal of Hydraulic Engineering* **112(6)**, pp 433-455.

Warn, A.E. (1982) Calculating Consent Conditions to Achieve River Quality Objectives. *Effluent and Water Treatment Journal* **22**, pp 152-155.

Young, P. and Whitehead, P.G. (1975) A Recursive Approach to Time Series Analysis for Multivariate Systems in G.C. Vansteenkiste (ed) *Computer Simulation of Water Resource Systems*.

Yoshida, K. (1989) Mathematical Models for Evaluation of the Fate of Chemicals in the Environment. *Eisei Kagakn* **35(5)**, pp 313-321.

Biographical Sketch

Sam James worked in the Civil Engineering Department of The University of Newcastle Upon Tyne from 1958 to 1989, where he was successively Lecturer, Senior Lecturer and Reader in Environmental Engineering. He was also a partner in Environmental Software Ltd and responsible for a number of riverine, estuarine, and marine models of water quality in various countries.