Chapter 13

Water Quality Modeling

The objectives of this chapter are:

- to introduce water quality concepts, monitoring, and standards,
- to provide a detailed discussion on river water quality modeling,
- to explain basics of lake water quality modeling, and
- to cover catchment and ground water quality models.

The ancient river valley civilizations that prospered in India, Egypt, and Mesopotamia were aware of the importance of the quality of water, although at that time the problems were not of serious nature. In recent years, with the growth of population and industrial activity, the quality of water has deteriorated at many places and has become an important issue all over the world. Clearly, water quality is closely linked to water use and to the state of economic development of the society. Although various countries have developed standards of water quality for different purposes which are being enforced, it has not yet been possible to provide water of desired quality to all the people. The quality of water is deteriorating sharply in many regions of the world and there are cases of poisoning of water by toxic chemicals, such as arsenic. According to the World Health Organization (WHO) estimates, more than one billion people drink unsafe water and 2.4 billion (40% of the human race) are without adequate sanitation. Every year, nearly 3.4 million people, mostly children, unnecessarily die due to water-related diseases (more than one million from malaria alone).

In view of the central role of supply of clean water in social health, organizations such as WHO strongly urge several basic measures, including purifying water (say, chlorination), and improving hygiene, as immediate means of improving social well-being in developing countries. Chlorination, for example, is a proven means of ridding piped water of disease-causing microorganisms. A good example of successful chlorination is to be found in the Maldives where a national control programme used it in wells and in oral rehydration salts against diarrhea. According to WHO, twenty years after the programme started, all of the Maldives islands have their own community rainwater collection tanks, and deaths from diarrhoea are virtually unknown. Elsewhere, good water management has almost eradicated guinea worm, a disfiguring, disabling disease which afflicted 50 million people in Africa and Asia in the mid-1900s. By 1999 that number had fallen to below 100,000. But poor irrigation water management has, in sharp contrast, led to a huge spread of schistosomiasis (snail fever) to areas of the world where it never existed before. According to WHO, an estimated 200 million people are infected today with schistosomiasis.

During the past 50 years there has been a strong emphasis on medical interventions, including, for example, drug use and this has tended to reduce the attention and priority given to safe water supply and adequate sanitation. With the growing resistance to antibiotics, insecticides and standard drugs, health authorities now understand the limitations of a purely medical approach. That makes safe water and sanitation more important than ever. Maintaining the quality of waters is an important aspect of sustainable development. Before discussing water quality, it is helpful to recall the physical properties of water.

13.1 RELEVANT PROPERTIES OF WATER

Two atoms of hydrogen and one atom of oxygen join together to form one molecule of water (H_2O). A noteworthy property of water is that it is denser than ice at its melting point. It is because of this property that ice floats on the surface of lakes and reservoirs in winter and the deeper layers of water are in liquid form and the aquatic life survives in these layers. Another noteworthy feature of water is its thermal properties. It has the highest specific heat (4.18 J/g/deg) of any known substance which means that the temperature of a large water body changes slowly. A very large amount of heat is needed for evaporation of water because its latent heat of vaporization is about 600 times larger than its heat capacity (the heat required to raise water temperature by 1° C). This, according to Maidment (1993), makes evaporation the dominant component of the energy balance associated with water cycle and about 23 percent of the solar radiation reaching the earth surface is absorbed by evaporating water. Vaporization of water also partly helps maintain the temperature of human body which contains about 70% water by weight.

The main cause of quality related problems is the molecular structure of water that makes water a nearly universal solvent. Due to this, it dissolves the largest number of substances, many of which are harmful leading to water quality problems. Water has a high surface tension which makes raindrops acquire the shape of spherical drops and there is capillary rise in soil zone.

The temperature of water is an important physical variable that affects its density, viscosity, surface tension, vapor pressure, solubility, etc. The temperature of a water body depends on the location, season, source, and depth of sampling point. Normally, the temperature of water in surface bodies varies from 0 to 35° C. Selected physical, chemical and biological characteristics of surface and ground waters are given in Table 13.1.

Table 13.1 Physical, chemical, and biological characteristics of various water sources [Adapted from Malina (1996)].

	Water source	
Characteristics	Typical surface water	Typical groundwater
Suspended solids, mg/L	> 50	-
Dissolved solids, mg/L	< 100	> 100
Temperature, °C	0.5 - 30	2.7 - 25
Turbidity (JTU)	10 – 50	-
	Chemicals: inorganic matter	
Alkalinity, mg/L as $CaCO_3$	< 100	> 100
Hardness, mg/L as $CaCO_3$	< 100	> 100
Chlorides, mg/L	50	200
Heavy metals, mg/L	-	0.5
Nitrogen, mg/L	< 10	< 10
Organic, mg/L	5	-
Nitrate, mg/L	< 5	5
pH, (units)	6 – 9	6.5 - 8
	Chemicals: organic matter	
Total organic carbon (TOC), mg/L	< 5	-
Pesticides, mg/L	< 0.1	-
Phenols, mg/L	< 0.001	-
Surfactants, mg/L	< 0.5	< 0.5
Oxygen, mg/L	7.5	7.5
Bacteria, MPN/100 mL	< 2000	< 100
Viruses, plaque forming units (pfu)	< 10	< 1

The range of a few key water quality parameters and their typical values are given in Table 13.2.

Table 13.2 Typical value and range of parameters of river water quality [Compiled from McCutcheon et al. (1993), Biswas (1981), and others].

Water quality parameter	Typical value	Observed range
Inorganic carbon (mg/L)	50	5 – 250
Total organic carbon (mg/L)	1 - 10	0.01 – 40
Dissolved organic carbon (mg/L)	1 - 6	0.3 – 32
Total organic matter (mg/L)	2 - 20	0.02 – 80
BOD (5 day) (mg/L)	3 – 15	1 – 100
Temperature (	10 – 20	0 – 30
Dissolved oxygen	4 – 9	0 - 20

13.2 WATER QUALITY MONITORING

The term monitoring indicates long term, standardized measurement and observation of the environment in order to define the status and trends in the uses of resources. In survey, a finite duration (usually short) intensive program is launched to measure and observe the quality of aquatic environment for a specific purpose. The term surveillance is used for a continuous specific measurement and observation for the purpose of water quality measurement and operational activities. Note that all the three activities require collection of data and therefore sometimes the term monitoring is used to denote all three. Usually the value of a water quality variable is a function of space and time. Therefore, one can write

$$c = f(x, y, z, t) \tag{13.1}$$

The quality of a water body may show rapid variations. In general, the variations are more in river, somewhat less in lakes, and much less in aquifers. Fig. 13.1 shows a schematic of facets of water quality monitoring. Monitoring and modeling of water quality variations require, inter alia, a detailed knowledge of hydraulics and hydrology of the water body. In case a program is launched from an operational point of view, the periods of worse conditions, such as summers when the flows are small, and the periods when the concentration of pollutants is likely to be highest, should be given more attention.

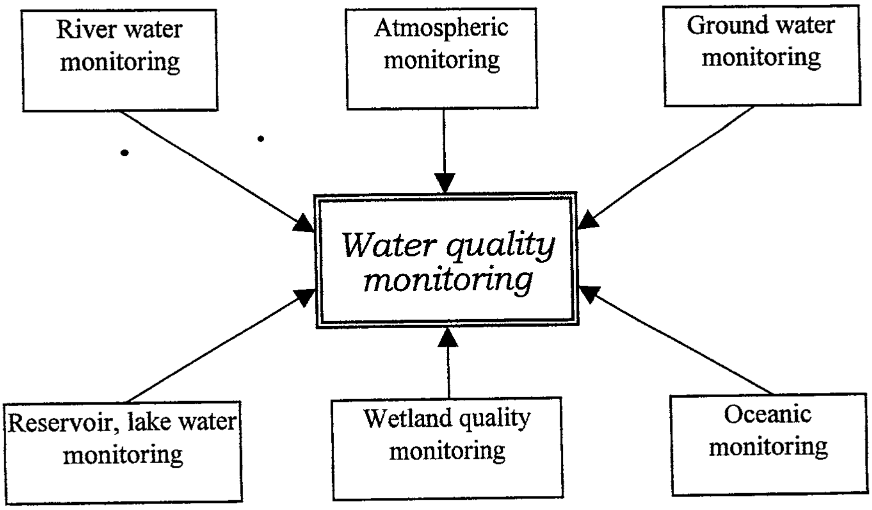


Fig. 13.1 Facets of water quality monitoring.

Guidelines regarding frequency of observation for trend monitoring were suggested by Chapman (1992). The characteristics of spatial and temporal variations in water quality, following Chapman (1992), are given in Table 13.3. The design of any water quality monitoring program should be periodically examined. The review should take into account new approaches, instruments, techniques, etc. The observers who are deployed for water quality samples and analysis must have the requisite background and training since these are specialized activities.

Table 13.3 Spatial and temporal variations in water quality variables.

Rivers	Lakes and reservoirs	Ground water
Spatial variations (x - longitudinal direction; y - transverse direction; z - vertical direction)		
In fully mixed narrow rivers - variability only in x. Wide rivers – variability in x and y, particularly downstream of sewage outfall or junction with a tributary.	High variability in z for most lakes. High variability in x, y, and z in irregularly shaped lakes. In reservoirs, variation also depends on purposes and operation.	Commonly, high variability in x and y. In multi-layer aquifers and in the unsaturated zone, high variability in x, y, and z may be present.
	Temporal variations	
Variation is closely related with discharge but a unique relation may not exist. High sediment load during floods. High BOD, low DO, higher concentration of pollutants during low flows.	Thermal stratification influenced by weather changes. Variations depend upon residence time.	Low temporal variation. Definite trend can be seen if the aquifer is hydraulically connected to a river or lake that receives pollutants.

The Global Environment Monitoring System (GEMS) was launched in 1970s to determine the status and trend of key environmental issues. The GEMS/WATER programme (see http://www.cciw.ca/gems) was established within the United Nations Environment Programme (UNEP) in 1975 with the twin objectives of improving water quality monitoring and assessment capabilities in participating countries, and determining the status and trends of regional and global water quality.

13.2.1 Monitoring Network

The location of sampling stations largely depends on the purpose of study. In general, sampling stations may be divided into two categories: i) basic stations, and ii) auxiliary stations. Basic stations are usually located at the mouth of main streams and major tributaries, downstream of river development projects, at or near hydrometric stations, gauge discharge sites, at state boundaries, upstream and downstream of waste outfalls, industrial and urban centers, and at points of water use. Auxiliary stations are established to investigate the effect of pollutants discharged into a stream, determination of assimilation capacity of stream and similar studies with a common objective. These stations are purposely related to each other and may be moved to another place or operated temporarily.

Data collected at these stations are used to interpolate stream quality at other points, or predict the water quality described under a set of given conditions.

13.2.2 Sampling Program

Water quality samples should be taken at places where the composition is expected to be homogeneous over the cross-section. Usually there will be no difficulty in locating such points in effluents discharged from pipes or small open channels. Sampling points in rivers should be well away from any possible disturbing influence, such as pools, stagnant zones, heavy growth of weed or sewage fungus, or points where ground water enters, unless it is desired to specifically study their effects on water quality.

Sampling frequency largely depends on the purpose of the network, the relative importance of the station, the variability of the data, and the accessibility of the station. The workload involved and the financial commitment for a decided frequency of sampling must match the available resources. At newly started stations, samples may be collected at a higher frequency so that within 2-3 years a sufficient number of observations are available for a statistical analysis to determine mean, variations, cycles, and trends in the relevant parameters used in monitoring the water quality. The frequency of sampling may be changed after such an evaluation. For basic station networks operated to collect baseline data, the sampling frequency may be from 3-4 times per year to monthly. In any event, at least one sample should be taken in each season. When stations are operated in relation to specific use, the frequency of sampling will be governed by that use. The sampling of raw water for water works may be carried out daily. Weekly or bi-monthly samples may be collected at a sampling station which is maintained downstream of a waste outfall to monitor the effectiveness of the waste water management program and its effect on the stream. Where the stream water is used for swimming and other recreational purposes, sampling may be confined only to the season of use.

The details of water quality monitoring critically depend on the level of deterioration of the water body. Clearly, the greater the deterioration of the water body is, more intense – in terms of the number of parameters and frequency of observation -- the monitoring is. The aim of such monitoring may be to identify the sources and causes of pollution, to decide a program of treatment, or to assess the effectiveness of remedial action.

Critical Parameters: The choice of water quality characteristics that are to be measured must necessarily be determined by local circumstances. In general, it will be necessary to compromise between the number of parameters measured and the marginal difference that information on each parameter makes to subsequent management decisions. The number of organic constituents present in water could be very large but it would be impractical to measure them all on a routine basis. Instead, it will be necessary to rely on non-specific tests, such as COD or TOC, to indicate the general level of organic pollution, together with a few specific tests for selected pollutants with particularly harmful properties.

As a general idea, the parameters to be measured may include the following: total organic carbon, BOD, cyanide, pesticides, suspended solids, nitrogen, fluoride, cadmium, chromium, copper, lead, nickel, zinc, mercury, boron, dissolved oxygen, pH value, and coliform bacteria. If the objective is to develop a model which would permit the evaluation of the influence of pollution control measures on the cost of treatment of public water supply, additional information might be needed on total hardness, alkalinity, calcium hardness, sulphate, phosphate, sodium, potassium, etc.

13.2.3 Water Quality Standards

Whether water from a given source can be used for a specific purpose critically depends on its quality. Even though adequate water may be available from a source, if the quality is not up to the mark, either it cannot be used or it has to be treated before use. Water quality standards are legally enforceable criteria that specify parameters, such as temperature, concentration of various pollutants etc. whose adherence makes water suitable for a given purpose. Clearly, the permissible limits depend on the intended use of a source, e.g., water from a particular source may be good for irrigation but it may not be suitable for drinking.

The continued advances in research on water quality and the growing concern with risks to health have caused various governments and international bodies to draw standards of water quality for various purposes. The WHO had issued water quality guidelines 1971. These were later revised by following a philosophy that emphasizes a risk-benefit approach in the formulation and enforcement of national standards. This new approach was contained in the publication *Guidelines for drinking-water quality,* issued by WHO (1996). Research findings and field experience continue to expand the knowledge base on water and health. The latest WHO guidelines and standards are available on its website at www.who.int/water_sanitation_health/ Water_quality/drinkwat.htm. Table 13.4 gives the bacteriological quality of drinking-water, and Table 13.5 lists substances and parameters in drinking-water that may give rise to complaints from consumers. The various national governments have drawn standards for use within the territory of their jurisdiction.

13.2.4 Water Quality Based Classification of River

Rivers are generally classified on the basis of annual average discharge in various categories: Large rivers > 1000 m^3/s, rivers 150-1000 m^3/s, streams 5-150 m^3/s, and small stream < 5 m^3/s. Note that these distinctions do not consider annual variations of river flow. In sub-tropical and arid zones, rivers often range from zero discharge during the dry season to large discharge during wet periods.

Knowledge of the natural water quality of a stream, its self-purification capacity and the effect of various wastes on its ecosystem is necessary for a planned development of its uses. While the overlying strata protect the ground water, a stream is highly vulnerable to activities of man in its basin. Also, they are one of the most extensively exploited water resources. Although water does not exist in streams in its pure chemical form, it may be classified as unpolluted in view of its beneficial use. A polluted stream tends to regain its natural quality with time as the water flows in it. Various physical, chemical and biological phenomena are responsible for this self-purification. Some conservative pollutants may persist for a long time before they are diluted to an insignificant level or are removed from the liquid phase due to physico-chemical reactions of precipitation and adsorption.

Table 13.4 Bacteriological quality of drinking-water[a] (Source: WHO website www.who.int).

Organisms	Guideline value
All water intended for drinking	
E. coli or thermotolerant coliform bacteria[b,c]	Must not be detectable in any 100-ml sample
Treated water entering the distribution system	
E. coli or thermotolerant coliform bacteria[b]	Must not be detectable in any 100-ml sample
Total coliform bacteria	Must not be detectable in any 100-ml sample
Treated water in the distribution system	
E. coli or thermotolerant coliform bacteria[b]	Must not be detectable in any 100-ml sample
Total coliform bacteria	Must not be detectable in any 100-ml sample. In the case of large supplies, where sufficient samples are examined, must not be present in 95% of samples taken throughout any 12-month period

[a] Immediate investigative action must be taken if either *E. coli* or total coliform bacteria are detected. The minimal action in the case of total coliform bacteria is repeat sampling; if these bacteria are detected in the repeat sample, the cause must be determined by immediate further investigation.

[b] Although *E. coli* is the more precise indicator of faecal pollution, the count of thermotolerant coliform bacteria is an acceptable alternative. If necessary, proper confirmatory tests must be carried out. Total coliform bacteria are not acceptable indicators of the sanitary quality of rural water supplies, particularly in tropical areas where many bacteria of no sanitary significance occur in almost all untreated supplies.

[c] It is recognized that, in the great majority of rural water supplies in developing countries, faecal contamination is widespread. Under these conditions, the national surveillance agency should set medium-term targets for the progressive improvement of water supplies, as recommended in Volume 3 of *Guidelines for drinking-water quality.*

One of the most efficient and effective ways to present numerical results is through the use of graphs and maps. The visualization of findings in the form of maps provides an easy and rapid comprehension of the situation. Additionally, such maps may show the location of human settlements, industrial plants, major water outfalls and intakes, water purification plants, power plants, etc. A band, the width of which indicates the mean discharge, represents the river course. Colors indicate the quality of the water. Usually the following color code is used:

Blue:	Category I, no pollution to slight pollution
Green:	Category II, moderate pollution
Yellow:	Category III, heavy pollution
Red:	Category IV, excessive pollution
Black:	Category V, zone of devastation.

Table 13.5 Substances and parameters in drinking-water that may give rise to complaints from consumers (Source: WHO Website www.who.int).

	Levels likely to give rise to consumer complaints[a]	Reasons for consumer complaints
Physical parameters		
colour	15 TCU[b]	appearance
taste and odour	—	should be acceptable
temperature	—	should be acceptable
turbidity	5 NTU[c]	appearance; for effective terminal disinfection, median turbidity =1 NTU, single sample =5 NTU
Inorganic constituents		
aluminium	0.2 mg/l	depositions, discoloration
ammonia	1.5 mg/l	odour and taste
chloride	250 mg/l	taste, corrosion
copper	1 mg/l	staining of laundry and sanitary ware (health-based provisional guideline value 2 mg/litre)
hardness	—	high hardness: scale deposition, scum formation low hardness: possible corrosion
hydrogen sulfide	0.05 mg/l	odour and taste
iron	0.3 mg/l	staining of laundry and sanitary ware
manganese	0.1 mg/l	staining of laundry and sanitary ware (health-based guideline value 0.5 mg/litre)
dissolved oxygen	—	indirect effects
pH	—	low pH: corrosion high pH: taste, soapy feel preferably <8.0 for effective disinfection with chlorine
sodium	200 mg/l	taste
sulfate	250 mg/l	taste, corrosion
total dissolved solids	1000 mg/l	taste
zinc	3 mg/l	appearance, taste
Organic constituents		
toluene	24–170 μg/l	odour, taste (health-based guideline value 700 μg/l)
xylene	20–1800 μg/l	odour, taste (health-based guideline value 500 μg/l)
ethylbenzene	2–200 μg/l	odour, taste (health-based guideline value 300 μg/l)
styrene	4–2600 μg/l	odour, taste (health-based guideline value 20 μg/l)
monochlorobenzene	10–120 μg/l	odour, taste (health-based guideline value

		300 µg/l)
1,2-dichlorobenzene	1–10 µg/l	odour, taste (health-based guideline value 1000 µg/l)
1,4-dichlorobenzene	0.3–30 µg/l	odour, taste (health-based guideline value 300 µg/l)
trichlorobenzenes (total)	5–50 µg/l	odour, taste (health-based guideline value 20 µg/l)
synthetic detergents	—	foaming, taste, odour
Disinfectants and disinfectant by-products		
chlorine	600–1000 µg/l	taste and odour (health-based guideline value 5 µg/l)
chlorophenols		
2-chlorophenol	0.1–10 µg/l	taste, odour
2,4-dichlorophenol	0.3–40 µg/l	taste, odour
2,4,6-trichlorophenol	2–300 µg/l	taste, odour (health-based guideline value 200 µg/l)

[a] The levels indicated are not precise numbers. Problems may occur at lower or higher values according to local circumstances. A range of taste and odour threshold concentrations is given for organic constituents.

[b] TCU, true colour unit.

[c] NTU, nephelometric turbidity unit.

13.3 RIVER WATER QUALITY MODELING

The river water quality models consist of a set of governing dynamic equations that describe hydrologic, thermal, and biochemical processes that take place in the riverine ecosystem. These are the equations of conservation of mass, momentum, and energy. However, because of incomplete understanding of some of the processes as well as different levels of detail, a whole lot of different models are available. Mostly one-dimensional models are used in river studies; higher dimensional models have been mainly employed to study lakes and estuaries. The earliest attempt to model water quality in rivers was made by Streeter and Phelps in 1925. Since that time, many additions have been made to improve the Streeter-Phelps model.

River water quality modeling has two components: 1) forecasting the developments in a basin and consequent effects on the water quality, and 2) forecasting of the changes in concentration of the pollutants within the stream channel. The second component has two problems. The first is the prediction problem, i.e., the solute concentration at a specific point in time and space are known and the solute concentrations at various times at various locations downstream are to be determined. The second objective involves formulating across the problem in a descriptive manner, i.e., a time series of solute concentrations along the stream is given and it is required to find what the dominant processes are that control the solute concentration.

Forecasting the concentration of contaminants which are stable in nature is simple since their concentration changes only due to dilution or evaporation. Concentrations of many biologically stable organic and inorganic substance change due to precipitation, sedimentation, adsorption and chemical reactions with other substances. These reactions are influenced by several factors such as pH, temperature, bed characteristics, etc., and they are to be considered separately for respective mixtures of substances and local conditions.

Similar to hydrographs, the plot of concentration of pollutants with respect to time is known as a pollutograph. The graph of pollutant load (concentration) multiplied by flow rate/time is known as loadograph. Pollutants may enter into a water body from a point source or a non-point source. As the name suggests, a point source indicates that the pollutants enter the water body through a well-defined outlet or locations as happens with municipal or industrial waste. Other examples of point sources include discharges and spills that occur due to accidents, e.g., when transporters of hazardous materials release contaminants into a water body. The pollutants from a non-point source come from flow distributed over large land surface; a typical example is runoff from agricultural areas. Non-point sources of solutes are distributed along the watercourse. Sediment and associated pollutants also originate from non-point sources and result from the interplay of a large number of factors, such as climate, precipitation (amount, intensity, and distribution), geology, soil properties, land use, and streamflow characteristics. Note that this differentiation between point and non-point is a bit confusing because if the waste from a large city is collected to a sewer system and discharged into a river at a well defined outlet, it will be termed as point source pollution, although the catchment producing waste is spread over a large area.

Pollution sources may also be roughly classified according to the time-pattern of outflow. Some sources continuously discharge waste into a water body while others may do it instantaneously or intermittently. Continuous sources dump pollutants into the water body over a long period of time. A common example of a continuous source is a municipal wastewater treatment plant. Although mass-loading rates may vary in time, most of these treatment plants continuously discharge effluents into the water body. It needs to be highlighted that the treatment of concentrated wastes is easier than dilute wastes.

The waste from an instantaneous source enters the water body over a very short period of time. Although truly instantaneous sources are hard to find, situations do arise in which solutes are added to the river over time intervals that are indeed very small relative to the time span of interest. The addition of pollutant to a water body in one gulp is one example of an instantaneous source. Another example is an accidental spill from a tanker where contaminants enter a river or lake in just a few minutes.

The riverine ecosystem can be schematically represented as a food web (Fig. 13.2). Organic debris of natural origin (leaves, humus, etc.) constitute nutrients for bacteria. The bacterial population degrades organic substances into inorganic compounds, mainly nitrates, phosphates and carbon dioxide (self-purification process) in aerobic conditions. These inorganic compounds are the principal nutrients for the phytoplankton, which consume them to make biomass through the process of photosynthesis in the presence of sun light. A useful by-product of photosynthesis is oxygen gas. Another source of oxygen in water is diffusion at the free surface, known as superficial reaeration. The oxygen that is made available through these two processes counterbalances the oxygen deficit due to bacterial activity.

The biochemical and chemical processes of a river are significantly influenced by hydraulic and thermal conditions. The main hydraulic variables that influence water quality are flow velocity, depth, and discharge. Obviously, an increase of discharge increases the dilution rate and decreases pollutant concentrations. An increase of flow velocity reduces biochemical self-purification since the travel time between two river sections reduces. The amount of sediment load being transported by a river depends on the flow velocity. Another important consequence of velocity variations is turbulence in flow. An increase in the turbulence definitely increases reaeration because there is better intake and mixing of oxygen at choppy layer at the surface. Due to this reason, considerably higher aeration takes place in shallow, fast flowing streams. In many water treatment processes, artificial aeration is an important activity. Besides aeration, turbulence also influences the ecological interactions within the food web; the efficiency of bacterial degradation processes which involve exoenzyme drops if turbulence increases. As far as the flow depth is concerned, the penetration of sunlight is small at greater depths and this causes a slowdown in photosynthetic processes.

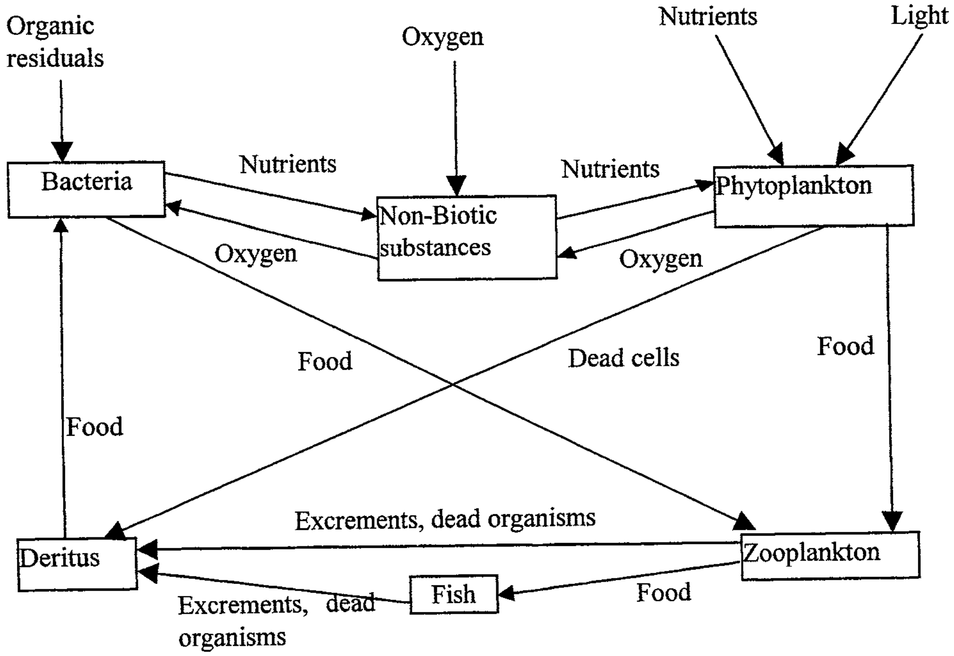


Fig. 13.2 Simplified representation of aquatic eco-system as a food web [After Gandolfi et al. (1996)].

Clearly, high organic loads cause a strong depletion of the dissolved oxygen in water. Sometimes this causes severe damages to higher order species and produces considerable amounts of mineral nutrients. Mineral nutrients may also directly enter into a river by various sources, such as treatment plant outflows, scour and leaching from agricultural lands, or some industrial processes. In rivers with low flowing velocities, the time of residence is quite large and in such cases, high contents of mineral nutrients can be assimilated by algae, giving rise to intensive algal blooms. As a consequence, the mass of phytoplankton may block the penetration of sunlight in deeper layers. This may cause massive death of organisms, which in turn causes oxygen consumption and a further increase of mineral nutrients. In this way, a degenerative phenomenon, known as *eutrophic cycle*, may be established in the water body.

Among nondegradable materials, heavy metals, even at relatively small concentrations, may seriously influence the bacterial metabolism. At times, this may lead to the death of bacteria. Oily substances form a thin film on the water surface thus reducing reaeration. The penetration of sunlight at deeper layers can be reduced due to high concentration of suspended solids.

Regarding thermal conditions, unless the temperature is very high, biochemical processes accelerate with increase in temperature. The solubility of gases in water decreases with rise in temperature. A direct fall out is slower intake of oxygen through superficial reaeration and higher biochemical-oxygen demand (BOD).

13.3.1 Components of a River Water Quality Model

In a detailed mathematical model of river water quality, all the biochemical, hydraulic and thermal phenomena must be described by means of differential equations. Gandolfi et al. (1996) suggested that the water quality model must be composed by three submodels: biochemical, hydraulic, and thermal submodels, and these could be coupled together as shown in Fig. 13.3a. Evidently, there will be interactions among the state variables of these submodels although some of the interactions will be stronger and some weaker. In particular, the influence of temperature variations (in the range of values normally encountered in most natural rivers) on the hydraulic conditions is negligible. Based on this reasoning, the structure of the water quality model can be simplified as shown in Figure 13.3b. These three submodels can be sequentially solved, beginning with the hydraulic submodel and ending with the biochemical one.

13.3.2 Hydraulic and Thermal Models

In one-dimensional unsteady flow process, two important variables are the flow depth h (or the area of flow cross-section A which is a function of h) and the mean velocity v (or discharge). The two pertinent equations are the mass balance and momentum equations. The St. Venant equations are the general form of these equations.

In a thermal model, one state variable, i.e., temperature, is adequate to provide the requisite information. The temperature is an input to the biochemical model and in view of this and observations about temperature above, one may skip the thermal model.

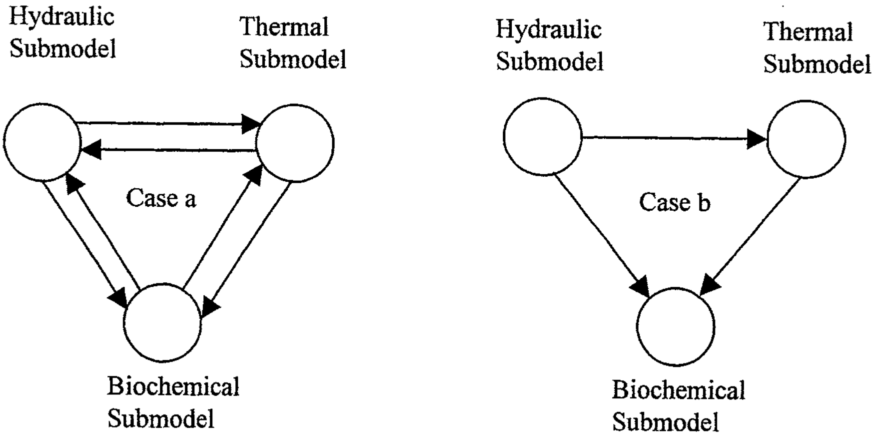


Fig. 13.3 Water quality model structure: a) the general case; b) when minor interactions are ignored [Source: Gandolfi et al. (1996)].

13.3.3 Biochemical Model

A large number of variables are involved in the biochemical model. The number of agents that are involved in the self-purification processes is so huge that it would be impractical, because of logistics and computational problems, to introduce a state variable corresponding to each of them. If one were to introduce all the interactions of a real-life case, the resulting model would be unmanageable. This calls for a need to reduce the number of variables either by substitution or by grouping similar variables and then letting one variable represent each group.

A pertinent variable that is a representative of the water quality status or the self-purification process in a river is the dissolved oxygen (DO) concentration. A detailed discussion on DO can be found in Section 13.4. BOD is the measure of the amount of oxygen needed for complete biochemical oxidation of all the matter present in a unit volume of water. Therefore, BOD is the aggregated variable representative of all the biochemically oxidizable compounds in that matter. Not all water quality problems require highly sophisticated models. In fact, many water quality decisions can be taken based on representative indicators, such as BOD.

It needs to be emphasized here that any biochemical model is a highly simplified representation of the processes that actually take place in the water body. Most parameters of the equations cannot be measured in the field and, therefore, these models require careful calibration. Of course, one needs to have sufficient field data to set-up the model.

13.3.4 Geochemical Processes

The discussion so far was focussed on physical processes that aid and affect solute transport. Although these processes play a large role in determining the fate of solutes, chemical and biological processes may have equally important impact on solute transport. Some of the basic geochemical reactions affecting solutes in natural waters are explained in what follows.

A dissolved chemical species may take part in two types of chemical reactions: homogeneous and heterogeneous. The reactions in which dissolved species interact with species of the same phase are known as homogeneous reactions. These reactions are termed as homogeneous because the species involved are in the same (dissolved) form. Some examples of homogeneous reactions are: acid-base, complexation, and hydrolysis reactions.

The second type of reactions in which a dissolved species may take part are heterogeneous reactions. These reactions involve species from more than one phase. Thus, a heterogeneous reaction may involve interaction of a dissolved phase species with a species in gas or solid phase. For example, the dissolved oxygen concentrations in water may be dependent on the oxygen in the atmosphere over the surface water body. If the water body is undersaturated in terms of dissolved oxygen concentrations, oxygen will enter the water body through the air/water interface and the concentrations of dissolved oxygen will increase. Conversely, if water becomes oversaturated with oxygen due to some reason, oxygen will escape to the atmosphere through the process of degassing and the concentrations of dissolved oxygen will decrease. Other examples of heterogeneous reactions include solid-phase reactions, such as precipitation/dissolution and sorption.

There are two fundamental approaches to study geochemical reactions in natural waters. The appropriate approach for a given problem depends on the rates at which relevant reactions occur, relative to the time scale of interest. If reaction rates are 'slow' relative to the study time scale, a kinetic approach is employed, wherein the dynamics of the system are studied. If reaction rates are relatively 'fast', an equilibrium approach is implemented to determine the steady-state composition of waters. Other factors, such as data availability, also play a role in determining the appropriate approach.

All geochemical reactions require some finite amount of time, τ_c, for completion. The required amount of time is dependent on the rate of reaction, r, such that τ_c and r are inversely related (Runkel and Bencala, 1995). A kinetic approach is often implemented when τ_c exceeds the time period of observation, τ_0. For example, τ_c for many biologically-mediated oxidation/ reduction reactions is on the order of days to years. If the interest is in the state of the system over the course of a day, a kinetic approach is needed to describe how the concentrations of the chemical species change over time. In this case, differential equations may be written to describe the temporal variation in species concentrations and kinetic rate constants (r) may be empirically determined. The equations may be solved to yield the species concentrations over time.

13.3.5 Sorption/ Desorption

Sorption is the process in which a dissolved species becomes associated with a solid surface. This is an important process that controls the concentrations of solutes in natural waters. The dissolved species that takes part in a sorption reaction is known as a *sorbate*, and the solid species with which it gets associated with is known as the *sorbent*. In case the dissolved species penetrates the sorbent, the process is known as *absorption*. The term *adsorption* is used to describe the interaction of the dissolved species with the surface or interface of the sorbent (Weber et al., 1991).

Sorption may have a significant effect on dissolved inorganic species in water. Morel and Hering (1993) noted that trace elements, such as zinc and copper, are known to sorb to hydrous ferric oxides. Kuwabara et al. (1984) found copper to sorb to the bed of a small stream.

There is close coupling between physical and geochemical processes in a river. The distribution of a solute mass among three phases, viz., dissolved, solid, and gas, is determined by geochemical reactions and in this way, they affect the amount of mass that is available for physical transport. The physical transport mechanisms affect the location of solute mass. This is subjected to various geochemical actions as it moves in water.

The coupling between transport and chemistry may be illustrated by examining a conceptual classification of geochemistry based on homogenous and heterogeneous reactions. This distinction between reaction types becomes important when considered within the context of physical transport. To begin with, the heterogeneous reactions are divided into three subclasses. In heterogeneous I reactions, a dissolved species interacts with a mobile solid species. Examples of heterogeneous I reactions include the formation of a precipitate in the water column due to oversaturated conditions, and the sorption of a dissolved species onto a particulate solid within the water column. Heterogeneous II reactions are those in which a dissolved species interacts with a stationary solid species. An example of a heterogeneous II reaction is the sorption of a dissolved species onto a stationary solid such as particles coating the streambed or debris in the channel. Finally, in heterogeneous III reactions, a dissolved species interacts with a gas phase, such as the degassing of dissolved oxygen to the atmosphere.

13.3.6 Pollutant Concentration and Load

Concentration is the primary measure of the quantity of a constituent in a fluid environment and is defined as

$$C = M/V \tag{13.2}$$

where C is concentration (mg/L), m is mass of constituent (mg), and V is volume of fluid (L). Note that the density of water is nearly 1.0 g/cm^3 and hence the units of mg/L and g/m^3 are numerically equivalent to *parts per million* (ppm) by mass in water. For variables that are not measured in mass units, concentration may be defined in terms of numbers. For example, bacteria are often measured as *most probable number* (MPN) per unit volume.

The impact of constituents on a water body is influenced by both the concentration and load. The term *load* may mean either the total mass M in a volume V of water (see eq. 13.2)

$$M = CV \tag{13.3}$$

or the mass flow rate L (mass/time) in water flowing with a discharge Q (m^3/s):

$$L = CQ \tag{13.4}$$

13.3.7 Transport of Solutes in Rivers

A *solute* can be defined as any substance or entity that is transported downstream by the flowing waters. Thus, solutes may be pollutants, such as pesticides and hydrocarbons, or naturally occurring substances, such as dissolved gases, nutrients, and trace elements. Study of the processes affecting solutes is important because pollutants may pose a threat to public health when the water of the affected body is used for drinking or recreational purposes. The impact of pollutants on the aquatic organisms that live in the stream ecosystem is also an important issue. The solutes that occur naturally are also of interest because they often interact with pollutants and change their toxicity. The concentrations of naturally occurring solutes are also affected by human activities and in many cases this significantly degrades the quality of water body. Nutrients also play a role in eutrophication -- the process in which abnormally high nutrient concentrations cause excessive plant growth.

The fate and transport of solutes in rivers depends on a number of processes. The most obvious and perceptible are the physical processes which cause solutes to move downstream and mix with other constituents in water. The residence time of a given solute in the system under study is often determined by physical transport characteristics. The additional processes that influence solute concentrations are the chemical, biological, and geochemical reactions that take place in the water body. The residence time effectively determines the time scales over which chemical and biological processes have an effect. All these factors make a close and complex coupling among the various processes involved in solute transport.

Consider that a dose of pollutant is released at the center of a free-flowing stream. A few important terms and processes related to its transport are defined below.

Flux: Flux is the rate of flow of mass or energy per unit area normal to the direction of flow. The transport of a constituent is measured by the flux; the common units are quantity per unit area per unit time. If the constituent is measured in units of mass, a typical unit of flux is g/m^2s.

The movement and concentration of a pollutant is affected by two important transport mechanisms: advection and dispersion.

Advection: Advection, also known as convection, is a bodily transport of the constituent due to the motion of the fluid. The constituent moves with the fluid velocity without change in concentration. The flux F due to advection is product of velocity and concentration:

$$F = UC \tag{13.5}$$

where U is velocity (m/s) and concentration C is in terms of quantity per unit volume (gm/m^3).

Advection does not alter the shape (distribution of concentration versus distance) of the constituent distribution as long as the velocity distribution remains uniform. Fig. 13.4a shows a case of pure advection. A dose of a dye is released into water at time t_0. At time greater than t_0, the location of dye changes as it moves in the downstream direction with water but its shape and concentration remain unaltered.

Dispersion: As the constituent moves in the downstream direction, small-scale mixing causes it to spread out, thereby increasing the volume and decreasing the concentration of the constituent-containing water. This process is called dispersion. Sometimes the terms dispersion and diffusion are used interchageably. See Holley (1996) for a detailed treatment of the subject. Dispersion is attributed to both molecular diffusion and velocity variations caused by shear stress. Molecular diffusion takes place due to random motion of particles. This is a significant mixing process in still water or laminar flow, such as a calm lake or ground water. In natural streams, the role of molecular diffusion is less and the effect of velocity variation becomes the dominant mixing mechanism. It is well known that in a river, the flow velocity increases with distance from the stream bed and is maximum at some point close to the water surface. In the lateral direction, the velocity is the maximum at the center and reduces as the bank is approached. These velocity variations cause considerable mixing as different particles move with different velocities.

The flux due to diffusion is given by Fick's law of diffusion. According to this law, the mass flux due to molecular diffusion is proportional to the concentration gradient. Thus, flux in the x direction would be:

$$F_x = -E_x \frac{\partial C}{\partial x} \tag{13.6}$$

where concentration C is expressed in units of quantity per unit volume and E_x is the longitudinal dispersion coefficient or diffusivity, with units of L^2/T. The negative sign indicates a positive flux in the direction of negative gradient (i.e., in the direction of decreasing concentration). When dispersion is the only transport process, the behavior of a constituent is shown in Fig. 13.4b. Here, the center of the constituent mass remains at the same place but the volume of constituent-containing water tends to increase with time.

The behavior of the constituent mass due to the combined effect of advection and dispersion is shown in Fig. 13.4c. Here, the location of the center moves downstream with time and its concentration goes on reducing with the passage of time.

In surface waters, most diffusion is by the process of turbulent diffusion. Therefore, in practice, diffusion often is used to account for all unknown factors in a problem, including undefined velocity fields, trapping of the constituent along boundaries, secondary currents, density effects, etc. If velocity fluctuations due to turbulence could be described exactly as a function of time and space, then turbulent transport could be analyzed as an advective process. Unfortunately, turbulent fluctuations ordinarily can only

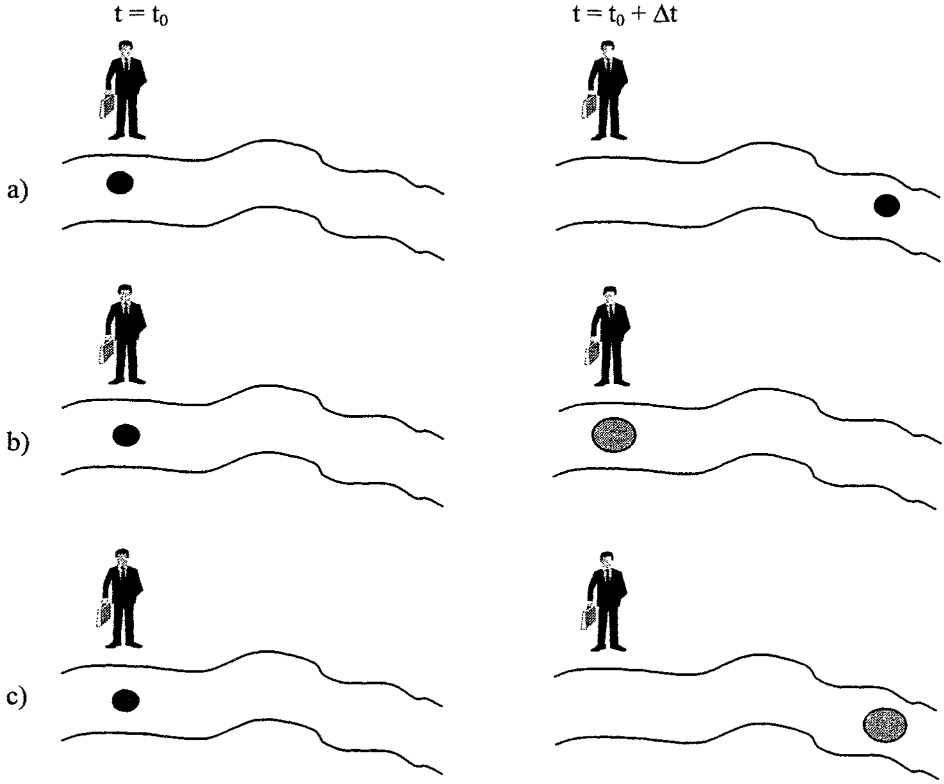


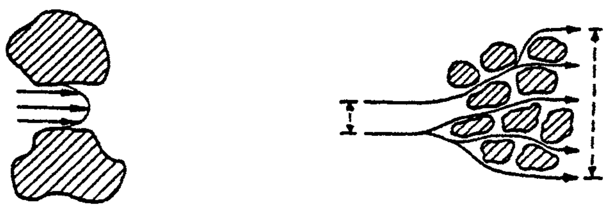
Fig. 13.4 Effects of advection and dispersion on a constituent. a) The case of advection only; the location of the constituent changes with time but its volume is constant. b) the case of dispersion only; the center of the constituent is stationary but the volume increases. c) combined effect of advection and dispersion; the location and volume of the constituent changes with time [After Runkel and Bencala, 1995].

be described statistically. Although eq. (13.6) is a convenient and widely used to describe turbulent transport, the diffusivities are usually unknown and must be either estimated by tracer method or empirical data. Otherwise it becomes calibration parameter for the site.

Dispersion is one of many processes which can reduce the concentration of contaminants transported by groundwater. It is a physical phenomenon of major importance which affects contaminant concentration as these materials travel in groundwater systems. This process will not only tend to mix contaminated flows with uncontaminated groundwater leading to reductions in concentration by dilution, but will also result in contaminants spreading longitudinally and transversely forming a typical plume. This process also results in the contaminants arriving at a distant location earlier than predicted by flow models which do not account for dispersion. It is important to note that the concentration of the contaminant that 'arrives early' will be less than the concentration reported by the flow models.

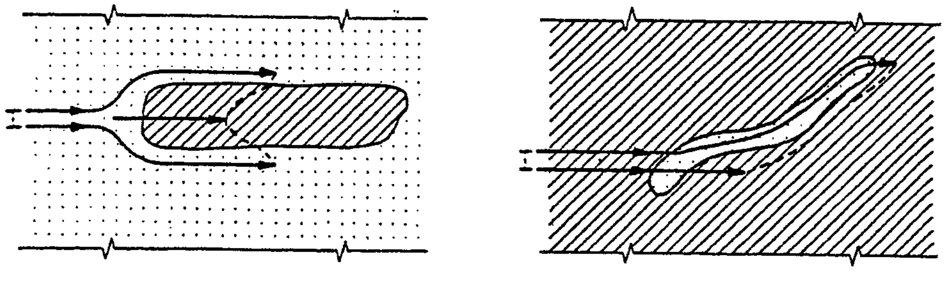
The general term dispersion refers to both the process of mechanical mixing during fluid advection and molecular diffusion due to the thermal-kinetic energy of the contaminant material. Diffusion, which is driven by concentration differences, is a dispersion process of importance only at low velocities. Dispersion due to mechanical mixing during fluid advection is referred to as hydraulic dispersion.

Hydraulic dispersion is generally separated into microscopic and macroscopic levels as shown in Fig. 13.5. Hydraulic dispersion is the spreading of distribution of contaminant material in groundwater systems and results from inherent heterogeneity of soil matrix geometry in all natural soil systems. Microscopic dispersion results from the numbers of pore pathways available to a slug of groundwater as well as the hydraulics of flow around individual soil particles. Macroscopic dispersion applies to the impact of small soil bodies or lenses present in larger soil bodies of significantly different hydraulic conductivity. This condition can lead to wide ranges in time of travel for contaminants depending on what route the ground water carrier takes. Hydrodynamic dispersion is the macroscopic outcome of the actual movements of individual tracer particles through the pores and includes two processes. One mechanism is mechanical dispersion which depends on both the flow of the fluid and the characteristics of



Individual Pores

Pore Channels



Soil lens of low hydraulic conductivity in a sandy aquifer

Soil lens of high hydraulic conductivity in a silty aquife

Fig. 13.5 Types of dispersion in ground water flow: (a) Microscopic dispersion, and (b) Macroscopic dispersion.

the porous medium through which the flow takes place. The process of water movement through saturated porous media involves both transport and adsorption of fluid. Advective and dispersive transports are the mass movement mechanisms associated with hydrodynamic dispersion. It is generally assumed that the amount of material transferred parallel to any given direction is the sum of the advective and dispersive mass transport components. Advective or mechanical mass transport is attributed to the variation of local microscopic velocity in the porous medium matrix. The dispersive transport phenomenon, or the so-called physicochemical dispersion or molecular diffusion, is caused by the existence of concentration.

13.3.8 Governing Advective-Diffusion Equation

From a spatial perspective, solutes enter surface waters through point and non-point sources. From the standpoint of environmental monitoring, point sources are relatively easy to quantify. Mass loading from these sources may be estimated by measuring the flow and solute concentration associated with a plant's effluent:

$$W = Q_e C_e \tag{13.7}$$

where W is the mass loading rate [M/T], Q_e is the volumetric flow rate for the point source, and C_e is the solute concentration in the effluent. In practice, calculations of mass loading rates are often considerably more complex than a straightforward application of eq. (13.7) because Q_e and C_e vary with time.

Since non-point sources of solutes are distributed along the watercourse, these are often diffuse, in that mass entering at any one point in space is relatively small, yet the aggregate mass loading rate is significant. An example of a non-point source is agricultural runoff that enters a stream as overland flow. During precipitation, runoff from cultivated fields may contain pesticide residues and fertilizer as well as suspended sediments that sorb contaminants. Loading due to this type of non-point source is represented by a lateral inflow term in the general transport equation. Another example of a non-point source is that of acid rain or acid deposition that arises due to combustion of fossil fuels. This loading may impact a watershed, leading to the acidification of surface waters.

The mass loading rates for non-point sources are often difficult to measure because the loads are not associated with a specific point in space and there might be large spatial variations. The pollutant load that may enter as lateral flow in the river may have considerable variation in the longitudinal (along the flow) direction. In case of acid deposition, an estimate of mass loading rates can be made by analyzing the rain samples collected at gauges that are installed at different locations in the study area. Here also, considerable variation in loading rates through the focus area can be expected. Solute sources and loading rates also vary with respect to time. These factors necessitate a carefully designed sampling program to monitor non-point sources of pollution.

An equation describing the spatial and temporal effects of advection and dispersion on solute concentration is developed using the law of conservation of mass. This law ensures that the mass is neither created nor destroyed and that the change of mass in a unit control volume of water is equal to the difference between the mass flowing in and leaving the control volume:

Time Rate of Change of Mass = Mass Inflow – Mass Outflow (13.8)

where each term in the equation is expressed in terms of mass per unit time. The governing equation for conservation of mass of a constituent can be derived by equating the change of mass in a control volume to the sum of the net (advective plus diffusive) flux through the control volume plus sources and sinks. The general three-dimensional form of the law in cartesian coordinates is

$$\frac{\partial C}{\partial t}+u\frac{\partial C}{\partial x}+v\frac{\partial C}{\partial y}+w\frac{\partial C}{\partial z}=\frac{\partial}{\partial x}\left(E_x\frac{\partial C}{\partial x}\right)+\frac{\partial}{\partial y}\left(E_y\frac{\partial C}{\partial y}\right)+\frac{\partial}{\partial z}\left(E_z\frac{\partial C}{\partial z}\right)-KC \qquad (13.9)$$

in which u, v, and w are the velocity components in the x, y, z directions, respectively; C is concentration in the turbulent flow; E_x, E_y, E_z are nonisotropic (a function of direction), nonhomogeneous (a function of location) turbulent diffusivities in the x, y, z directions; and first-order decay (with coefficient K) is assumed. Eq. (13.9) can be applied to two-dimensional problems by averaging in one coordinate direction. For example, if averaging is in the z direction, the two-dimensional, nonisotropic, nonhomogeneous form in cartesian coordinates is

$$\frac{\partial(hC)}{\partial t}+\frac{\partial(uhC)}{\partial x}+\frac{\partial(vhC)}{\partial y}=\frac{\partial}{\partial x}\left(hE_x'\frac{\partial C}{\partial x}\right)+\frac{\partial}{\partial y}\left(hE_y'\frac{\partial C}{\partial y}\right)-hKC \qquad (13.10)$$

For this equation, the concentration and u and v velocities (in the x and y directions) are vertically averaged over the variable depth $h(x,y)$. Thus E'_x and E'_y include a diffusive mixing component due to shear-flow dispersion. Eq. (13.10) can be simplified if the depth is constant in space and time, since h can then be eliminated from each term.

The one-dimensional form of the advective-dispersion equation commonly applied in streams is

$$\frac{\partial C}{\partial t}+\frac{\partial(UC)}{\partial x}=\frac{1}{A}\frac{\partial}{\partial x}\left(AE_L\frac{\partial C}{\partial x}\right)-KC \qquad (13.11)$$

In eq. (13.11), U = Q/A is the average longitudinal velocity, $A(x)$ is the cross-sectional area at any location, and $E_L(x)$ is the longitudinal dispersion coefficient. The advection-dispersion equation describes the spatial and temporal variation in solute concentration C:

$$\frac{\partial C}{\partial t}=-U\frac{\partial C}{\partial x}+D_L\frac{\partial^2 C}{\partial x^2} \qquad (13.12)$$

where U is the advective velocity [L/T], and D_L is the longitudinal dispersion coefficient [L^2/T]. Coefficients U and D_L are assumed to be constant in space and time.

Although the variables of river water quality vary in three spatial dimensions, for practical purposes, a one-dimensional description is generally adequate. It is assumed that the variables show appreciable variation only along the length of flow and that the variation in respect of depth and width of the cross-section is negligible. The requirements of data and other resources of higher dimensional models are large in comparison with one-dimensional models.

Gandolfi et al. (1996) described a general form of the one-dimensional balance equation, valid for the generic component P which can be any water quality constituent or the biomass of a population whose concentration is p. Let t be the time, l the spatial coordinate, v the mean velocity of the fluid in the cross section of area A, and D the longitudinal dispersion coefficient. Then, the equation becomes

$$\frac{\partial(Ap)}{\partial t}+\frac{\partial(Avp)}{\partial l}-\frac{\partial}{\partial l}\left[AD\frac{\partial p}{\partial l}\right]=E_p+AI_p \qquad (13.13)$$

where E_p represents the external sources and sinks of the constituent p, and I_p represents all the phenomena that take place inside the river and influence the concentration p (e.g., decay, sedimentation). The first term on the left hand side represents the variation of p with respect to time as seen by a stationary observer at the river bank, while the second and third terms represent, respectively, the convective and diffusive components of the transport process. All the variables that appear in eq. (13.13) are functions of space and time. The equations of the three sub-models can be obtained by substituting p with the appropriate variable and defining the source and sink terms.

A multitude of analytical solutions is available for eq. (13.11) to (13.13). One taxonomic breakdown considering the similarities and structure is to consider instantaneous and continuous sources (in time), and point (three-dimensional), line (two-dimensional) and plane (one-dimensional) injections in space. For homogeneous, nonisotropic turbulence, the solutions may be reduced to the Gaussian form.

For solutions, a point source means that the contaminant release of mass M is concentrated at a single point and can diffuse in all three coordinate directions. A line source means that the contaminant release is spread uniformly over the length h of a line and diffuses only in the x-y plane perpendicular to the line. A plane source means that the contaminant release is spread uniformly over a plane surface of area A and diffuses only in the x direction perpendicular to the plane.

13.4 MODELING OF OXYGEN IN RIVERS

Since oxygen is crucial for all biological life and is an indicator of water quality, its modeling is of central importance in river water quality studies. A detailed treatment of the topic is in order.

13.4.1 Dissolved Oxygen (DO)

The biological life that is present in water, including the organisms that are responsible for the self-purification processes, depends on the dissolved oxygen for survival. Oxygen is not much soluble in water and the DO content of natural waters varies with temperature, atmospheric pressure, dissolved solids, turbulence, the photosynthetic activity of algae and plants, and atmospheric pressure. The solubility of oxygen decreases as temperature and salinity increase. In fresh waters, DO at 1 atmospheric pressure ranges from 15 mg/L at 0°C to 6 mg/L at 40°C. Huber (1993) has provided tables of DO saturation concentration at sea level at various temperatures.

Variations in DO occur seasonally, or even during a day as a function of temperature and biological activity. Biological respiration, including that related to decomposition processes, reduces DO concentrations. Waste discharges high in organic matter and nutrients can lead to decreases in DO concentrations as a result of the increased microbial activity during the degradation of the organic matter. As the oxygen solubility is less when the water temperature is high, the dissolved oxygen in water is deficient during summer season when temperatures are high and flow in the river is small.

The waste material present in water is degraded by two processes: aerobic and anaerobic. In aerobic processes, oxygen is used for oxidation of organic matter and the end products are relatively harmless. In anaerobic processes, slow degradation without oxygen takes place and the end products are unwanted or even harmful. Thus, it is important that wastes are degraded through aerobic route. Since the solubility of oxygen in water is low, it is desirable that wastes are treated before they are dumped in a water body so that the quality of water does not deteriorate below a certain minimum level at any place.

The level of DO indicates the degree of pollution by organic matter, the destruction of organic substances and the level of self-purification of the water. Concentrations below 5 mg/L may adversely affect the functioning and survival of biological communities and may lead to the death of most fish below 2 mg/L.

Determination of the DO concentration is important in water quality management since oxygen is either involved in or influences nearly all chemical and biological processes in water bodies. There are two main methods to determine DO. The titration method involves the chemical fixation of oxygen in a water sample collected in an air-tight bottle. Fixation is carried out in the field and titration in the laboratory. The method is time-consuming but can give a high degree of accuracy. It is suitable for most kinds of sources of water. The alternative oxygen probe method is quick and can be used in-situ or for continuous monitoring, although its accuracy is somewhat less.

DO is of limited use as an indicator of pollution in groundwater, and is not useful to evaluate the use of groundwater for normal purposes. In addition, the determination of DO in groundwater requires special equipment and is, therefore, not widely carried out.

13.4.2 Biochemical Oxygen Demand

The amount of oxygen consumed by indigenous micro-organisms in water while degrading under aerobic conditions is known as biochemical oxygen demand (BOD). It is defined as the amount of oxygen required for the aerobic micro-organisms present in the sample to oxidise the organic matter to a stable inorganic form. BOD is an important indicator of the status of quality of water. BOD tests are routinely carried out to determine the quality of water body. Sometimes, the chemical oxygen demand (COD) is determined which is an indirect, although somewhat inaccurate, indicator of BOD. The BOD tests take several days while COD tests can be performed in a few hours.

BOD is an approximate measure of the amount of biochemically degradable organic matter present in a water sample. The method is subject to various complicating factors, such as the oxygen demand resulting from the respiration of algae in a sample and the possibility of oxidation of ammonia. The presence of toxic substances in a sample may affect microbial activity leading to a reduction in the measured BOD.

Unpolluted waters typically have BOD values of 2 mg/L or less. Typical BOD concentrations for rivers are 2 to 15 mg/L; values up to 65 mg/L have been observed in practice. Those rivers that receive wastewaters may have considerably higher BOD particularly near the point of wastewater inflow. BOD of the raw sewage may be about 600 mg/L, whereas it should come down to 20 to 100 mg/L after treatment, depending on the treatment process followed.

Standard laboratory tests are used to determine BOD by measuring the amount of oxygen consumed after incubating the sample in the dark at 20°C temperature for a specific period of time. Usually this period is five days and this is denoted by BOD_5. The oxygen consumption is determined from the difference between the dissolved oxygen concentrations in the sample before and after the incubation period.

BOD_5 can be calculated as $BOD_5 = D_o - D_1$ in which D_o and D_1 are the DO concentrations (mg/L) at time 0 and 5 days, respectively. BOD_5 test can also be used to characterize municipal and industrial wastewaters. However, in these tests, in addition to dilution water, acclimated seed organisms, nutrients, and the presence or absence of toxic substances must be considered. As mentioned above, the samples are incubated at 20°C in standard BOD_5 analyses. However, if the samples are incubated at some other temperature, the rate coefficient can be adjusted using the relationship:

$$K_5 = K_{20}\,\theta^{(r-20)} \tag{13.14}$$

where $\theta = 1.024$ for pure water. The BOD remaining at time *t* is

$$L_t = L * 10^{-kt} \tag{13.15}$$

The amount of BOD that has been exerted (satisfied) at time *t*, *y*, is

$$y = L - L_t \tag{13.16}$$

where *L* is the ultimate BOD (mg/L). Therefore

$$y = L(1 - 10^{-kt}) \tag{13.17}$$

Recently, online, continuous BOD meters for wastewater plants have been introduced. Some of these systems have good reproducibility and correlation with standard five-day BOD tests. Standard features include automatic line washing, sensor auto-calibration and automatic control of sample volume for three months of maintenance-free operation. Since the correlated BOD of a sample can be measured in as little as 20 minutes, the instrument enables users to monitor BOD trends before a wastewater plant problem gets out of hand, evaluate the toxicity of influents and their effect on wastewater treatment plant loading and monitor effluent quality. BOD_5 levels from 0.5 to up to 10,000 mg/l can be measured.

The instrument used is basically an online bioreactor in which a suspension of microorganisms (biomass) is aerated until it reaches the endogenous respiration stage. When a wastewater sample is added, the microorganisms begin to degrade it rapidly, causing an increase in the oxygen uptake rate (OUR) and a decrease in DO compared to the levels during endogenous respiration. When the organic matter in the sample is consumed, the microorganisms return to the endogenous stage.

13.4.3 Chemical Oxygen Demand (COD)

COD is a measure of the oxygen equivalent of the organic matter in a water sample that is susceptible to oxidation by a strong chemical oxidant. COD is widely used as a measure of the susceptibility to oxidation of the organic and inorganic materials present in water bodies and in the municipal and industrial wastes. The COD test of natural water yields the total quantity of oxygen that is required for oxidation of a waste to carbon dioxide and water (McCutcheon et al. 1993). In a BOD test, only biologically reactive carbon is oxidized while in a COD test, all organic matter is converted to carbon dioxide. The test for COD does not identify the oxidisable material or differentiate between the organic material and inorganic material present. Similarly, it does not indicate the total organic carbon present. Consequently, the COD values are higher compared to BOD. Nevertheless, COD is a useful variable that can be rapidly measured; the COD test can be performed in 3 hours against 5 days required for a BOD_5 test.

The COD concentrations observed in surface water resources typically range from 20 mg/L or less in unpolluted waters to greater than 200 mg/L in waters receiving effluents. Industrial wastewaters may have COD ranging from 100 mg/L to 60,000 mg/L (Chapman 1992).

13.4.4 Reaeration

Reaeration is the physical absorption of oxygen from the atmosphere by water. It occurs at the air-water interface if a non-equilibrium condition between air phase and the water phase exists for oxygen. Reaeration is the dominant natural means by which a water body may recover DO concentrations. From the point of view of water quality management, it is important that physical reaeration process taking place in a channel is clearly understood and the reaeration amount is correctly estimated. The theoretical background related to reaeration coefficient that controls this process is available in many studies including Rao (1999). As per two-film theory, mass transfer occurs through the gas and liquid interfaces until a dynamic equilibrium is established. The rate of transfer of oxygen from the atmosphere to the body of the liquid is generally proportional to the difference between the existing concentration C and the equilibrium or saturation concentration C^* of oxygen in the liquid (Rao, 1999). Mathematically, it can be written as

$$\frac{dm}{dt} = K_L A(C^* - C) \tag{13.18}$$

where m is the mass of oxygen, K_L is the coefficient of diffusion of oxygen in the liquid; and A is the area through which oxygen is diffused. Also,

$$\frac{dm}{dt} = V_1 \frac{dC}{dt} \tag{13.19}$$

where V_l is the volume of the liquid. Thus, using eqs. (13.18) and (13.19), one obtains

$$\frac{dC}{dt} = K_L (\frac{A}{V_1})(C^* - C) \tag{13.20}$$

Parameter $K_L(A/V_1)$ is generally denoted by $(K_2)_T$ and is widely termed as the oxygen transfer or reaeration coefficient at temperature T (°C). The value of $(K_2)_T$ is related to the value $(K_2)_{20}$ as follows:

$$(K_2)_{20} = (K_2)_T / \theta^{(T-20)} \tag{13.21}$$

The measurement of the reaeration coefficient requires considerable effort, both in the field and in laboratory. The required time and funds may not be available in many cases and therefore, many efforts have been made to relate the reaeration coefficient with channel characteristics. Besides the theoretical approaches to define the reaeration coefficient, a large number of predictive equations have been developed to relate the reaeration coefficient K_2 with the mean flow velocity (V), shear stress velocity (V_*), depth of flow (H), Froude number (F_r) and the channel bed slope (S). Moog and Jirka (1998) concluded that slope is an essential component of reaeration equations and proposed two predictive equations, based on slope criteria. These are:

$$K_2 = 1740\, V^{0.46} S^{0.79} H^{0.74} \quad for\ S > 0.00 \tag{13.22}$$

$$K_2 = 5.59 S^{0.16} H^{0.73} \quad \text{for S} < 0.00 \tag{13.23}$$

where V is the velocity of stream water (m/s), H is the flow depth (m), S is slope, and F_r is the Froude number. Thackston and Dawson (2001), while re-calibrating reaeration equations, observed that reaeration equations should not be applied for very high Froude numbers, where the influence of turbulent water is prevalent. Maier and Dandy (1996) used ANNs to predict water quality parameters.

13.4.5 Modeling of Dissolved Oxygen

The pair of differential equations that provide mass balances for BOD and oxygen deficit in a stream segment with constant flow and geometry is (Chapra, 1996):

$$U\frac{dL}{dx} = -k_r L \tag{13.24}$$

$$U\frac{dD}{dx} = -k_a D + k_d L \tag{13.25}$$

where U is average stream velocity (m/d), L is the carbonaceous BOD concentration (mg/L), x is the distance downstream from the discharge point (m), k_r is total removal rate of BOD by decomposition and settling (1/d), D is the dissolved oxygen deficit (mg/L), k_a is the areation rate (1/d), and k_d is the removal rate of BOD by decomposition (1/d). The deficit is related to the oxygen concentration c by

$$c = c_s - D \tag{13.26}$$

where c_s is the saturation concentration for dissolved oxygen (mg/L).

Equations (13.24) and (13.25) are written for a steady state condition and simulate the spatial distribution of oxygen below a treatment plant. Variations in time are not considered in this simple representation. Further, these ignore longitudinal dispersion and sources and sinks of oxygen, such as photosynthesis, respiration, and sediment oxygen demand. These equations can be solved for the BOD and DO concentration below a single point source of sewage as

$$L = L_0 \exp[-(k_r/U)x] \tag{13.27}$$

and

$$c = c_s - D_0 \exp[-(k_a/U)x] -[\exp\{-(k_r/U)x\} - \exp\{-(k_a/U)x\}]*k_d L_0/(k_a - k_r) \tag{13.28}$$

where L_o and D_o are, respectively, the concentrations of BOD and oxygen deficit at the mixing point where the waste is discharged.

Assume that the flow in a river is Q_u and BOD L_u when a sewer with flow Q_s and BOD L_s meets it (see Fig.13.6). After complete mixing, the resulting BOD L_0 can be obtained by a simple mass balance:

$$L_0 = (Q_u L_u + Q_s L_s) / (Q_u + Q_s) \tag{13.29}$$

As the flow moves downstream in the river, BOD is subject to advection and diffusion/ dispersion. A sink term ($-K_1L$) is included in the advective-diffusion equation (13.15) with C replaced by L, and other source/sink terms can be added optionally. For the steady-state condition, $\partial L/\partial t = 0$ in eq. (13.15), and the ordinary differential equation is readily solved to give

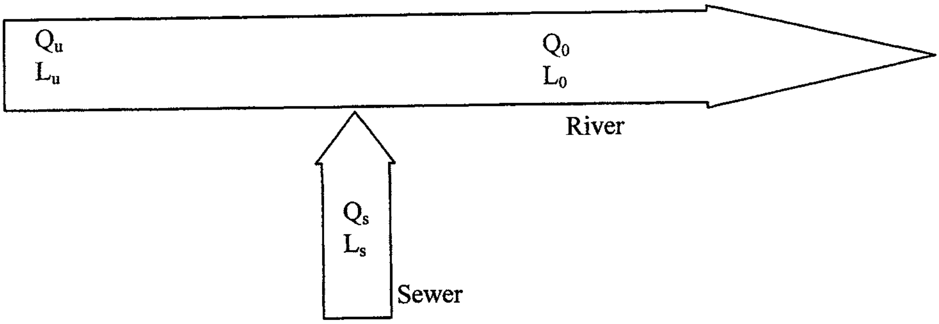


Fig. 13.6 Schematic of a point source discharging in a river.

$$L(x) = L_0\, e^{mx} \tag{13.30}$$

where L(x) is the BOD distribution downstream of the initial condition *L*, and the exponent *m* is

$$m = -K_1 / U \tag{13.31}$$

Since travel time t = x/U, eq. (13.24) can be simplified as

$$L(x) = L_0 \exp(-K_1 t) \tag{13.32}$$

in which *L* a simple exponential decay as a function of *t*.

In the DO balance, the term $-K_1L(x)$ is a sink and reaeration at air-water interface is a source. Terms can be added to represent other sources and sinks due to photosynthesis, sediment oxygen demand, etc. Considering only the BOD sink term and the reaeration source term in one-dimensional advective-diffusive equation (neglecting dispersion), the steady-state DO deficit *D(x)* (Medina et al. 1981) is

$$D(x) = [K_1L_0/(K_2 - K_1)]*[e^{mx} - e^{rx}] + D_0\, e^{rx} \tag{13.33}$$

where $D(x) = [C_s - C(x)]$, C_s is the saturation DO concentration, D_o is the initial, well-mixed deficit at $x = 0$, $r = K_2/U$, and K_2 is the reaeration coefficient. Note that the effect of dispersion is important for estuaries where the flow velocity is low but dispersion can be neglected for rivers.

Eq. (13.33) describes the classical DO *sag curve*, due to the typical shape of the curve shown in Fig.13.7. As the pollutants enter the river, oxygen is consumed in degradation and therefore the deficit increases. The oxygen from atmosphere enters the river through reaeration at the water-air interface. DO goes on decreasing as long as the BOD oxidation exceeds reaeration till a minimum concentration or maximum deficit D_c is reached. From this point onwards, the reaeration process dominates and DO increases until saturation is reached. In this way, a 'sag' is produced in the DO curve. Note that this description is a highly simple case and there may be additional BOD sources or DO sinks in a real-life problem.

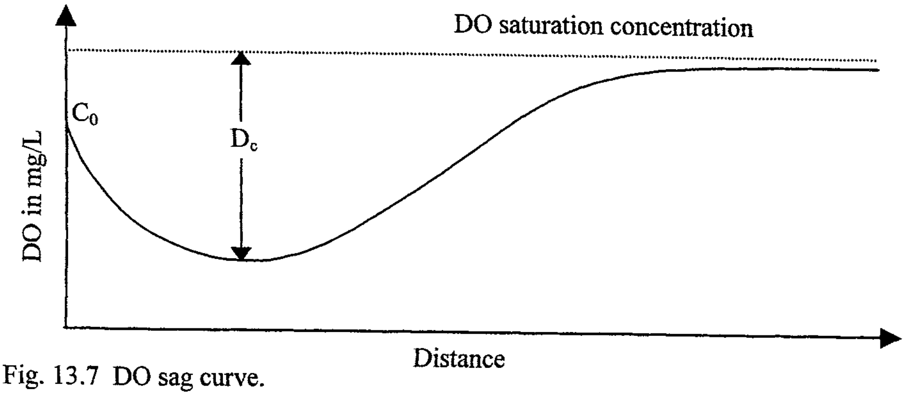


Fig. 13.7 DO sag curve.

13.5 CATCHMENT-SCALE WATER QUALITY MODELS

Sediment and sediment-associated pollutants that reach a water body originate largely from non-point sources in the catchment and result from a complex interplay of numerous forces. Of special importance are (1) climate, in general, and the nature, amount, and intensity of precipitation, in particular; (2) orientation, degree, and length of slopes; (3) geology and soil types; (4) land use; (5) condition and density of the channel system; (6) particle settling velocity; and (7) streamflow regime. The uncertainty in estimation of pollutants largely depends on the variability of these factors.

The term *loading function* describes calculation procedures to estimate the average inflow of non-point pollutants or chemical loads over a time period or a storm event from an individual land use category. A number of different loading functions have been developed and are in use. These functions are used only for preliminary or rough calculations. For detailed and improved estimates, simulation models are used which perform hydrologic, soil erosion and transportation, and chemical/biological pollutant computations over certain time interval. The resulting values for each variable of interest, such as runoff, sediment, and pollutant load, can be analyzed to get the desired information.

The development and application of catchment-scale water quality models have been largely driven by the need for tools that can be used to evaluate two issues. These are non-point source pollution effects (i.e., exposure and/or loadings assessment), and chemical management plans, such as agricultural best management plans for fertilisers and pesticides or, more recently, the total maximum daily loads (TMDLs), including both point and non-point contaminant sources. Catchment scale water quality models must represent dominant processes that determine the interaction between the following state variables: water, temperature, sediment, dissolved oxygen, nutrients (nitrogen and phosphorus species) and bacteria (coliforms), pesticides and other toxic organics, metals, and selected biological variables (phytoplankton, benthic algae, zooplankton, herbivorous fish, predatory fish).

With the exception of biological variables, all the other above listed variables can be critical to modeling water quality the in presence of non-point sources, both urban and non-urban. Temperature is important in modeling all hydrodynamic, water quality, and soil processes. Estimation and prediction of sediment transportation and deposition is useful for many applications related to design and management. Dissolved oxygen is a useful indicator of water quality and its modeling is needed to support analyses of nutrients and biological parameters. The important nitrogen species are ammonium, ammonia, nitrite, nitrate, and organic nitrogen. The phosphorous species that must be considered are orthophosphorus and organic phosphorus. Additional chemicals that should be modeled by a comprehensive water quality model include pesticides and other toxic organics, and metals. Note that these two categories include a large number of abiotic variables and hence a generalized approach is necessary. The general physical and chemical processes important for fate and transport are adsorption/desorption, diffusion, atmospheric deposition, volatilization, and chemical reactions/degradation. The processes that need to be considered for biological variables depend on the trophic level.

A large number of computer models are available for water quality modeling of a catchment. Donigian et al. (1995) carried out a comprehensive study of a number of models. Among the models for full-scale simulation for urban areas, four models namely, DR3M-QUAL, HSPF, STORM, and SWMM, were found to be the best. DR3M-QUAL is a version of the USGS Distributed Routing Rainfall Runoff Model that includes quality simulation (Alley and Smith, 1982). Runoff generation and subsequent routing use the kinematic wave method, and parameter estimation assistance is included in the model. The Hydrological Simulation Program – Fortran (HSPF) is the culmination of hydrologic routines that originated with the Stanford Watershed Model in 1966 and eventually incorporated many non-point source modeling efforts (Bicknell et al., 1993). This model has been widely used for non-urban non-point source modeling. It incorporates field scale models for non-point loadings into a catchment and basin-scale analysis framework that includes fate and transport in one-dimensional stream channels. Several flow routing and water quality options are available in the model. The Storage, Treatment, Overflow, Runoff Model (STORM) developed by the Hydrologic Engineering Center (HEC, 1977) was among the first continuous simulation models in urban hydrology.

The Storm Water Management Model (SWMM) was originally developed as a single-event model specifically for analysis of combined sewer outflow. Its capabilities were later enhanced and the Version 4 of the model (Huber and Dickinson, 1988) performs both continuous and single-event simulation. It can simulate backwater, surcharging, pressure flow and looped connections (by solving the complete dynamic wave equations), and has a variety of options for quality simulation, including traditional buildup and washoff formulations as well as rating curves and regression techniques. *Buildup* is a term that represents all of the complex spectrum of dry-weather processes that occur in an urban area between storms, including deposition, wind erosion, street cleaning, etc. All such processes lead to an accumulation of solids and other pollutants that are then *washed off* during storm events.

The MOUSE (Modeling of Urban Sewers) model was developed by the Danish

Hydraulic Institute, Denmark. Included in the package are modules for generation of runoff from rainfall, sewer routing (the S11S model), and a simple quality routine that uses the constant concentration approach (Jacobsen et al., 1984).

Chemicals, Runoff, and Erosion from Agricultural Management Systems (CREAMS) was developed by the U.S. Department of Agriculture – Agricultural Research Service (Knisel, 1980) for analysis of agricultural best management practices for pollution control. CREAMS is a field scale model that uses separate hydrology, erosion, and chemistry submodels connected together by pass files. Runoff volume, peak flow, infiltration, evapotranspiration, soil water content, and percolation are computed on a daily basis. Daily erosion and sediment yield, including particle size distribution, are estimated at the edge of the field. Plant nutrients and pesticides are simulated and storm load and average concentrations of sediment-associated and dissolved chemicals are determined in runoff, sediment, and percolation through the root zone. CREAMS can also simulate user-defined management activities, such as aerial spraying or soil incorporation of pesticides, animal waste management, and agricultural best management practices.

The Areal Non-point Source Watershed Environment Response Simulation (ANSWERS) is an event based, distributed parameter model capable of predicting the hydrologic and erosion response of agricultural watersheds (Beasley and Huggins, 1981). Application of ANSWERS requires that the catchment be subdivided into a grid of square elements, each of which should be small enough so that all important parameter values within its boundaries are uniform. Within each element, the model simulates the processes of interception, infiltration, surface storage, surface flow, subsurface drainage, sediment drainage, and sediment detachment, transport, and deposition. The output of one element then becomes an input source to an adjacent element.

The surface water quality models can be classified in two categories: *far-field* models which simulate quality in entire sections of a water body and mixing zone models which simulate *near-field* dilution processes. The far-field models can be sub-divided on the basis of water body type, i.e., rivers, lakes and reservoirs, and estuaries. The models to simulate water quality defer from one another mainly in terms of their representation of four key attributes: dimensionality, time, hydrodynamics and pollutant loadings.

Dimensionality determines how a model represents spatial features of the water body. Most river and stream models are one-dimensional and can be applied to branching systems. Two-dimensional models can cover either longitudinal and lateral (X/Y) or longitudinal and vertical (X/Z) dimensions. "Box" models can be applied in 1, 2, or 3 dimensions.

Time determines how a model can represent the water body dynamics. Steady-state models predict concentrations that do not vary in time. These are useful primarily for rivers under low-flow design conditions. Both dynamic and quasidynamic solutions predict concentrations that vary with time. Quasidynamic solutions allow some major forcing functions, such as flow, loading, or solar effects on photosynthesis, to vary with time.

All receiving water quality models require information on the movement of water. Some provide this information in the input data set. These models are steady or quasidynamic in nature. Others require input information on flow or velocity; still others can either accept input flows, or be linked to simulated hydrodynamics. Some water quality models provide for the hydrodynamic calculations internally. Most, however, require linkage to an external hydrodynamics file.

Almost all models simulate advection and dispersion. Most 1-D riverine models do not require dispersion because most rivers are not highly dispersive and the model network and solution techniques introduce some degree of numerical dispersion. All models allow the user to input steady pollutant loads. Some allow the specification of variable loads from the input data set. A few models provide internal or external linkage to non-point source loading simulations.

One of the most widely used models is QUAL2E (Brown and Barnwell, 1987). The enhanced model is capable of simulating several water quality constituents. A finite difference scheme is used to solve the one-dimensional advection-dispersion mass transport and reaction equation. The model can predict DO, CBOD, temperature, and phytoplankton dynamics as affected by organic material and nutrients. It has nine state variables: total algal biomass, BOD, DO, ammonia, nitrites, nitrates, organic nitrogen, organic phosphorus, and orthophosphates.

13.6 WATER QUALITY IN LAKES AND RESERVOIRS

A lake is a partially enclosed inland body of fresh water surrounded by land. Lakes vary in size from many thousands of square kilometres in area and many metres in depth to only a few square kilometres and depths of less than 10 metres. Lakes are used for many purposes including municipal and industrial water supply, recreation, navigation, fishing, power generation, etc. During warm weather, lakes are heated by the incident solar energy. During cold season, they loose heat to the atmosphere and thereby cool down. It is well known that warm water is lighter and therefore, it floats on colder denser water. The maximum density of water occurs at 4° C. The result is thermal stratification of lakes.

On the basis of thermal characteristics, lakes are usually divided into three zones: epilimnion, hypolimnion, and metalimnion. The *epilimnion* zone is the upper layer of the lake consisting of the warmer, lighter water. The downward movement of this water requires displacement of the denser and colder waters in the lower region of the lake and there is therefore, a thermal resistance to mixing. Warm waters in the epilimnion zone are circulated by winds and do not go far below the surface but move along the top of the cold water zone and then returns to the surface. The *hypolimnion* zone is comprised of the non-circulating cold mass of water in the bottom layers of the lake during the stagnant period. The hypolimnion zone has little or no opportunity to gain heat from the sun or oxygen from the atmosphere during the warm weather seasons. The *metalimnion* zone, known as *thermocline*, is the transition zone between the epilimnion and hypolimnion and is the area in which steep temperature gradients are found. Because of the difference in densities of epilimnion and hypolimnion waters, the thermocline acts as a barrier to the downward movement of the lighter waters. The various chemical and biological processes that take place in a lake are significantly influenced by this thermal stratification.

13.6.1 Differences between Lakes and Reservoirs

Although the lakes and reservoirs appear to be similar on a casual look, there are many fundamental differences between them and these also influence the chemical and biological processes that take place. The differences in capacity-inflow ratio and water level fluctuations in lakes and reservoirs are largely responsible for this difference in behavior. A small residence time means that many species do not have an opportunity to reproduce in most reservoirs. The important differences between natural lakes and man-made reservoirs are summarized in Table 13.4.

Table 13.4 Important differences between natural lakes and man-made reservoirs.

Feature	Natural lake	Man-made Reservoir
Age	1000s of years	100s of years
Capacity-inflow ratio	Large	Wide range
Water level fluctuations	Small	Usually large and seasonal
Location of maximum depth	Commonly near the center	Close to the dam
Source of inflows	Surface and subsurface	Predominantly surface
Outlet of water	Surface and subsurface	Almost totally surface
Catchment : water surface area	Small	Large
Shape	Mostly oval or circular	Usually linear or dendritic
Sediment and nutrient loading	Low	High
Bio-diversity	Higher	Lower
Primary productivity	Lower	Higher
Water quality gradients	Concentric	Longitudinal

Age wise, natural lakes are usually very old; some of them date back to thousands of years while most large reservoirs were made during the past century. Both natural lakes and artificial reservoirs receive a wide variety of sediments and nutrients as inputs and these get accumulated and deposited. There are large variations in deposition rates depending on the catchment properties as well as the properties of the water body (including regulation in case of reservoirs). In general, the rate of sedimentation in man-made reservoirs is much higher compared to natural lakes. The process of sedimentation leads to a gradual reduction in the storage capacity (see Chapter 12) and over time, the lake or reservoir may ultimately reduce to a marshy land. Many programs have been launched world over to recover the storage capacity by removal of sediments and bio-mass through mechanical means.

Geometrically, lakes and reservoir are quite different and the reason lies in their origin. Natural lakes are formed at local depressions and are typically circular or oval shaped. The central portion is deepest in a lake. In contrast, the site for a reservoir is decided based on many factors; a deeper reservoir will have less surface area and less loss of water due to evaporation. Such a reservoir is created where river slopes are high. The upstream end of a reservoir has shallow depth and the maximum depth is near the dam. Since most of the flow enters at the farthest upstream end and leaves at the downstream end, there is a strong longitudinal flow and density currents may also be present.

Some of the products of biological processes settle and combine with the inorganic components of the sediments present at the lake bottom. A variety of pollutants, such as pesticides, trace elements, metals, non-biodegradable substances, etc. also enter the lake and are responsible for many problems.

13.6.2 Chemical Considerations

The most serious challenges to the use of lakes from water quality angle have been *eutrophication* and inflow of toxic chemicals. Naturally, eutrophication or 'lake enrichment' has been one of the most intensely studied subjects in water quality modeling. A water-quality analysis of lakes commonly involves questions of deleterious effects due to increased nutrient (nitrogen and phosphorous) supply. The deleterious effects are increased life and growth of a lake's biota, especially algae and macrophytes (large aquatic plants) with a consequent increase in turbidity and color, possible reduction in dissolved oxygen, and change in nature of the fish population. The degree of eutrophication is largely dependent on nutrient concentration in the lake waters. As summarized in Table 13.5, in-lake nitrogen and phosphorus concentrations are a reflection of the trophic status of a lake.

Table 13.5 Trophic status of lakes [Sources: NAS/NAE (1972), USEPA(1974)].

Water-quality variable	Oligotrophic	Mesotrophic	Eutrophic
Total phosphorus, g/L	< 10	10 - 20	> 20
Chlorophyll a, g/L	< 4	4 - 10	> 10
Secchi depth, m	> 4	2 - 4	< 2
Hypolimnetic oxygen, % saturation	> 80	10 - 80	< 10

Some authors have defined the trophic status of lakes on the basis of phosphorus concentrations alone. Alternately, indices have also been suggested to denote the trophic state of lakes. Reckhow and Chapra (1983) describe the use of a regression equation that relates values of Secchi disk readings and concentrations of phosphorus, nitrogen and chlorophyll *a*. Considerable efforts are made by lake and reservoir managers to control nutrient levels to reduce vegetational growth and thereby enhance the use of lakes. Nutrients in this context are usually considered to include phosphorous, nitrogen, carbon, and silica in various chemical forms.

Nitrogen and phosphorus are required for growth of algae. On the basis of their relative presence, the trophic status of a lake is determined. Phosphorus is of paramount importance in lake eutrophication. According to Thomann and Mueller (1987), when the ratio of the total nitrogen (N) to the total phosphorus (P) is less than 13, lakes are nitrogen-limited. When this N/P ratio is in the range 13 to 21, the lakes are known as nutrient-balanced and if N/P > 21, then it is phosphorus-limited. The term 'phosphorus-limited' implies that additional phosphorus is required to produce additional algal growth (Huber 1993). Most lakes are phosphorus-limited, especially those for which non-point-source runoff is the dominant source of phosphorus. Note that these limits (13 and 21) are approximate only and depend on algal species. The clear lakes with low biological productivity and poorer in nutrient materials and organic life are termed as *oligotrophic*. The lakes with high biological productivity are referred to as *eutrophic*. Such lakes are rich in nutritive materials and contain an abundance of plankton organisms, shore vegetation, and animal life. In between fall *mesotrophic* lakes which have an intermediate level of biological productivity.

Lakes contain a wide variety of physical and chemical substances. These ranges from floating debris, suspended materials, dissolved inorganic matter, nutrients, metals, organics and dissolved oxygen. Of these, dissolved matter, suspended solids, nutrients and dissolved oxygen are among the most important constituents in assessing the productivity of lakes. Dissolved matter or total dissolved solids is a measure of the total inorganic substances dissolved in water. These substances include major chemical ions, such as calcium, magnesium, sodium, potassium, carbonates, sulphates and chlorides as well as dissolved metals. Suspended solids in the lake water are, for the most part, finely suspended particles of insoluble material, including sand, silt, clay, debris from vegetative growth, algae, chlorophyll and other substances. These materials originate from shore erosion through wind and wave action, turbidity inputs, biological activities and from pollution sources. Nutrients play a very significant role in the life of a lake.

Dissolved oxygen is an important factor in the health of lakes. It is essential to the production and support of biological life in lake waters and necessary to the decomposition and decay of organic wastes and deceased organisms. Oxygen is consumed by the respiration of plants and animals, by bacterial decomposition of organic matter and by the chemical oxidation of waste substances. It plays an important role in the organic cycle of lakes.

13.6.3 Biological Considerations

Biological substances in lakes consist of different life groups of organisms including bacteria, fungi, phytoplankton, zooplankton, benthic fauna, aquatic plant life and fish. Each of these organisms is an essential part of the biological community in lakes and each is critical to the overall balance and stability of lake environment. Out of these, the phytoplankton and zooplankton, benthic fauna, and fish are the most commonly studied.

Lake stratification is driven by seasonally variable forces: solar energy, inflowing water temperature, and variable suspended solid concentrations. If temperature profiles are measured year round, the temperate zone in lakes and reservoirs will demonstrate a strong summer stratification due to solar heating of surface waters, but isothermal conditions occur during winter, culminating in density gradients and allowing the entire water column to mix vertically, a process called turnover. During turnover, nutrients which have accumulated in the deeper water are returned to the surface where they can promote algal growth in the summer as more solar radiation is received, daylight hours increase, temperatures rise and ice covers melt away.

The continuous cycling of carbon between inorganic and organic forms is attained by the use of solar energy in photosynthesis. The process converts the solar energy into chemical energy. The process of photosynthesis can be expressed by the following chemical equation:

$$6CO_2 + 6H_2O \overset{Photosynthesis}{\underset{\text{Re}\,spiration}{\Leftrightarrow}} C_6H_{12}O_6 + 6O_2 \tag{13.34}$$

13.6.4 Lake Mass Balance

A simple mass balance equation for a lake can be written as (Young and Dolan, 1995):

$$V\frac{dC}{dt} = \sum_i W_{TRIB,i} + \sum_j W_{PTS,j} + \sum_k W_{NPS,k} + W_{ATM} - J_{SED}A_s - J_{EVAP}A - QC - kCV \tag{13.35}$$

The lake has volume, V, an outflow rate of Q, a contaminant of concern with water column concentration, C. It receives loads of the contaminant from tributaries $\Sigma W_{TRIB,i}$, direct point sources $\Sigma W_{PTS,j}$, external direct non-point sources $\Sigma W_{NPS,k}$, and atmospheric sources ΣW_{ATM}. The lake loses mass due to the net of sedimentation, resuspension, diffusion, and bioturbation over the sediment with surface area A_s, (J_{SED} A_S), by evaporation/volatilization over the water surface with area A, ($J_{SED}A$), and which reacts within the water column by a first-order process with rate law $-kC$.

When contaminant transport occurs by pure advective processes, the average load, L [MT^{-1}], delivered to a receiving water during some specific time interval, t [T], through an interface of area, A [L^2], for a contaminant that is carried by water flowing at an instantaneous velocity, v [LT^{-1}], and concentration, C [ML^{-3}], may be described by the equation:

$$S = \frac{1}{\Delta t}\int_{\Delta t}\int_A v\{A(\tau),\tau\}C\{A(\tau),\tau\}dAd\tau \tag{13.36}$$

If contaminant transport occurs by purely diffusive or dispersive processes along the instantaneous concentration gradient normal to the interface, dC/dz [ML^{-4}], with a transport coefficient, D_z [L^2T^{-1}], then eq. (13.37) may be used to represent the average load to the receiving water:

$$S = -\frac{1}{\Delta t}\int_{\Delta t}\int_A D_z\{A(\tau),\tau\}\frac{dC\{A(\tau),\tau\}}{dz}dAd\tau \tag{13.37}$$

Eqs. (13.30) and (13.31) are one-dimensional, idealized, deterministic simplifications of the complex, stochastic situation that exists and determines loads during contaminant transport. If it were possible to monitor continuously in time and space and with absolute accuracy all boundaries of a receiving water body, then one could compute loads without uncertainty, at least in theory. Even if monitoring with that intensity were technologically feasible, however, it would be impractical. Nevertheless, these equations can serve to illustrate the major sources of uncertainty that affect estimates of chemical loading and other forcing functions of interest for aquatic system modeling. In particular, any condition or change in conditions that alters any of the variables in eq. (13.36) and (13.37) will affect, in turn, the resulting estimate of load. By corollary, uncertainty in the variables of eq. (13.36) and (13.37) will propagate through the relationship to affect the load estimate. Any quantity, therefore, that produces uncertainty in flow velocities, concentrations, dispersion or diffusion coefficients, or concentration gradients can lead to uncertainty in contaminant loading estimates.

The dominant source of input to water and chemicals to most lakes is surface inflows and outflows. Depending on the factors such as the behavior of the inflowing streams and their number, accuracy required, and funds available, a suitable monitoring program is devised. The commonly used methods of estimating the inflow of chemical and sediments include measurements of their concentrations at discrete times and estimating the total loading by multiplying the concentration with discharge. Although this method is most popular, it may give erroneous results, particularly if large amounts of chemicals enter the water bodies during a short period of high flows. An improved approach is to develop a relationship between flow and pollutant concentration and then estimate loadings using these relations.

An important way of exchange of water and chemicals from a lake is through atmosphere. Rain and precipitation that directly falls on the lake surface constitutes input, while evaporation is the process through which the outflow of water from a lake takes place. Chemicals enter the lake through deposition of particles and absorption of gases to the water surface. Depending on the circumstances and location, atmospheric loading can be an important source of chemicals, particularly for the lakes that have large surface areas. Sometimes, chemical composition of precipitation is determined to estimate chemical loading. However, this method may not give reliable results for which on-site monitoring using collectors is necessary. These collectors collect precipitation and other deposition to the lake. Data of pan evaporimeters are most commonly used to estimate evaporation.

Seepage through sub-surface processes is another source of exchange for lakes. If the groundwater contains large concentrations of constituent matters, seepage inflows can be an important source of chemical inputs. Seepage is commonly estimated as the residual term in the lake water balance equation. However, all the errors of estimation in individual components of water balance will be aggregated in seepage terms, making it error prone and will not give correct results when there is inflow as well as outflow of water and chemicals through seepage. In some basins, due to geologic formations, there might be inflow due to seepage at one end and outflow at the other end. The water balance approach will clearly give wrong results in such cases. In the flownet approach, a network of piezometers is set up in the catchment of the lake to determine the water table gradients. The inflows and outflows can be estimated using governing groundwater equations.

13.7 GROUNDWATER QUALITY

Groundwater has long been regarded as the best resource of water for any type of use. The groundwater is used for different purposes, the major ones being community water supply, agriculture, and industrial processes. Each type of use requires certain water quality criteria which determine whether the groundwater in question is suitable for the purpose. Although it is generally well protected from contaminating influences, the very uses for which it is deployed are causing its degradation. In some cases, excessive abstraction of groundwater has caused a gradual degeneration and a number of serious pollution problems in large groundwater bodies. The need to conserve vitally important aquifers as raw water sources calls for careful management of groundwaters with respect to their quantity and quality. In general, groundwater contamination is irreversible, i.e., once it is polluted, it is difficult to restore the quality over a short span of time.

Rocks and soils are the two main components which influence the groundwater quality. The interaction of rocks and water is a complex process due to a great variety of rocks and environmental conditions. Soil and rock basically can be distinguished from one another in that soil contains organic and inorganic constituents. Inorganic constituents in soil range from 90 to 95% while rock is almost completely inorganic. Soil is the result of the total interaction of water, air, climate, plant and animal organisms with rocks.

Groundwater, although protected by the soil cover, is subject to quality changes as a result of activities of man on the overlying cover. The most important pollution sources include:

- Domestic waste water infiltrated into the aquifer through cesspools or septic tanks,
- municipal sewage (due to leaks in sewerage system) or percolation from waste ponds, etc.,
- leachates from garbage dumps and sanitary landfills,
- industrial wastes from mining, refineries and oil industries, metal processing, and other industries,
- cooling water infiltration through cooling water recharge wells,
- accidental discharges through petroleum products,
- irrigation-return flows, and
- artificial recharge with treated sewage.

The self-purification of groundwater occurs due to a variety of physical, chemical and biological processes. Physical processes include dispersion and filtration. Dispersion causes dilution of wastes and filtration favors reduction in the amounts of substances associated with colloidal or larger-sized particles. The geochemical processes include complexation, acid-base titrations, oxidation-reduction, precipitation-solution, adsorption-desorption. Biological processes include decay and respiration, cell synthesis, etc.

Unlike surface water pollution, the damage to groundwater is not readily 'visible' and may not be detected until it is seriously polluted. The analysis of any groundwater problem requires sound knowledge of the geological and hydrological conditions of the aquifer that is subject to pollution. The basic network of groundwater observation points consists usually of production wells and piezometers. In most cases, however, there might be a need for additional monitoring points for groundwater levels and selected quality parameters.

Sampling and analysis of groundwater can be executed in two ways: (1) Direct measurement of groundwater quality in test hole. For this purpose a probe is lowered or permanently installed in the observation well. Pollution indicators, such as electrical conductivity and temperature, can be easily measured this way. (2) Water samples are pumped from the observation well. If accurate measurements of pH, redox potential, and electrical conductivity are desired, it will be necessary to analyze these parameters at the site. For other parameters samples can be preserved by adding an appropriate preservative and analysis can be carried out in the laboratory. The selection of analytical parameters has to be made according to the objectives of the monitoring program.

13.7.1 Models for Groundwater Quality

Groundwater modeling is concerned with simulating the hydrologic behavior of sub-surface systems. These days, it is the preferred method to understand the movement of water and the pollutants and for regulatory purposes. Contaminant transport models are a step beyond flow models. These models include all the considerations incorporated in flow models plus relationships which are designed to track the contaminants of interest and determine the change in their concentration with time. The continuity equations for contaminant transport simulations include not only terms for dispersion and flow but also other processes, such as chemical and biological reactions which quantify the expected changes in contaminant concentrations with time as this material travels through the soil system of interest. The controlling concept is that the total mass is always accounted for. Models that are used to predict the groundwater contaminant transport can be classified into three categories:

(a) *Advection Models:* These models define the movement of contaminants as a result of groundwater flow only. A slug of water carrying contaminants moves through the soil system along with groundwater flow. Contaminants are transported with no change in concentration with distance.

(b) *Advection-Dispersion Models:* When the concept of dispersion is introduced into the model, a term is included which provides for dispersion related mixing and spreading and leads to time-related changes in contaminant concentration. The dispersion term takes into consideration molecular diffusion, microscopic dispersion, and macroscopic dispersion. Generally, because of the scale of applications in terms of land area involved and relatively high flow velocities, molecular diffusion is of small consequence compared to micro- and macro-dispersion.

(c) *Advection-Dispersion-Chemical/Biological Reaction Models:* Another step in model sophistication is the inclusion of the effects of reactions which change the concentration of transported contaminants. The reactions may be chemical or biological and can be incorporated into advection-only models or advection-dispersion models. Because of the current lack of knowledge regarding subsurface reaction kinetics, only chemical processes, such as ion exchange and adsorption, have been considered in most applications.

An additional class involves coupling of geochemical models with groundwater flow models. Such models are complex and were developed to study the chemistry of natural waters. These are not designed for application to contaminant transport problems. Their applications have been limited to simulate the evolution of groundwater quality along regional groundwater flow paths in systems dominated by calcium-magnesium-sulphate reactions. Application of this modeling approach to meet industry needs appears to be of limited value.

Consider the transport of a contaminant in a saturated flow through a porous medium. The term contaminant refers to any species of interest in a solution. The symbol C denotes the concentration of a contaminant, i.e., mass of contaminant per unit volume of the solution. It is assumed that the porous medium is homogeneous and isotropic with respect to dispersivity, the flow regime is laminar, and in general, variations in contaminant concentration cause changes in the density and viscosity of the liquid. These, in turn, affect the flow regime. The equation describing the mass transport and dispersion of dissolved chemical constituents in a saturated porous medium may be written as

$$\left[\frac{\partial C}{\partial t}+\frac{\partial}{\partial x_i}(V_i C)\right]-\left[\frac{\partial}{\partial x_i}\left(D'_{ij}\frac{\partial C}{\partial x_j}\right)+q'_c\right]=0 \quad \mathrm{i,j}=1,2,3\ldots \tag{13.38}$$

where D'_{ij} is the coefficient of hydrodynamic dispersion, V_i is the component of seepage velocity, q'_c is the mass flux of source or sink, and x_i are the Cartesian coordinates. The theoretical basis and the derivation of the diffusion-convection equation are discussed in detail by Bear (1979). In eq. (13.38) the first term represents the time rate of change of the contaminant concentration. The second term describes the advective transport of C in the x_i-direction, which is proportional to the seepage velocity. The third term is the transport (redistribution) of C due to dispersion and the molecular diffusion. Finally, the last term represents the time rate of production or decay of C.

The advective dispersion equation is a nonlinear partial differential equation of parabolic type. The relation is nonlinear because of the advective term, and because of the transport coefficient which is a function of the dependent variable V. The advective term is nonsymmetric and has been a principal source of difficulty in the numerical solution of the advective dispersion equation. Bobba and Singh (1995) have described the initial and boundary conditions for this equation and have discussed the many finite difference and finite element schemes that are used in contaminant transport models.

Among the models for groundwater quality, perhaps the most popular is the MODLFOW model. MODFLOW is a MODular 3-dimensional finite difference groundwater FLOW model developed by McDonald and Harbough (1988) of the USGS, USA. It simulates steady and non-steady flow in three dimensions for an irregularly shaped flow system in which the aquifer layer can be confined, unconfined, or a combination of confined and unconfined. Flow from external sources, such as flow to wells, areal recharge, evapotranspiration, flow to drains, and flow through river, can be simulated.

MODFLOW uses a modular structure wherein similar program functions are grouped together. The modular structure consists of a main program and a large number of independent subroutines called "modules". The modules, in turn, have been grouped into "packages". Each package deals with a specific aspect of the hydrological system to be simulated. For example, the option 'well package' simulates the effect of wells, the 'river package' simulates the effect of river, etc.

The three-dimensional unsteady movement of groundwater of constant density through porous earth material in a heterogenous anisotropic medium can be described by the following partial differential equation:

$$\frac{\partial}{\partial x}\left(K_{xx}\frac{\partial h}{\partial x}\right)+\frac{\partial}{\partial y}\left(K_{yy}\frac{\partial h}{\partial y}\right)+\frac{\partial}{\partial z}\left(K_{zz}\frac{\partial h}{\partial z}\right)-W=S_s\frac{\partial h}{\partial t} \tag{13.39}$$

where K_{xx}, K_{yy}, K_{zz} denote the hydraulic conductivity along major axes [LT^{-1}], h is the potentiometric head [L], W is the volumetric flux per unit volume and represents sources and/or sinks of water [T_{-1}], S_s is the specific storage of the porous material [L^{-1}] and, t is time [T]. Possible inflow/outflow terms (W) are recharge from rainfall, artificial recharge through wells, pumping through wells, evapotranspiration loss, recharge from river/canal cells, outflow into a river/canal cell, inflow/outflow across a boundary cell, outflow through drains, spring flow, etc.

MT3D is a Modular 3-Dimensional solute Transport model for simulating changes in concentration of *single species* miscible contaminants in groundwater considering advection, dispersion and some *simple chemical reactions* with various types of boundary conditions and external sources or sinks in groundwater systems. The model was developed by Zheng (1992).

MT3D is based on a modular structure to permit simulation of transport components independently or jointly. It interfaces directly with the USGS finite-difference groundwater flow model MODFLOW for the head solution, and supports all the hydrologic and discretization features of MODFLOW. It has been accepted by practitioners and researchers alike and applied in numerous field-scale studies throughout the world. The modular structure of the MT3D transport model makes it possible to simulate advection, dispersion, source/sink mixing, and chemical reactions independently.

13.8 CLOSURE

Water quantity and quality are an integral part of the natural hydrologic environment. These two processes are in continuous dynamic interactions. Heavy dependence of the modern society of chemical products is fraught with environmental degradation, health hazard, and pollution of precious natural resources. Therefore, proper assessment, development, and management of water resources requires full understanding of the environmental processes and their interactions. Historically, water quantity has been the governing factor in determining water use. However, in a world that is increasingly aware and conscious of development that does not damage the environment, the modeling of water quality has occupied the central stage in water resources utilization. A large number of water quality models are available these days and provide critical inputs in decision making.

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