

nated water is higher than would be expected from a simple admixture of seawater sufficient to produce the observed chloride concentration in the contaminated water, probably owing to the exchange of calcium held on exchange sites on aquifer minerals for sodium in solution in the advancing saltwater front.

Detection and tracing of seawater contamination using stable isotopes of hydrogen and oxygen, or long-lived radioactive isotopes such as carbon-14, should have a considerable potential. Hanshaw, Back, Rubin, and Wait (1965) described this technique.

Large withdrawals of ground water from wells near the shoreline of Los Angeles County, Calif., has caused extensive inland contamination of ground water by seawater intrusion. Remedial measures undertaken there since the 1940's to control the situation have been described in many published reports, for example, that of Banks and others (1957). Seawater intrusion was controlled by injecting freshwater through wells into the contaminated aquifer close to the shoreline so as to build up a freshwater barrier. More recently, a similar procedure has been used farther south, in Orange County, Calif. (Hammer and Elser, 1980).

#### APPLICATION OF WATER-QUALITY MEASUREMENTS TO QUANTITATIVE HYDROLOGY

Certain types of water-quality determinations can be used to measure or estimate water-discharge rates or quantities of stored water. Various kinds of "chemical" measuring techniques suitable for surface streams have been in use for many years (Corbett and others, 1945, p. 88-90; Rantz and others, 1983, p. 211-259). One of these has been applied extensively to determine the rate of solute movement, or time of travel of water through a reach of a river, a value that cannot be estimated accurately from stream-discharge records. In this procedure, a readily detectable solute is added to the stream in the form of a concentrated slug, and the length of time required for the material to appear at a downstream point is measured. In recent years, many measurements of this kind have been made with dyes such as rhodamine WT in response to the need for time-of-travel data in pollution studies and for other applications. Inorganic materials also can be used as tracers, and Nelson and others (1966) used radioactive materials introduced into the Columbia River by nuclear facilities at Hanford, Wash., to trace the flow times in that stream. An index of U.S. Geological Survey time-of-travel studies was assembled by Boning (1973).

The salt-dilution method of measuring flow rate of a stream consists of adding, at a constant rate, a known quantity of tracer, usually sodium chloride, and measuring the concentration of chloride in the water upstream from

the point of addition and far enough downstream that mixing is complete. The flow must remain constant during the time the measurements are being made, and enough time must be allowed so that the concentration at the downstream point is stable. This provides enough information for calculating the discharge rate of the stream. The method can be used in systems in which other procedures are impossible because of inaccessibility or extremes of turbulence or velocity. Amounts of salt added need not be large enough to affect water quality adversely.

The mathematical basis for calculating discharge by the tracer method is the mass-balance equation cited previously in connection with the relation of stream-water quality to discharge. The water discharges in a system of this type are related by the equation

$$q_1 + q_2 = q_3,$$

where  $q_1$  is the discharge upstream,  $q_2$  is the discharge of the tagging solution, and  $q_3$  is the discharge downstream from the point of addition of  $q_2$ . To express the discharge rate for the tracer ion, one may write the equation

$$c_1 q_1 + c_2 q_2 = c_3 q_3,$$

where the  $c$  terms are the concentrations known or observed at the points at which the  $q$  values are taken. When the technique is used as described above, all the  $c$  terms and  $q_2$  are known: hence, the two equations provide values for  $q_1$  and  $q_3$ .

This procedure for evaluating discharges has potential hydrologic uses that seem not to have been used widely. Water-quality changes occur in river systems owing to inflows of water of a different composition, and a combination of sampling and flow measurement might be used to help determine quantities that cannot be measured directly.

A simple example of a system that can be evaluated this way is a stream low in dissolved-solute concentrations that receives inflow from a saltwater spring. If the spring inflow is accessible for measurement, the streamflow can be measured by analyzing samples of water collected from the spring and from the stream above the inflow point and from the stream far enough below the inflow to assure complete mixing, and then determining the springflow. If the springflow cannot be measured directly, as is more commonly the case, a single measurement of riverflow and analysis of samples at the three necessary points can provide a basis for calculating spring inflow.

It is true that the usual procedure would be to measure flow above and below the inflow zone and to determine inflow by calculating the difference. If the

riverflows are fairly large, however, the probable magnitude of the measuring error may easily exceed the quantity of inflow.

At Clifton, Ariz., the San Francisco River receives enough inflow from hot saline springs that issue from gravel in the streambed to alter the composition of the river water considerably at normal stages of flow. The composition of the inflowing water was determined by sampling one point of spring discharge that was above the river level, and samples of river water were obtained upstream and downstream from the inflow zone. The discharge was measured by means of a current meter at the downstream site. Table 23 contains the analyses and the calculated and measured discharges. Although the calculated inflow is a little more than 2 ft<sup>3</sup>/s, almost all this amount occurs below the water surface in the stream, where it is not noticeable to the casual observer and is not measurable by direct means. The correlation of dissolved-solids and discharge data for the San Francisco River below the inflow zone at Clifton was discussed earlier.

In areas where interconnections between ground-water and surface-water systems are of interest, detailed studies often include seepage measurements. These consist

of a series of measurements of riverflow and tributary inflow taken in a downstream direction, with unmeasured gains and losses between measuring points being ascribed to ground-water inflows or losses of streamflow to the ground-water reservoir. Such measurements can provide considerably more information if water samples are taken at all measuring sites. The analyses of the samples help show where both inflow and outflow may be occurring between measuring points and help refine the investigator's understanding of the hydrologic system. Data of this kind were used, for example, to help evaluate details of the hydrology of the Safford Valley, Ariz. (Gatewood and others, 1950).

In studies of surface streams and related inflows and outflows, enough measurements and observations usually can be made to provide for a detailed evaluation. Although it would be helpful to be able to estimate ground-water flow rates and the contributions from point and diffuse sources of recharge by chemical techniques, the inherent complexity of ground-water chemistry and flow patterns and the difficulty of obtaining truly representative samples severely limit the tracer approach.

For example, there are serious problems inherent in deciding whether ground-water samples from wells ade-

**Table 23.** Analyses of water from Clifton Hot Springs and from the San Francisco River above and below Clifton, Arizona

[Date below sample number is date of collection. c, calculated. Source of data: Hem (1950)]

Constituent	1		2		3	
	Jan. 10, 1944		Jan. 10, 1944		Jan. 10, 1944	
	mg/L	meq/L	mg/L	meq/L	mg/L	meq/L
Silica (SiO <sub>2</sub> ) .....					58	
Iron (Fe) .....					.19	
Calcium (Ca) .....	44	2.20	72	3.59	860	42.91
Magnesium (Mg) ....	12	.99	13	1.07	41	3.37
Sodium (Na) .....	58	2.52	156	6.78	2,670	116.10
Potassium (K) .....						
Bicarbonate					142	3.63
(HCO <sub>3</sub> ) .....	204	3.34	206	3.38	109	1.79
Sulfate (SO <sub>4</sub> ) .....	17	.35	19	.40	153	3.19
Chloride (Cl) .....	70	1.97	270	7.62	5,800	163.58
Fluoride (F) .....	.8	.04	.8	.04	3.0	.16
Nitrate (NO <sub>3</sub> ) .....	.2	.00	.5	.01	7.5	.12
Dissolved solids:						
Calculated .....	302		633		9,790	
Hardness as						
CaCO <sub>3</sub> .....	160		233		2,310	
Noncarbonate	0		64		2,220	
Specific conductance (micromhos at 25°C).	547		1,160		16,500	
Discharge (cfs) .....	58(c)		60		2.1(c)	

1. San Francisco River, 2 mi above Clifton, Ariz.

2. San Francisco River at gaging station at Clifton, Ariz.

3. Clifton Hot Springs seep opposite Southern Pacific Lines depot. Temperature, 43.4°C.

quately represent the entire thickness of aquifer penetrated and whether the tracer ions used move with the same speed as the water itself. There are, however, a number of examples that can be cited in which chemical techniques of measurement have been useful.

Many investigations of direction and rates of ground-water movement have been made by studies that involved injection of slugs of salt, dye, or radioactive material. The idea is by no means new. Slichter (1902) conducted a number of studies in which salt solution was added to one well and its appearance monitored in adjacent wells; he referred to similar work done in Europe at earlier times by Adolph Thiem. More recent experiments of this type were described by Kaufman and Orlob (1956).

Any tracer material that may be added must be similar in density and temperature to that of the ground water, and large amounts might constitute objectionable pollution. Where movement is through large fissures or cavernous openings, a tracer technique becomes more simple and useful. Additions of organic dye have been used to trace water movement through limestone and to identify pollution sources in such systems.

Material that is naturally present is also potentially useful for tracing flow and for estimating rates of movement. Radioactive material present naturally includes tritium, carbon-14, and lead-210. The half-life of lead-210 and its chemical properties limit its usefulness as a ground-water tracer. The use of isotopes, both radioactive and stable, has produced an extensive literature already referred to (Rodehamel and others, 1971; Friedman and O'Neil, 1977).

Some of the water stored in McMillan Reservoir in the Pecos River north of Carlsbad, N. Mex., escapes through solution openings in gypsum, but the outflow apparently is all or nearly all returned to the river through springs located a few miles downstream from the reservoir. Many investigations of this system have been made. Theis and Sayre (1942, p. 54–58) used the observed pattern of chloride concentrations in the reservoir and spring water to develop an empirical equation relating water emerging at the springs to water that had been stored in the reservoir at earlier times. From this, the volume of storage in the ground-water system feeding the springs was estimated. At a section of the river a few miles farther downstream, Claassen (1981) calculated the rate of enlargement, by dissolution in the circulating water, of channels in gypsum beds using data on quality of river water and ground water.

Kaufman and Orlob (1956) observed that chloride ions seemed to move at effectively the same rate as water through porous material. In fact, the retardation of chloride in their experiment was a little less than that of tritium, which participated to some extent in exchange reactions, even though the tritium actually was incorpor-

ated in water molecules.

Some aquifers can be considered conduits having fairly well defined boundaries. Water moving down such channels may show quality changes related to side inflows or to other factors. Plate 3, a water-quality map of part of Safford Valley, Ariz., shows how the composition of ground water in the alluvial fill, which was considered by Gatewood and others (1950) to be a hydrologic unit, changes downstream. The inflow of fresher water from the south side of this section of the valley is evidently large compared with the amount of rather saline water moving downstream in the fill at the upstream end of the reach. The relative magnitudes of flow can be estimated by the composition of the influent water and the mixture.

Admittedly, the effects of other factors, such as river stage and pumping for irrigation, may influence the results of calculations. Where the data can be obtained, however, water-quality maps offer a method of extending estimates of both ground-water flows and the relative amounts of water contributed from different sources.

In an early study of ground-water and surface-water relationships along the Illinois River at Peoria, Ill., Larson (1949) used water-quality data to estimate the proportions of river water and ground water in a pumped well near the stream. Chemical studies to evaluate sources of water in wells along the Platte River in Nebraska were described by Barnes and Bentall (1968). Konikow and Bredehoeft (1974) prepared maps of water quality for ground water in the Arkansas River valley downstream from Pueblo, Colo. This study used mathematical modeling to compute probable future water quality in the aquifer.

### Mathematical Simulations—Flow Models

The simple equation of conservation of mass introduced earlier is an underlying physical principle from which much more detailed mathematical simulations of flow in single or multiphase systems can be derived. The increase in emphasis on mathematical treatment of hydrologic systems is probably the most significant development in the field of hydrology during the past 20 years.

Hydrologic systems are dynamic in the sense that water, solutes, and energy are in motion within them, influenced in various ways by the physical properties of the channels or passages through which the motion occurs and by those effects that relate to the driving energy, or hydraulic head. Interrelationships of this kind can be represented by systems of partial differential equations based on the principle of conservation of mass, which, for example, might be capable of predicting how a ground-water system would be affected in space and time by postulated local head changes. These equations can be designed to show propagation of such changes in space along two or even three coordinates. Solutions for systems of partial differential equations like these can be

readily produced by modern computer techniques. They would be prohibitively laborious if done by other methods.

More closely related to the subject of water chemistry are the various types of transport models that deal with fluid and solute movement. These also consist of arrays of partial differential equations that relate rates of movement of water in one or more dimensions to change in transported substances associated with the water. Factors treated by such models commonly include dispersion, or mixing, advective transport, diffusion along concentration gradients, and behavior of sources and sinks in the system for the material being transported.

These mathematical models are based on principles of physics. The incorporation of chemical factors is generally necessary to simulate successfully the behavior of dissolved material being transported. For a few types of material it can reasonably be assumed that the solute does not participate in chemical or adsorptive interactions with anything else in the system, and its behavior then can be modeled accurately by means of the physical transport equations.

A slug of nonreactive (conservative) solute added to a river, as in a chemical spill, will be perceived at a downstream point as an increase in concentration of that solute with time to a peak, followed by a decrease to background levels. Characteristically, the concentration plotted against time for sites short distances downstream from the spill will display a sharp rise to a peak, followed by a slower decline to background. As the distance downstream increases the peak is attenuated, finally becoming very faint. The shape of the peak and the degree of attenuation are related to the hydraulic characteristics of the system as well as to the extent of interaction of solute with other components of the system. A prediction of height and duration of the downstream peak obviously is possible if the system is characterized well enough.

In practice, the modeling of solute transport in streams is complicated by chemical interactions and by difficulties in evaluating physical parameters. Nevertheless, many stream system models have been developed, often by using results of field experiments and observations on the particular reach of stream that is being modeled. Theoretical concepts may define the general structure of the model, but some of the necessary numbers must be obtained by fitting and by trial and error. This may produce a model that can be used only for the stream for which it was developed, but such models have been used effectively for predicting the response of streams to sewage effluents and some of the related biochemical effects that can be observed in rivers. A review of some of the work on modeling of phytoplankton in rivers and other water bodies was given by DiToro and others (1971). Development of a model for transport of added tracers in a small

mountain stream having "pool-and-riffle" characteristics was described by Bencala and Walters (1983).

In most ground water systems the flow characteristics are materially different from those in open channels. A large area of solid surface generally is encountered by each unit volume of water moving through the system. In a fine-grained sediment, the surface area contacted by each liter of water transmitted may amount to thousands of square meters per meter of travel. The quantity of cations in exchange sites on this large area may well be as large as, or larger than, the quantity in solution in a liter of water. With the slow rates of water movement that might be expected in some systems—perhaps only a few tens of meters a year—there is a maximum of opportunity for completion of any interaction that might occur between solutes and surfaces. Cations will be adsorbed or dissolved in accordance with selectivity behavior of the sites, but it can be expected that such systems will extract introduced trace metal cations effectively because so many sites are available. Even where the proportion of sites occupied at equilibrium by adsorbed trace metals is small, their low initial concentration can easily be decreased to undetectable levels.

Many models of transport of conserved solutes in ground water are described in the literature. Robertson (1977), for example, modeled the transport of tritium in basalt and associated soils in Idaho, and Bredehoeft and Pinder (1973) described a model they applied to a chloride-contamination problem in a limestone aquifer in Georgia.

Where there is solute-solid interaction, an approach that has been used is to assume that a local equilibrium condition is rapidly attained. A model by Rubin and James (1973) for an ion-exchange process in ground water used this approach coupled to a physical-transport model. A general review with some mathematical methods for studying transport of solutes in aqueous systems was given by Lerman (1979). The broader subject of mathematical modeling of ground water was reviewed briefly by Appel and Bredehoeft (1976), who gave a substantial number of literature references to solute-transport models for ground water. A review of water-quality-assessment model techniques for surface-water systems was prepared by Hines and others (1975).

In general terms, ground-water systems and water in such environments as soil or unsaturated zones or lakebed sediments are characterized by slow water movement and by very much slower movement of many solutes. Models of such systems need to give major emphasis to evaluating the chemical and related processes that cause this differential, and the mathematical structure of the model should be appropriate to the chemistry of the system (Rubin, 1979, 1983).

A study by Jackson and Inch (1980) of the movement of the radioactive nuclides strontium-90 and cesi-

um-137 through a sand aquifer demonstrated the use of several kinds of chemical and transport models. The rate of movement observed for strontium-90 was about 3 percent, and the rate of cesium-137 movement, about 0.3 percent of the ground-water movement rate in that system.

In surface-water systems the bulk of the water moves much more rapidly than in the systems cited above. However, the modeling of solute transport in such systems is complicated by the additional effect of a moving solid phase (suspended and bed sediment) interacting with solutes, as well as by much more important photochemical and biochemical factors.

As noted in earlier sections of this book dealing with chemical equilibrium, solids that participate in an equilibrium are usually assumed to be at standard state (activity=1). Therefore, models using equilibrium assumptions are somewhat limited in their capacity to evaluate systems in which the changing nature and quantity of participating solids at various places in the system is a matter of concern.

In those ground-water systems in which chemical processes may represent a more sensitive aspect of the model than physical transport, the appropriate models to use may be those in which chemical rather than physical processes are emphasized. Wigley and others (1978) and Plummer and Back (1980) demonstrated that one can describe flow rates in regional limestone aquifer systems and can develop much other information on their hydrologic properties by studies of major element chemistry, mass balances, and isotopic distributions. The principles used in these models were reviewed by Plummer and others (1983).

In theory, at least, the modeling of solute behavior in a carbonate system can be based on fairly simple equilibrium chemistry. The modeling of reactive solutes in granular aquifer material is a much more difficult task, and one that has by no means been reduced to a routine exercise.

The development of a mathematical model that has predictive usefulness is a substantial contribution to applied hydrologic science, but it is necessary to tailor the model to the specific system to which it is to be applied. *A proper perspective needs to be maintained, for some evaluations of hydrologic systems can be made with less detailed models than others.* The term "model" need not imply a massive computer-programmed approach. In any event, a conceptual model laid out in rather simple terms must always precede it. The more detailed model is then developed to fulfill the requirements of the study.

## RELATION OF QUALITY OF WATER TO USE

An immediate purpose of the usual quality-of-water study is to determine if the water is satisfactory for a proposed use. Accordingly, the subject of water-analysis interpretation must often include some consideration of

standards and tolerances that have been established for water that is to be used for various purposes. Standards for water to be used for drinking and other domestic purposes have been established in many countries. Published literature contains tolerance levels and related data for constituents of water to be used in agriculture, in industry, for propagation of fish, and for a number of other specific purposes.

Water that is to be used as a public supply may be employed for many purposes. Therefore, the standards used to evaluate the suitability of water for public supply generally are more restrictive than those that would be applied to water for a small domestic or farm supply, although not necessarily more rigorous for individual components than the limits that apply for many industrial uses.

Water from mineral and hot springs is used medicinally in many places, and the mystic qualities of natural warm springs have been of great interest to man since prehistoric time. Medicinal uses have been summarized by Licht (1963) and will not be considered here.

An extensive survey of water-quality standards and review of the literature on the effects of solutes on uses of water was prepared by McKee and Wolf (1963). More recently, the U.S. Environmental Protection Agency sponsored a thorough study of water-quality and water-use interrelationships by a committee named by the National Academy of Science (NAS-NAE, 1972). Water uses for which standards were suggested include (1) recreation and aesthetics, (2) public water supplies, (3) freshwater aquatic life and wildlife, (4) marine aquatic life and wildlife, (5) agricultural uses, and (6) industrial water supplies. The subject can be considered only rather briefly here.

## Domestic Uses and Public Supplies

Besides being chemically safe for human consumption, water to be used in the home should be free of undesirable physical properties such as color or turbidity and should have no unpleasant taste or odor. Harmful micro-organisms should be virtually absent; however, they are not usually considered in ordinary chemical analyses. The presence of harmful micro-organisms is considerably more difficult to ascertain than most other properties of water, but it is a highly important consideration. Over the years, great progress has been made in decreasing the incidence of waterborne disease, especially typhoid fever and cholera, and in the United States these two diseases have become rare.

Filtration of water taken from surface-water sources and disinfection, usually by addition of chlorine, have been the most effective means of controlling harmful organisms. In recent years increasing attention has been given to the occurrence in water of the protozoan *Giardia lamblia*, which can cause intestinal disturbances (giardia-