

water with surface areas of minerals as large as is normally expected in shale or in sandstone. The opportunity for water to pick up solutes from these metamorphosed rocks is, therefore, small, and water from slate or quartzite also is likely to contain low concentrations of solutes. Analysis 16-8, figure 50, represents water from a quartzite in Alabama. Limestone may be converted to marble without much chemical change, and the processes of solution in such a marble are much the same as those in limestone. If the original limestone was impure, however, it could yield a marble containing some minerals less soluble than calcite.

Processes of metamorphism generally involve aqueous solutions, and the alteration products that result may include hydrolyzate minerals. The release of water from some types of rocks during metamorphic processes can be expected. White (1957a) examined natural waters for possible features of their composition that could be attributed to metamorphism of rocks. Among the properties cited by White as possible indications of a metamorphic influence on water composition were high concentrations of sodium, bicarbonate, and boron and relatively low concentrations of chloride. Analysis 18-5 is for water described by Barnes and others (1967) to issue from a zone of alteration of ultrabasic rock to serpentinite.

The first three analyses in figure 50 represent waters that passed through metamorphosed rocks long after the processes of metamorphism were completed. In contrast, the water represented by analysis 18-5 is actively participating in the ongoing metamorphic process.

INFLUENCE OF ACTIVITIES OF HUMANS

All life forms interact with their environments in various ways. As a result of these interactions, complex ecologic structures have evolved, structures in which diverse life forms interact with one another in supportive as well as in predatory ways. One might view the present-day Earth-surface environment as having been shaped in many ways through these life processes interacting with their surroundings over the span of geologic time. Certainly this is true for the development of soils—and it has been thought by many geochemists that the atmosphere has attained much or all of its oxygen from activity of photosynthetic organisms. A more extreme view was expressed by Lovelock and Margulis (1974), who suggested that the life processes of organisms established and continue to maintain the composition of the atmosphere at an optimum for living species to thrive. It is perhaps less clear how natural waters might have been made more hospitable over a long time span by such processes, but one may readily observe ways in which organic processes currently maintain water bodies in a state favorable for life (oxygen and nutrient balances, for example).

Many human activities have adverse consequences for the environment. As human populations increase and civilizations become more and more technologically developed, the adverse effects become obvious, and they have been a matter of deep concern to thoughtful observers for more than a century. When human activities cause a decline in the quality of natural waters we use the term "pollution." This word has deep connotations and water pollution is difficult to define scientifically. For the purpose of this discussion it is defined as man-caused deterioration of water quality that is sufficiently severe to decrease substantially the usefulness of the resource, either by humans or by some other life form deemed to be beneficial.

In a broad general sense one can describe the interaction of life forms with their environment in the terms of thermodynamics. Life processes themselves, for example, involve an expenditure of energy to produce a form of internal order (decreased entropy). When the organisms die, the second law of thermodynamics predicts that this order will be largely destroyed and its stored energy partly released, with an increase in entropy in the products of decay. The energy loss is not total, however, and over geologic time large amounts of available energy have been stored, in coal and petroleum, for example.

The rise of modern civilization has brought with it a large and increasing use of energy, from fossil sources and more recently from nuclear fission. Much of this energy is employed in ways that influence the physical environment, as in agriculture, timber harvesting, and mining. These activities could be likened to increases in degree of order—at least humans generally consider the results beneficial. The side effects on natural water may sometimes be severe enough to constitute pollution as defined here. This general view of pollution problems has been discussed by Stumm and Morgan (1981, p. 724-725).

Some of the energy expended by an industrial civilization is used to produce entropy decreases that can be more exactly defined thermodynamically. The conversion of iron oxide ore to metallic iron, and the recovery of other metals from ores, give products that are thermodynamically unstable (that is, low in entropy). Their conversion to more stable forms can be a source of water pollution as the metals react with their environment. Production and use of synthetic organic chemical compounds also pose a pollution threat, one that may be difficult to evaluate because these substances would not be present in the environment under natural conditions.

From these considerations a generalization can be made: Industrial civilizations can be expected to have substantial intrinsic environmental effects, and some may bring about pollution of natural water as this has been defined here. Some parts of the definition are subjective. Specifically, the definition requires that judgments be

made as to what constitutes a substantial impairment of usability of the water and which of such impaired uses are sufficiently beneficial to justify concern. It is in these areas that conflicts occur, and generally they cannot be resolved by scientific methods alone.

Much of the subject of water-pollution control and problems relating to it are beyond the scope of this book. However, there are many ways in which natural-water chemistry, as discussed here, can be applied to help understand, predict, and remedy pollution problems. It is necessary to recognize that environmental change attributable to humans is unavoidable and that some deterioration in water quality may be acceptable if alternatives entail unacceptable social costs.

Detection of lower and lower levels of organic or inorganic pollutants has become relatively easy. The improved ability to identify such materials in solution has resulted from improved technology and application of analytical chemistry. The fact that a particular substance is present does not, however, establish the existence of pollution as it is defined here. Various other aspects need to be considered. The major tasks to which scientific contributions can be made include such things as determining form, stability, and transport rates and mechanisms for pollutant species, predicting the probable effects of current or foreseeable practices in waste disposal or product use, assessing the impacts of artificial sources versus natural sources, and providing methods for identifying the most significant existing and potential pollution problems.

Stumm and Stumm-Zollinger (1971) discussed the subject of water pollution and presented a thoughtful analysis of many ecologic aspects and implications of the subject. Some aspects of the topic are discussed further here, and some were touched earlier in this book.

High densities of populations of human or other biological species inevitably encounter metabolic-waste-disposal problems, and these problems may be greatly magnified in industrial civilizations that produce large volumes of waste products. Waste accumulations in excessive amounts may occur in colonies of some of the lower forms of life and may cause the colonies to die out. The intelligence of humans as individuals is certainly sufficient to recognize, understand, and cope with problems related to waste management. Unfortunately, as in many other aspects of human behavior, the intelligence and ethical standards of social groups seem to lag far behind the levels attainable by individuals. Thus, many aspects of both cause and cure of water pollution lie in the area of the social rather than the physical or biological sciences.

Waste-disposal practices may be classified into three major categories on the basis of the general aim of the process: (1) processes that convert the waste to innocuous or reusable material, (2) processes that disperse the waste

into a diluting medium, and (3) processes in which wastes are stored in a place where it is supposed they cannot later become a nuisance or a hazard. Failure of any of these processes to work satisfactorily can cause pollution problems.

Techniques of waste disposal in which organic waste is converted to innocuous forms are commonly used in sewage-disposal plants. Natural processes that produce similar results occur in oxygenated river water; however, heavy loading of streams with organic waste produces many undesirable effects, and the natural process of purification may easily become overwhelmed. Many inorganic wastes must either be dispersed into the environment in such a way as to avoid objectionable concentrations in any locality or be stored where they can do no harm.

Some common ionic species may be dispersed into the environment with no serious problems. Chloride, for example, may not be objectionable if maintained at a low enough concentration, and it can be conveyed to the ocean, where it will cause no significant effects. Some other solutes, however, may tend to accumulate and become concentrated in such places as stream sediment or biota and can be released from such accumulations in unexpected ways to cause troublesome local concentrations.

A method of disposal used in some places for obnoxious wastes is to inject them into deep aquifers that contain salty water. This generally amounts to storing the waste, but it is a method of storage whereby control over the material cannot be maintained. More positive controls generally are required for the highly dangerous wastes produced in some nuclear processes. Highly radioactive material is presently being stored in tanks or in solid form, which minimizes the possibility of escape.

Whatever the technique of waste disposal used, the increasing density of population in many areas makes it more and more likely that any water sampled will be affected in some way by the activities of humans. The added material may not fit the term "pollution" in the sense that the water becomes unusable, but it may have a measurable effect on major or minor dissolved-ion concentrations. Addition of organic matter to ground water may provide a reductant for oxidized minerals and may cause changes in the geochemical balance of the system, and changes in pH may cause rock minerals to dissolve.

Although some polluted surface waters can be restored to reasonable quality fairly rapidly by decreasing waste loads or concentrations, the process can be costly. A polluted ground water, on the other hand, may be so slow to recover that it becomes necessary to think of the pollution of aquifers as almost irreversible once it has occurred. For this reason, great care is needed to protect ground-water aquifers. Incidents of contamination of ground water from septic tanks, sewage and industrial

waste-disposal systems, solid-waste disposal practices, and natural-gas and petroleum-storage leaks as well as other topics related to the general subject of ground-water pollution have been receiving attention for a long time. Many were described at a pioneering symposium sponsored by the U.S. Public Health Service (U.S. Public Health Service, 1961). Control and abatement of the pollution of ground water that has resulted from faulty waste-disposal practices has been a growing problem in urban and rural areas. A bibliography of papers on ground-water contamination prepared by Bader and others (1973) included more than 700 references.

Continued concern about ground-water contamination is evidenced by the number of papers on this topic published in professional journals—a total of 19 in the 1984 volume of the journal "Ground Water," for example. Increased interest in and research on this and other aspects of environmental pollution in recent years also is evident in the number of popular articles in mass media and the new scientific and technical journals, such as "Environmental Science and Technology," "Journal of Environmental Quality," "Water, Air and Soil Pollution," and others that publish research in this field.

During recent decades the usual and preferred procedure for disposal of solid wastes has been to bury them in so-called sanitary landfills. Although, in theory, wastes in a properly designed and managed landfill should not be a contamination threat, in practice many of these landfills have not been protected from infiltration of water from the surface or from lateral movement of ground water through them, and leachate has contaminated neighboring ground water and surface water. Examples on Long Island, N.Y., cited by Kimmel and Braids (1980), showed that such leachates commonly are high in bicarbonate, chloride, and sodium and can have excessive amounts of dissolved metals, especially iron. Effects of landfill leaching also have been studied extensively in Europe (Golwer and others, 1975). Landfill leachates may also contain a wide variety of organic compounds. A case study relating to ground water contamination from a landfill in the Atlantic City, N.J., area (Sharefkin and others, 1984) illustrates the chemical complexity of potential leachates. These authors point out the high costs of correcting this type of problem.

In a society with highly developed industrial and agricultural technologies, a large number of organic and inorganic products are manufactured and used that would not be able to enter the environment naturally. Inevitably, some of these products, or their residues or byproducts, enter the hydrosphere. When their presence is discovered a surge of publicity and general concern may follow, along with pressures for various kinds of action to correct or lessen the problem. During the past several decades attention has been drawn, for example, to lead and mercury in the aqueous environment and to various

common and exotic organic substances, as already noted. A matter of more recent concern worldwide is the occurrence of rainfall having a low pH—the "acid rain" problem. Most of these environmental releases are forms of indirect pollution in the sense that the objectionable material was not being formally consigned to receiving water as a waste effluent.

One aspect of a form of indirect pollution of water mentioned above is the intrusion of seawater. This subject has been selected for further discussion here because it illustrates some of the subtleties of pollution effects and is an area in which both hydrologic and chemical knowledge is essential in achieving control.

Saltwater Intrusion

Both surface and underground waters may be contaminated by saline water where opportunity for contact occurs. The activities of humans may aid in bringing about contamination but are by no means required. Along seacoasts there is a saltwater-freshwater contact zone both in streams and in aquifers that extend under the sea.

The relation between seawater and freshwater in aquifers along the seacoast generally can be described by hydraulic relationships. The effect of man's withdrawal of water from the landward parts of these aquifers may have far-reaching effects on the position of the saltwater-freshwater interface. The hydraulics of coastal aquifers have been studied extensively in the field and by means of laboratory models. It is generally agreed by hydrologists that the boundaries between freshwater and saltwater in coastal aquifers depend on the balance of forces in a dynamic system. Normally, freshwater moves seaward continuously at a rate that is related to the head above mean sea level in the freshwater aquifer. As Hubbert (1940) pointed out, the result of this movement is that in an unconfined system freshwater discharges into the sea through the saturated zone from the high-tide line for some distance offshore. Cooper (1959) described how the movements of fresh- and saltwater along a contact zone tend to produce a diffuse zone of mixing rather than a sharp interface.

In a confined or semiconfined aquifer that is open to the sea at some distance offshore, a similar dynamic circulation pattern can be expected. So long as a high head of freshwater inland is maintained in the aquifer, freshwater will discharge into the ocean at the outcrop of the aquifer and will maintain the zone of contact with salty water in the aquifer a considerable distance offshore. Pumping inland will reduce the head of the freshwater, and because head changes are transmitted rapidly through the system, the flow of freshwater seaward will be decreased. The head may decline enough to stop entirely the seaward flow of freshwater past the interface. With

the decreased freshwater flow, the system will be unstable, and saltwater will invade the aquifer. The saltwater front will move inland to the point where the reduced freshwater head is again sufficient to produce a balancing seaward movement of freshwater past the interface.

Overdevelopment of coastal aquifers can greatly decrease the freshwater head and can bring about conditions favorable for the migration of saltwater inland. The migration of the saltwater front, however, is rather slow, as it represents actual movement of water in the system under low gradients with high resistance. The appearance of salty water in a well may not occur until some years after the head decline has reached serious proportions. The rate of movement of some of the ions in the saltwater front will be influenced by ion exchange, and diffusion and head fluctuation will cause the interface to become a transitional zone rather than a sharp front.

Saltwater intrusion into highly developed aquifers is a serious problem in many places along continental margins and has occurred in other places where nonoceanic saltwater was drawn into an aquifer when hydraulic heads were altered. Hydrologists are frequently confronted with the need to recognize incipient stages of saltwater intrusion so that steps can be taken to correct the situation.

The composition of average seawater is given in table 2. Chloride is the major anion, and it moves through aquifers at nearly the same rate as the intruding water. Increasing chloride concentrations may well be the first indication of the approach of a seawater contamination front. In an area where no other source of saline contamination exists, high chloride concentrations in ground water can be considered rather definite proof of seawater contamination. If important amounts of chloride could come from other sources, however, the establishment of definite proof of the seawater source may be difficult.

Components of seawater other than chloride may be used to identify contamination, but difficulties are encountered in using them. Magnesium is present in seawater in much greater concentration than is calcium. A low calcium:magnesium ratio may sometimes be indicative of seawater contamination. The presence of sulfate in anionic proportion similar to that of seawater also might be indicative. Because of possible cation-exchange reactions and sulfate reduction in the aquifers that can be expected to occur when seawater is introduced, the proportions of anions and cations in the first contaminated water to reach the sampling point cannot be expected to be exactly the same as those of a simple mixture of seawater and freshwater. It is indeed likely that even after moving only a short distance through an aquifer the water in the advancing saltwater front will have little superficial resemblance to a simple mixture. After the exchange capacity of the aquifer has been satisfied and equilibrium reestablished, the water transmitted inland

will be virtually unaltered seawater; however, a considerable volume of water may need to pass before this stage is reached. Because of the cation-exchange effects, the removal of the introduced ions from a contaminated aquifer by restoring seaward movement of freshwater also will tend to be slow.

Minor constituents of seawater may, in some instances, aid in determining whether a particular aquifer has been contaminated by seawater or by some other saline source. Incipient stages of contamination cannot generally be detected by these constituents. Piper and others (1953) were confronted with the need to differentiate seawater contamination of an aquifer from contamination by connate brine and had some success in doing this by comparing iodide, boron, and barium concentrations in the suspected water. The constituents that might be expected to be useful in identifying sources should be selected by using knowledge of the composition of contaminating solution and by considering the chemical and exchange behavior of the solutes.

Table 22 gives analyses of water from a well in the Los Angeles, Calif., area before and after contamination by seawater. The calcium concentration in the contami-

Table 22. Analyses showing the effects of seawater contamination in the Gaspar water-bearing zone, Dominguez Gap, Los Angeles County, California

[Date below sample number is date of collection. Source of data: Piper, Garrett, and others (1953, p. 227)]

| Constituent | 1 | | 2 | |
|---------------------------------------|--------------|-------|--------------|--------|
| | Jan. 8, 1923 | | Apr. 4, 1928 | |
| | mg/L | meq/L | mg/L | meq/L |
| Silica (SiO ₂) | | | 20 | |
| Iron (Fe) | | | .97 | |
| Calcium (Ca) | 27 | 1.35 | 438 | 21.86 |
| Magnesium (Mg) | 11 | .90 | 418 | 34.38 |
| Sodium (Na) | 82 | 3.57 | 1,865 | 81.10 |
| Potassium (K) | | | | |
| Bicarbonate (HCO ₃) | 235 | 3.85 | 193 | 3.16 |
| Sulfate (SO ₄) | 40 | .83 | 565 | 11.76 |
| Chloride (Cl) | 40 | 1.13 | 4,410 | 124.38 |
| Fluoride (F) | | | .0 | .00 |
| Nitrate (NO ₃) | | | 1.8 | .03 |
| Dissolved solids: | | | | |
| Calculated | 318 | | 8,200 | |
| Hardness as | | | | |
| CaCO ₃ | 113 | | 2,810 | |
| Noncarbonate | 0 | | 2,650 | |

1. Well 4/13-35 M3, Southern California Edison Co., West Gaspar Well, Los Angeles, Calif., before contamination by seawater.
2. Same well; water contaminated by intrusion of seawater.

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